

Understanding Environmental Pollution

Third Edition

Understanding Environmental Pollution delivers a concise overview of global and individual environmental pollution for undergraduate courses, presenting the tools for students to assess environmental issues. This edition contains more than 30% new material, assessing pollution from an international perspective, including air and water pollution, global warming, energy, solid and hazardous waste, and pollution at home. Both the sources and impacts of pollution are addressed, as well as governmental, corporate, and personal responsibility for pollution. Pollution prevention is emphasized throughout.

- Non-technical language encourages greater understanding of sometimes complex issues.
- “Delving deeper” exercises enable students to apply their learning.
- New chapter on the chemistry basics of pollution.
- Introduces toxicology and risk assessment, assisting students in understanding why chemicals are of concern and how they are regulated.

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or will remain, accurate or appropriate.

This book is dedicated to Dr. Stanley J. Idzerda of Saint Joseph, Minnesota.

Dr. Idzerda, a renowned LaFayette scholar, was the first Director of the Honors College at Michigan State University when as a student I came to know him. I owe him everlasting thanks for his contributions to my life. He was unfailingly helpful, seemed never to notice my faults, and always accentuated my positive attributes.

Contents

<i>Preface</i>	<i>page ix</i>
<i>Acknowledgements</i>	<i>xii</i>
<i>List of abbreviations and acronyms</i>	<i>xiii</i>
1 Understanding pollution	1
2 Reducing risk, reducing pollution	34
3 Chemical toxicity	57
4 Chemical exposures and risk assessment	89
5 Air pollution	117
6 Acid deposition	155
7 Global warming	170
8 Stratospheric ozone depletion	213
9 Water pollution	236
10 Drinking water pollution	286
11 Solid waste	311
12 Hazardous waste	348
13 Energy	374
14 Persistent, bioaccumulative, and toxic	410
15 Metals	425
16 Pesticides	456
17 Pollution at home	483
18 Zero waste, zero emissions	511
19 Chemistry: some basic concepts	539
<i>Index</i>	<i>562</i>

Preface

In the early 1990s, I could not find a textbook from which to teach an *Issues in Environmental Pollution* course. So began the writing of class notes, added to by student concerns, misunderstandings, questions, and an ever-increasing volume of information on the issues. The result was the text, *Understanding Environmental Pollution*. It summarizes the basics of many pollution issues, using language understandable to those with a limited science background, while remaining useful to those with more. Four questions are addressed for each pollutant or category of pollutants: what is the pollutant of concern? Why is it of concern? What are its sources? What is being done to reduce, or sometimes eliminate, its emissions into the environment? The impact of pollution on environmental health receives frequent attention with case descriptions posing reflective questions to the reader. Policy issues are often interwoven into the text. As are guidelines on what we, as individuals can do to reduce pollution. This text is not technical, yet provides the basics and, for a number of issues, much detail.

This third edition of *Understanding Environmental Pollution* has been updated and much revised. On the basis of requests, a short chapter on chemistry basics has been added. This edition places greater emphasis on pollutant movement among water, air, soil, and food, and pollutant transformation and degradation. The movement of pollutants across human boundaries is addressed. As are the problems that pollution events can sometimes bring to sites far removed from points of origin. Edition three also places greater emphasis on pollution problems in less-developed nations. China is used to illustrate the major environmental downsides of rapid industrialization occurring with few controls on pollution. The interaction between pollution and poverty is often noted. Most references include Internet addresses, except for those websites not open to the general reader. Many are easily accessed government sites.

A framework: Chapters 1 through 4 provide basic information on pollution and the issues that it poses, and on reducing pollution.

- Chapter 1 addresses the striking ways in which humans are impacting their environment and its ability to provide natural services. It asks us to define pollution for ourselves: high pollutant levels are obviously of concern, but how do we address those that are very small? And, how does an increasing population or large-scale technology impact the environment?
- Chapter 2 introduces *comparative risk assessment* and society's attempts to lower risks including major US laws passed to lower pollution. The chapter moves on to concepts to be used in the rest of the book: the waste management hierarchy with its stress on pollution prevention; and *industrial symbiosis*: treating wastes as resources.

- Chapter 3 introduces toxicity and factors affecting whether a chemical will have adverse effects. It presents the paradoxes with which we must grapple as we think about how or even, in some cases, whether to lower the emissions of a pollutant.
- Chapter 4 examines *chemical risk assessment*. Again, the issue of paradoxes is raised as society systematically, but often inadequately works to understand and describe the risk of particular chemicals and the more difficult problems of the risks associated with mixtures of chemicals.

Basics of pollution issues: Chapters 5 through 12 overview specific pollution issues, especially those starting with emissions into air or water, but in which the pollutants often move on to other environmental media.

- Chapter 5 delves into the principal pollutants in ambient air, the concerns they raise, their sources, and our efforts to reduce emissions. Movements across the globe of massive amounts of pollutants such as dust and smoke are reviewed. So are less prevalent air pollutants.
- Chapters 6, 7, and 8 examine global change issues that originate with air pollutants. In Chapter 6, acid deposition and our success in curbing it is explained. As are some continuing problems, which include increasing levels of acid deposition in Asia. Chapter 7 addresses global warming. Global warming, of necessity, receives greater emphasis in this edition although the many relevant issues are difficult to cover in one chapter. The text overviews not just government efforts to lower greenhouse gas emissions, but also those of businesses, cities, and states. Experience gained with the Kyoto Protocol is noted, while simultaneously looking forward to a more robust treaty. In Chapter 8, the Montreal Protocol is lauded for its success in eliminating major pollutants involved in stratospheric ozone depletion; remaining problems are also noted.
- Chapters 9 and 10 examine water pollution and drinking-water pollution, respectively. Chapter 9 emphasizes nonpoint source pollution, and the difficulties in reducing such emissions as compared to point sources. The *nitrogen glut* is examined along with *dead zones*, now a problem of global dimensions. Chapter 10 inspects drinking-water contaminants and drinking-water purification and the conundrums raised by disinfecting water. Problems relating to pathogenic organisms in drinking water are emphasized, especially in less-developed countries. The tragedy of arsenic poisoning in Bangladesh is also examined.
- Chapters 11 and 12 summarize just two of the many wastes that society produces, municipal solid waste and hazardous waste, respectively. Chapter 11 looks at the enormous quantities of solid waste that we produce, and the increasing difficulties that it poses to societies working to deal with it, especially those of less-developed countries. The increasingly prominent role of plastics as a damaging waste is discussed. Chapter 12 summarizes hazardous waste, its sources and treatment, and hazardous waste sites. It shows too how non-hazardous wastes such as discarded computers can, improperly dealt with, become hazardous.

Specific pollutants and pollution issues: Chapters 13–17

- Chapter 13 is devoted to the pervasive pollution produced by fossil fuel production and use. It reviews the ways in which many of the issues examined in earlier chapters are energy related. Alternative sources of energy are examined along with the environmental pluses and minuses associated with each.
- Chapters 14 and 15 introduce persistent, bioaccumulative, toxic (PBTs) pollutants. The problems caused by PBTs are out of all proportion to their environmental concentrations. Organic PBTs and metal PBTs are examined in Chapters 14 and 15, respectively.
- Chapter 16 summarizes pesticides and pollution related to the use of pesticides. Alternatives to the use of synthetic pesticides are reviewed. As are the differing approaches and philosophies involved in using pesticides in conventional agriculture as compared to organic and integrated pest management.
- Chapter 17 brings us to home settings, focusing on pollutants within our homes. Many pollutants are often found at higher levels inside our homes than outside. How can we reduce, or even eliminate, many of them? The chapter also discusses the hazardous products that we use.

Hope for meaningful change: Chapter 18

- Chapter 18 addresses the ideal of *zero waste*, *zero emissions* using two major approaches, dematerialization and detoxification. The tools we use in moving toward these ends are examined. The chapter also introduces some businesses, cities, and even whole countries that are making zero waste, zero emissions their goal.

Chemistry: Chapter 19

- Chapter 19 introduces some basics of chemistry. It was written in response to requests to provide more information on why pollutants act as they do. Several elementary explanations of pollution events using chemistry are provided.

Acknowledgements

I continue to extend warm gratitude to my husband, Dr. John C. Hassler, who has faithfully and with much patience over three editions of this text cared for my computer hardware and software. For this edition he, as a Ph.D. physical chemist, also reviewed the new chapter on chemistry.

List of abbreviations and acronyms

(Chemical Abbreviations listed separately below)

AC	Alternating current
ADI	Acceptable daily intake
AIDS	Acquired Immune Deficiency Syndrome
ATSDR	Agency for Toxic Substances Disease Registry (a US agency)
BOD	Biochemical oxygen demand
Bt	<i>Bacillus thuringiensis</i> (a bacterium)
Btu	British thermal unit (a unit of energy)
CAA	Clean Air Act (a US law)
CAFE	Clean Air for Europe
CDC	Centers for Disease Control and Prevention (a US agency)
CDM	Clean Development Mechanism
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act (Superfund) (a US law relating to hazardous waste sites)
CPSD	Consumer Product Safety Division (a US agency)
CRT	Cathode ray tubes
CSO	Combined sewer overflow
CWA	Clean Water Act
DBP	Disinfection by-product
DC	Direct current
DfE	Design for the environment
DOE	Department of Energy (a US agency)
EMF	Electromagnetic field
EPA	Environmental Protection Agency (a US agency)
EPR	Extended producer responsibility (also called <i>take-back</i>)
ETS	Environmental tobacco smoke
EU	European Union
EV	Electric vehicle
FAO	Food and Agriculture Organization (a UN agency)
FDA	Food and Drug Administration
FFDCA	Federal Food Drug and Cosmetics Act (a US law)
FFV	Flexibly fueled vehicle
FIFRA	Federal Insecticide Fungicide and Rodenticide Act (a US law)
GCM	General Circulation Model
GEO	Genetically-engineered organism

GI	Gastrointestinal
HAP	Hazardous air pollutant, also referred to as toxic air pollutant
HEPA	High efficiency particulate air (filter)
HHW	Household hazardous waste
HW	Hazardous waste
INDOEX	Indian Ocean Experiment
IPCC	Intergovernmental Panel on Climate Change
IPM	Integrated pest management
IR	Infrared
KWh	Kilowatt-hour
LCA	Life-cycle assessment
MACT	Maximum available control technology
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MEI	Maximally exposed individual
MIC	Methylisocyanate
µg /dl	Micrograms per deciliter (a concentration)
µg /l	Micrograms per liter (a concentration)
MOPITT	Measurements of Pollution in the Troposphere
MPG	Miles per gallon
MSW	Municipal solid waste
MTD	Maximum tolerated dose
NAPAP	National Acid Precipitation Assessment Program (program evaluating acidic deposition)
NAS	National Academy of Sciences (US body of scientists formed by a Congressional act)
NASA	National Aeronautic and Space Administration (a US agency)
NICAD	Nickel-cadmium batteries
NIMBY	Not in my backyard
NOAA	National Oceanic and Atmospheric Administration (a US agency)
NOAEL	No observed adverse effect level
NPL	National Priority List (a US list of high-priority hazardous waste sites)
NRC	National Research Council (an arm of the US NAS)
NTP	National Toxicology Program (a US program evaluating chemical toxicity)
ODP	Ozone depletion potential
OECD	Organization for Economic Cooperation and Development (organization of 30 prosperous nations)
p ²	Pollution prevention
PBT	Persistent, bioaccumulative, toxic
pCi/l	Picocuries per liter (a unit of concentration for radioactive substances)
PM	Particulate matter
PM ₁₀	Particulate matter that is less than 10 microns in diameter
PM _{2.5}	Particulate matter that is less than 2.5 microns in diameter
PNGV	Partnership for a New Generation of Vehicles

POP	Persistent organic pollutant
ppb	Parts per billion (a unit of concentration)
ppm	Parts per million (milligrams per liter, a unit of concentration)
ppt	Parts per trillion (a unit of concentration)
PSC	Polar stratospheric cloud
PV	Photovoltaic
RCRA	Resource Conservation and Recovery Act (a US law)
RDF	Refuse-derived fuel
RfD	Reference dose
SDWA	Safe Drinking Water Act (a US law)
SS	Suspended solids
SUV	Sports utility vehicle
TRI	Toxic Release Inventory (US list of chemicals released into environment)
TSCA	Toxic Substances Control Act (a US law)
TUR	Toxics use reduction
UN	United Nations
UNDP	UN Development Program
UNEP	UN Environmental Program
UNICEF	UN International Children's Emergency Fund
USDA	US Department of Agriculture
USGS	US Geological Survey (a US agency)
UV	Ultraviolet
WHO	World Health Organization (a UN agency)
WMH	Waste management hierarchy
WMO	World Meteorological Organization (a UN agency)
ZEV	Zero-emission vehicle

Chemical abbreviations and formulas

BaP	Benzo[<i>a</i>]pyrene (a PAH formed during combustion)
¹⁴ C	Carbon-14 (a radioactive form of carbon)
CCA	Chromated copper arsenate (used to protect wood against decay)
CCl ₂ F ₂	Freon-12 (the best-known CFC)
CFC	Chlorofluorocarbon (an ozone-depleting chemical)
CFC-12	Freon (the best-known CFC)
CH ₄	Methane (a greenhouse gas)
ClO	Chlorine monoxide (in the stratosphere it promotes ozone depletion)
CO	Carbon monoxide (a toxic chemical formed by incomplete combustion)
CO ₂	Carbon dioxide (a greenhouse gas)
DDE	Dichlorodiphenyldichloroethene (a DDT degradation product)
DDT	Dichlorodiphenyltrichloroethane (a once common, but now banned, insecticide)
DEHP	Di(2-ethylhexyl) phthalate (used in plastic to make it flexible)
DES	Diethylstilbestrol (a potent synthetic estrogen)
Dioxin	2,3,7,8-TCDD (sometimes refers to the whole dioxin family)

DMSO	Dimethyl sulfoxide (chemical promoting transport of chemicals across skin into body)
DNA	Deoxyribonucleic acid (genetic material)
H ⁺	Acid hydrogen ion (an ion that makes water acid)
HCFC	Hydrochlorofluorocarbon (a substitute for CFCs)
HCHO	Formaldehyde (a chemical found in many household products, often as a residual)
HCl	Hydrochloric acid (a common acid)
HFC	Hydrofluorocarbon (a substitute for CFCs)
⁴⁰ K	Potassium-40 (a radioactive form of potassium)
MIC	Methylisocyanate (responsible for massive Bhopal explosion)
MTBE	Methyl tertiary butyl ether (a chemical added to gasoline to provide oxygen)
N	Nitrogen
N ₂	Nitrogen (diatomic nitrogen, the form found in the atmosphere)
N ₂ O	Nitrous oxide (a greenhouse gas, also used as anesthetic, known as “laughing gas”)
NO ₂	Nitrogen dioxide (a common air pollutant, which also leads to acid deposition)
NO _x	Nitrogen oxides (common air pollutants that contain nitrogen)
O	Single oxygen atom
O ₂	Oxygen (diatomic oxygen, the form found in the atmosphere)
O ₃	Ozone (triatomic oxygen, a common air pollutant)
PAH	Polycyclic aromatic hydrocarbon (common pollutants formed during combustion)
PBDE	Polybrominated diphenyl ether (a fire-retardant chemical which is persistent and bioaccumulative)
PCB	Polychlorinated biphenyl (now banned chemicals once commonly used in electrical equipment to prevent fires)
PERC	Tetrachloroethylene (perchloroethylene, a dry-cleaning solvent)
PET	Polyethylene terephthalate (a common plastic often used to make soft-drink bottles)
PFC	Perfluorocarbon (a greenhouse gas)
PFOS	Perfluorooctane sulfonates (stain repellants and fire fighting chemicals, environmentally persistent and bioaccumulative)
Po	Polonium (a naturally found radioactive element)
PVC	Polyvinylchloride (a plastic)
Rn	Radon (a naturally found radioactive gas)
SF ₆	Sulfur hexafluoride (a potent greenhouse gas)
SO ₂	Sulfur dioxide (a common air pollutant, which also leads to acid deposition)
TBT	Tributyltin (biocide used to coat maritime ships to prevent growth of fouling organisms)
TCDD	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin (most toxic form of dioxin commonly called “dioxin”)
²³⁸ U	Uranium-238 (a radioactive isotope of uranium)
VOCs	Volatile organic compounds (or volatile organic chemicals)

“the very basis for life on earth is declining at an alarming rate.”

Former UN Secretary, General Kofi Annan

Chapter 1 asks some basic questions: what is pollution and why is it important? What causes pollution? Is it always harmful? How do pollutants change once in the environment? Section I emphasizes the major impacts we humans exert on Earth’s natural systems while reminding us of our profound dependence on the services provided by those systems. Section II asks why pollution happens. What substances pollute and where do they come from? We look at what happens to pollutants once released, and the effects exerted, sometimes at great distances from their point of release. Section III examines the catastrophic 1984 explosion in Bhopal, India. It also considers the opposite extreme: should we be concerned about very low levels of pollutants? We then move to impoverished parts of the world where pollution sometimes devastates human health. Section IV introduces root causes of pollution – growing human populations, growing consumption, and large-scale technology. Section V asks us to face ourselves, to see that our actions have environmental consequences, sometimes in ways we don’t suspect.

SECTION I

Humans are massively changing the Earth

A 1997 article in the journal, *Science*, Human domination of Earth’s ecosystems spoke of humanity’s impact on the environment.¹ See Figure 1.1 from left to right. 1. Up to one half of Earth’s land surface has been transformed by human action. 2. The percentage of the concentration of the atmospheric greenhouse gas, carbon dioxide, that results from human action. 3. The percentage of accessible surface fresh water on Earth being put to use by humanity. 4. The percentage of nitrogen fixation caused by humans is more than all natural terrestrial sources combined. 5. The percentage of plant species in Canada that humanity has introduced from elsewhere, i.e., invasive or exotic species. 6. The percentage of bird species on Earth that became extinct in the past two millennia (largely) from human activity. 7. The percentage of major marine fisheries that are fully exploited, overexploited, or depleted.

Ten years after the article, human domination has continued to increase. A 2007 report from the United Nation’s Environmental Program (UNEP) stated: “The human population is

¹ Vitousek, P.M., Mooney, H.A., Lubchenco, J., and Melillo, J.M. Human domination of Earth’s ecosystems. *Science*, **277**, July 25, 1997, 494–499 <http://mk.geog.uu.nl/homepages/Peter/teaching/Themes/Vitousek.pdf>.

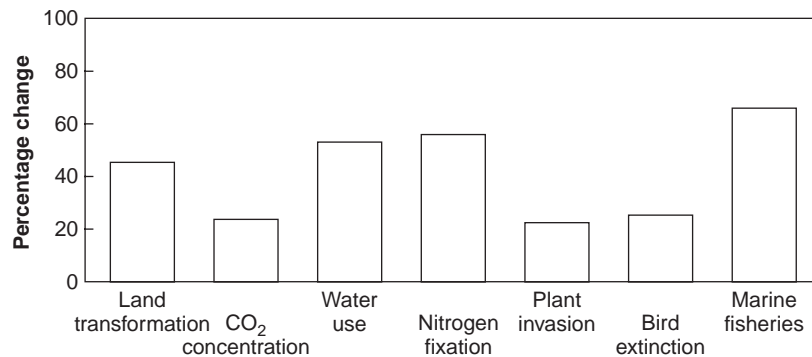


Figure 1.1

Human domination of Earth's ecosystems. Credit: Reprinted with permission from AAAS

living far beyond its means and inflicting damage on the environment that could pass points of no return.”² One example: as much as one-third of ocean fisheries are in collapse, two-thirds may be so in 2025, and all major ocean fisheries may be gone by 2048. As the “Human Domination” article stated: “The rates, scales, kinds, and combinations of changes occurring now are fundamentally different from those at any other time in history; we are changing Earth more rapidly than we are understanding it. In a very real sense, the world is in our hands and how we handle it will determine its composition and dynamics, and our fate.”

To the student: Chapter 1 describes major and discouraging problems. However, the chapter's purpose is to provide the background from which we can consider solutions. Solutions are assuredly difficult, but human willingness and energy can lead to surprising changes.

Nature's services

We may ignore pollution if its source is a local factory that provides employment. “That’s the smell of money” we might say. Many of us still fail to recognize our total dependence on our environment or recognize that all human employment depends on nature’s services. For a summary of nature’s services, see Table 1.1.

Examples of nature's services (ecosystem services^{3,4})

Protecting drinking water

New York City spent hundreds of millions of dollars to buy ~70 000 acres (~28 000 hectares) of land along streams and rivers in the Catskill Mountains to the city’s

² Kanter, J. U. issues “final wake-up call” on population and environment. *International Herald Tribune*, October 25, 2007, <http://www.ihf.com/articles/2007/10/25/europe/enviro.htm>.

³ Daily, G. C. *Nature's Services, Societal Dependence on Natural Ecosystems*. Washington DC: Island Press, 1997.

⁴ *Ecosystem Services: A Primer*, Ecological Society of America, 2000–2005. <http://www.actionbioscience.org/environment/esa.html> [August 2008].

Table 1.1 What are nature's services?

Type	Examples
Provisioning	Food (plants and animals), water, fuel (such as wood and dung)
Regulating	Climate (including temperature and precipitation), water purification and waste treatment, pollination, preventing soil erosion (as with grasses and trees), storm protection (as with mangroves and coral reefs)
Supporting	Services necessary to produce other ecosystem services including soil formation, nutrient cycling, production of oxygen (from photosynthesis)
Cultural	Spiritual values, a "sense of place," recreation and ecotourism

Nature's services, also called "ecosystem services" are the benefits people obtain from the natural world. These services directly affect people and also support services needed to maintain the other services." (See Millennium Ecosystem Assessment, <http://www.millenniumassessment.org/en/Framework.aspx>.)

north – the watershed⁵ that provides its drinking water.⁶ It then restricted use of that land, forbidding activities such as the application of pesticides and fertilizers that would pollute watershed streams and rivers. ■ The city also protected the land from development, leaving trees and grasses in place. Roots of grasses and trees hold the soil in which they grow, preventing it from eroding and running off into streams during rainstorms. Rooted vegetation also slows the rain falling through its foliage down into the soil. Leaf and other vegetation litter on the ground absorb and slow water too. These factors lessen the risk of flooding during heavy rains. And, as water seeps downward to groundwater, the soil traps pollutants contained in the rainwater. Because groundwater is in contact with surface water, keeping groundwater clean helps to provide clean surface water. The rainwater allowed to seep into groundwater replenishes it. ■ By protecting the Catskills' from pollution and recognizing the natural water filtration capability of undeveloped land, the City avoided having to build a \$6 billion treatment plant to purify its drinking water, plus the \$300 million a year it would have cost to run the plant. The City saved billions of dollars by protecting natural services – also called ecosystem services. Other American cities are following New York City's example, e.g., Austin Texas has purchased 20 000 acres (~8000 hectares) of land around its Edwards Aquifer.

Preventing floods

China is taking similar action to help curb flooding there. Lester Brown described the major 1998 floods along the Yangtze River basin in China, floods continuing for many weeks, and causing many billions of dollars in damage⁷. Afterwards, the Chinese government traced part of the flooding to deforestation along the Yangtze River, so they banned tree cutting in the upper reaches of the basin. They calculated that the value of living trees is three times the value of cut trees.

⁵ To get a sense of a watershed, see Figure 9.3.

⁶ Carlton, J. Cities spending millions on land to protect water supplies. *The Wall Street Journal*, 04 January, 2006.

⁷ Brown, L. Eco-economy, building an economy for the earth. Chapter 8, *Protecting Forest Products and Services*. Earth Policy Institute, 2001, http://www.earth-policy.org/index.php?/books/eco/eech8_intro.

Global climate change

In Chapter 7, we will see how important it is to limit atmospheric levels of carbon dioxide (CO₂), the major greenhouse gas. Human actions, especially burning fossil fuels, release large amounts of CO₂. Regulating the amount of CO₂ in the atmosphere requires the protection of trees and other vegetation that take up CO₂ from the atmosphere. Tropical forests are especially important. One scientist stated, “We’ll never solve the climate challenge unless we address the loss of tropical forests, [a loss] which puts out as much carbon dioxide as all the planes, trains, and cars worldwide.”⁸

Urban trees⁹

The organization American Forests, using satellite and aerial imagery, showed that tree cover in twenty US cities had declined by 30% over three decades, a disturbing loss of shade, cooling, and aesthetic value. Fewer trees also means more runoff of storm water, which otherwise could seep into groundwater while also removing pollutants. Fewer trees also mean more air pollution because the stomata in tree leaves can help remove air pollutants, and sticky or hairy leaves filter particulates from air. ■ Using a computer-based geographic information system, American Forests determined how much pollution urban trees remove, and then calculated the economic loss of cutting the trees down. In Washington, DC the cut trees would have removed ~354 000 pounds (over 160 000 kg) a year of major air pollutants including carbon monoxide, sulfur dioxide, and ozone. With fewer trees to trap storm water, storm water runoff increased by 34%. It costs Washington, DC about \$226 million per year to trap and treat the additional runoff. Despite tree losses, the average city still has about 30% tree cover, and American Forests believes that this could reasonably increase to at least 40%.

Stabilizing soil depends on more than trees

Grass is also tremendously important for holding soil in place. Indeed, the greatest environmental catastrophe in American history, the “dust bowl” occurred in the Midwestern states after farmers cleared massive areas of native grasslands. They cleared the grassland to grow ever increasing amounts of wheat. As long as rainfall was ample, catastrophe was averted, but as the region fell into a prolonged drought in the 1930s, wind whipped up the unprotected soil on 100 million acres (40.5 million hectares) and blew it, sometimes many hundreds of miles away (see Figure 1.2). Untold numbers of farms were destroyed as they were denuded of productive soil. Great numbers of animals, both domestic and wild, died. Humans suffered greatly too, many dying of “dust pneumonia.” Many thousands left the land that could no longer be farmed. US President Franklin D. Roosevelt, in the late 1930s, asked: why did the Great Plains blow away? What made this land die? It was difficult for him to accept that human action was responsible. Beginning in the late 1930s, a major

⁸ Source: Stephanie Meeks of The Nature Conservancy. She is working with the World Bank to provide incentives to people to preserve rain forests. Their effort is called Cool Earth.

⁹ Fields, S. If a tree falls in the city (ecosystem services of urban trees). *Environmental Health Perspectives*, **110**(7), A390, July, 2002.



Figure 1.2 Dust storm approaching Stratford, Texas (April 18, 1935). Credit: NOAA George E. Marsh Album

effort began to restore the land, to plant windrows of trees, and to check erosion. However, it took many years for recovery, and some land was never restored. These Midwestern states now largely depend on irrigation to water their crops. The water comes from the Ogallala aquifer, another resource that is being depleted. A fascinating depiction of this tragedy is given by Timothy Egan in his book, *The Worst Hard Time*.¹⁰

- Undeveloped land provides a multitude of other natural services: home to wildlife, timber for careful lumbering operations, recreation and aesthetic value. It is also cooler than cleared land.
- Undeveloped wetlands, whether located in forests or elsewhere trap eroded soil, preventing its runoff into streams and lakes. Wetland plants and microorganisms purify polluted runoff carried there. Wetlands provide flood protection as noted in the Yangtze example. They also provide habitat to multiple bird and other species.

Other ecosystem services

It is not possible to count the many services that nature provides, but Table 1.1 notes some major services, and other examples follow.

- Nature provides seafood, wild game, forage, timber, biomass fuels, and natural fibers.
- Trees and other vegetation take up the greenhouse gas carbon dioxide, while releasing the oxygen necessary to our lives.
- The atmosphere's ozone layer protects us from the sun's ultraviolet radiation.
- Worms and other organisms, and vegetation enhance soil fertility.
- Nature provides the insects, birds and other animals that pollinate many food crops. Birds and some insects eat many agricultural pests.
- Many species of fungi and bacteria, insects, and worms degrade organic waste materials, a vital

¹⁰ Egan, T. *The Worst Hard Time, the Great American Dust Bowl*. Boston: Houghton Mifflin Co., 2006.

function. Organic wastes include sewage, dead vegetation, and animal matter, and natural as well as anthropomorphic organic pollutants. Some larger creatures eat wastes too – vultures are essential to scavenge dead animals in some places. Waste-degrading creatures could live without humans, but we cannot live without them.

Among services that you might not think of, consider glaciers, many of which are now melting as the climate warms. Glaciers provide water to many of the world's major rivers, which in turn provide drinking water, and water used for agriculture, hydroelectric dams, industry, and, of course, water for the countless other species that live on Earth. Or think about the soil that, in many places around the world is undergoing *desertification*, conversion into deserts. Desertification lessens the land available for human habitation, for agriculture, or habitat for our fellow species. Moreover, as land undergoes desertification we see increasing numbers of dust storms, often badly impacting people, plants, and animals living hundreds, even thousands of miles from those storms.

Vital species

We do not know which species are absolutely vital to life on Earth, but we know that a great many are needed to maintain the multitudes of ecosystem services (see Box 1.1). We also know that humanity is destroying and disrupting habitat, and producing pollution. In the process, species are going extinct at a rate perhaps 100 times greater than the natural rate. ■ Coral is one example of a vital species. Coral reefs play an irreplaceable role in the marine environment. They provide habitat for marine species that are integral to the ocean's food chain. They provide a livelihood to a hundred million people in less-developed countries in jobs such as fishing and tourism. Beyond the marine environment, coral reefs protect the coastline from flooding and coastal erosion. But coral reefs are being lost through pollution from eroded soil carried in runoff along with chemical pollutants; global warming is also playing a deadly role.

Questions 1.1

1. In a paragraph, describe how protecting land from development, as New York City did, helps to provide clean water.
2. Coral reefs are a vital living resource that is being destroyed. What is another?
3. What did Harvard biologist, E. O. Wilson mean by saying "We need invertebrates but they don't need us"?
4. What natural services do the following provide? (a) Grasslands (b) Estuaries (c) Microorganisms.
5. When you think about vital species, what are two species (other than domestic animals) that come to mind? What services do these species provide?
6. How can pollution result from: (a) Deforestation? (b) Grassland loss? (c) Wetland loss?
7. Technology can mimic some natural services such as purifying water, albeit often at high cost. What technology – one that is already known or one that you can envision – can: (a) Provide clean drinking water at a reasonable cost? (b) Rebuild agricultural soil damaged by erosion? (c) Rebuild soil damaged by salt buildup? (c) Produce adequate food in the absence of fertile soil?

Box 1.1

"Less forgiving than our planet"

A facility known as *Biosphere 2* was designed to test a supposition often made by economists – that technology can substitute for natural life support systems. Biosphere 2 was to model a spacecraft that could allow humans to travel in space indefinitely. Within the structure, everything was to be sustainable. Built in the State of Arizona at a cost of \$200 million, the 3.2 acres (1.3 hectares) of Biosphere 2 are a closed-off mini-Earth containing tiny *biomes* – a marsh from the Florida Everglades, an equatorial rain forest, a coastal desert, a savanna with a stream and grasses from three continents, an artificial mini-ocean with a coral reef, plus an orchard and intensive agricultural area. Its underbelly holds a maze of plumbing, generators, and tanks. In 1991, eight people started living in Biosphere 2 to test its ability to support life. They lived within the facility for two years. The first year went well, but in the second, crops failed, and people grew thin. They became dizzy as atmospheric oxygen levels fell from 21% to 14% – a level typical of a 14 000 feet (4270 m) elevation. This occurred because excessive organic matter in the soil absorbed oxygen from the air as did the type of concrete used. Atmospheric carbon dioxide “spiked erratically,” while nitrous oxide rose to levels hazardous to brain function. Vines and algal mats overgrew other vegetation. Water became polluted. The Biosphere initially had 3800 plant and animal species. Among the 25 introduced vertebrate species 19 died out over the two years, and only a few birds survived. All the Biosphere’s pollinators – essential to sustainable plant communities – became extinct. Excitable “crazy” ants destroyed most other insects. In 1997, Columbia University took over Biosphere 2 for use as an educational facility designed to teach Earth stewardship, a place to “build planetary managers of the future.” Its research efforts included studying the effects of various levels of the greenhouse gas carbon dioxide on plant communities. That effort ended and the University of Arizona is now in charge. Someone noted that Biosphere 2 is less forgiving than our planet. But Earth is a closed system too. History records many examples of civilizations that failed or grew weak after severely impacting their local environments.¹¹ But survivors often moved on to other environments. Today, many people still struggle to “move on,” but there are fewer and fewer fresh locales into which Earth’s huge population can move.

The technical problems of Biosphere 2 could probably be solved. But for the whole Earth, or major parts of it, can we substitute technology for nature’s services, for breathable air, or for fertile clean soil?

What is happening to Earth’s ecosystems?

Keeping in mind our absolute dependence on Earth’s ecosystems and the major stresses on them, how well are they still providing their natural goods and services? The first systematic examination of this question was a four-year \$20 million study, the Millennium Ecosystem Assessment (MEA).¹² Carried out by 1400 scientists worldwide under the aegis of the UN

¹¹ Diamond, J. *Collapse, How Societies Choose to Fail or Succeed*. New York City: Viking, 2004.

¹² (1) Stokstad, E. Taking the pulse of Earth’s life-support systems, *Science*, **308** (5718), April 1, 2005, 41–43. (2) *Global Economic Growth Continues at Expense of Ecological Systems*. Worldwatch Institute, January, 2008. <http://www.worldwatch.org/node/5456>.

Environment Program's (UNEP), the MEA evaluated the health of the planet's forests, coastlines, inland waters, shrub lands, dry lands, deserts, agricultural lands, and other ecosystems vital to human and natural welfare. Helping investigators to envision what was happening were 16 000 photographs donated by the US National Aeronautics and Space Administration (NASA). Taken from space by satellite, these showed changes occurring in the 1990s in biomes such as coastlines, mountains, and agricultural land.

In 2005 MEA provided some answers as to what is happening to ecosystem services. Their report revealed that *at least 60% of services supporting life on Earth* including fresh water, fisheries, and many other services are being used unsustainably. The report, *Living Beyond Our Means: Natural Assets and Human Well-being*¹³ has shown that we are using about 1.25 Earths' worth of resources, even while human population and consumption continues to increase. Consequences of environmental degradation could become more obvious in coming years. Although results were extremely worrisome, the study pointed toward means by which we can improve ecosystem management, a topic that we will examine throughout this text.

SECTION II

Pollution

When pollution is obvious

If you read that a *pollutant* is "any substance introduced into the environment that adversely affects the usefulness of a resource" you may yawn. But pollution literally hits you if you live in a city where emissions from cars, trucks, and motorbikes sting your eyes, congest your nose, cause your head to ache, or tighten your breathing. ■ In the 1960s and '70s, pollution in the United States, a wealthy country, was often blatant. Some rivers were obviously polluted by industries operating on their banks. Oil floating on the surface of Ohio's Cuyahoga River caught on fire more than once. One fire in 1959 burned for 8 days. ■ Air pollution was obvious too. In industrial cities soot drifted onto streets and clothing, and into homes. Severe air pollution episodes increased hospital admissions killing sensitive people. Trash burned in open dumps. ■ Heavy pesticide use killed fish, birds, and other animals. ■ The new century finds the environment in industrialized countries improved. But continuing population growth in the United States, and unrelenting, indeed accelerated, land development may be reversing some of that progress. And the United States, once an environmental leader, abandoned that role in the first decade of the twenty-first century.

Just as a weed is "a plant out of place," a pollutant is "a chemical out of place." Oil enclosed within a tanker is not a pollutant. Spilled into the environment, it is. However, doing harm often involves more than being out of place. A small oil spill may go unnoticed,

¹³ See <http://millenniumassessment.org/en/index.aspx>, home page of the MEA, which links to the report's summary and other reports including *Living Beyond Our Means*. Also see the World Resources Institute's *EarthTrends* at <http://earthtrends.wri.org/> for more useful information on Earth's ecosystems.

Table 1.2 Terms used to describe pollutant concentrationppm = parts per million ^a

ppb = parts per billion (one thousand times smaller than ppm)

ppt = parts per trillion (1 million times smaller than ppm)

ppq = parts per quadrillion (1 billion times smaller than ppm)

To grasp these concentrations, consider the following:

1 ppm = 1 pound contaminant in 500 tons (1 million pounds)

1 ppb = 1 pound of contaminant in 500 000 tons

1 ppt = 1 pound of contaminant in 500 000 000 tons

1 ppq = 1 pound of contaminant in 500 000 000 000 tons.

For a different perspective, think about periods of time:

1 ppm is equivalent to 1 second in 11.6 days

1 ppb is equivalent to 1 second in 32 years

1 ppt is equivalent to 1 second in 32 000 years

1 ppq is equivalent to 1 second in 32 000 000 years.

^a ppm, ppb, etc. refer to parts by weight in soil, water, or food. In air, they refer to parts per volume.

but a large one can be disastrous. Circumstances are important too. If the oil is of a type easily degraded, or one that evaporates easily, or if wind blows the spill quickly away from a shoreline, there may be little harm. But, coming ashore, oil may devastate animals, birds, and other shore-dwelling organisms.

Almost any substance, synthetic or natural, can pollute. However, it is synthetic and other industrial chemicals that are emphasized here. If we learn that industrial chemicals in a water body are obviously impairing the ability of birds to reproduce, or are associated with fish tumors we all agree that the water is polluted. But what if only tiny amounts of industrial chemicals are present and living creatures are apparently unaffected? Is the water polluted? Some would say “yes,” arguing that chronic effects could result, i.e., adverse effects resulting from long-term exposure to even very low concentrations of a substance. ▪ The word *waste* differs from *pollutant*, although a waste can be a pollutant too. Waste refers to material such as garbage, trash, construction debris, materials that have reached the end of their useful life. ▪ See Table 1.2 for a description of how pollutant concentrations are described.

Pollution is often less obvious if you live in a wealthy country where the twentieth century brought cleaner air and drinking water, sewage treatment, safe food laws, and food refrigeration. But it took many years and many billions of dollars to reach those results. And wealth does not guarantee an unspoiled environment. For example, parts of the American Appalachian Mountains suffer destruction and pollution resulting from mountaintop-removal mining (described later). Or think about wealthy Hong Kong. In the 1990s, the beaches of this island were too polluted for swimming. High concentrations of hazardous industrial metals, livestock waste, and human waste polluted its rivers, and large amounts of trash polluted the harbor. However, between 1993 and 2000, hazardous metal discharges

were reduced from 15 432 lb/day (7000 kg/day) to 4409 lb/day (2000 kg/day). And, Hong Kong increasingly collects and treats sewage before releasing it into the harbor. However, air pollution remains critical. In the mid-1990s, exhausts from motor vehicles resulted in 25% of the population suffering from respiratory problems. Today, despite better air pollution controls, heavy smog often blankets Hong Kong. Although, up to half of this enters Hong Kong from nearby Chinese cities in Guangdong Province. But part of the imported pollution comes from facilities owned by Hong Kong companies – operating on the mainland with poor pollution controls.

Why does pollution happen?

Unless you assume that people and industry deliberately pollute, why does pollution occur? It happens because no process is 100% efficient. Consider your own body – it cannot use 100% of the food you eat. ▪ The gastrointestinal (GI) tract does not break down the fiber in the food you eat, and this is excreted from the body as solid waste. ▪ Enzymes in the gut do break down other foods into molecules that can cross the GI wall into the bloodstream, which carries the nutrition throughout your body. But the body cannot use 100% of the nutrient value, and a portion is excreted into urine as water-soluble waste. ▪ Also, your body cannot convert all the potential energy in food into useful energy – part becomes waste energy.

As with your body, no other process, natural or human, such as manufacturing or fuel burning, is 100% efficient: each produces pollution and waste, and waste energy. See Box 1.2. Lack of prevention, carelessness, unwillingness to invest in good technology, or lack of appropriate technology aggravates the waste and pollution produced. Architect William McDonough and chemist Michael Braungart observe, “Pollution is a symbol of design failure.” In other words, wastes need not be wastes and pollutants need not be pollutants. We should be able to return these to the manufacturing process, or else make sure the wastes involved are able to biodegrade harmlessly in the environment. We will return to this later.

What substances pollute?

Almost any chemical or material from either human or natural sources can pollute. See Table 1.3. Also see Pollutant Sources below.

Natural pollutants

This text emphasizes anthropogenic pollutants (i.e., pollutants produced by human activity), but natural chemicals can also pollute. This happens dramatically when an erupting volcano spews out huge quantities of rocks, ash, chlorine, sulfur dioxide, and other chemicals. Other natural chemicals can pollute too, but sometimes human actions allow natural substances to reach dangerous levels as in the following illustrations: 1. *Radon* is a naturally radioactive chemical, a gas that arises from transformations occurring in underlying rocks and soil

Table 1.3 An introduction to pollutant types

CATEGORY	EXAMPLES
Organic chemicals	Polychlorinated biphenyls (PCBs), oil, many pesticides
Inorganic chemicals	Salts, nitrate, metals and their salts
Organometallic chemicals	Methylmercury, tributyltin, tetraethyl lead
Acids ^a	Sulfuric, nitric, hydrochloric, acetic
Physical ^a	Eroded soil, trash
Radiological ^a	Radon, radium, uranium
Biological	Microorganisms, pollen

^a Acids, as well as physical and radioactive pollutants can be either organic or inorganic – sulfuric acid is inorganic, acetic acid (found in vinegar) is organic. Biological pollutants are mostly organic, but contain inorganic components.

Box 1.2**Gasoline combustion**

Gasoline is primarily composed of hydrocarbons (molecules containing hydrogen and carbon) plus small amounts of contaminants. During combustion, the hydrocarbons are converted into the products shown below, subsequently released in the vehicle's exhaust. Notice that oxygen (O_2) is involved in almost all of the reactions. Waste energy is released as heat.

During combustion, hydrocarbons react with atmospheric oxygen (O_2) yielding the products shown:

- The carbon in hydrocarbons \rightarrow carbon dioxide (CO_2 , a gas)
- The hydrogen in hydrocarbons \rightarrow water (H_2O)

Because combustion in a gasoline engine is far from 100% efficient . . .

Hydrocarbons + $O_2 \rightarrow CO_2 + H_2O$ + *incomplete products of combustion*. These include carbon monoxide (CO), soot (fine black carbon particles), volatile organic chemicals (VOCs) and lesser amounts of chemicals including PAHs. (Burning gasoline in a laboratory in an enriched oxygen atmosphere, could force combustion to completion, i.e., to $CO_2 + H_2O$.)

The contaminants in gasoline also react with atmospheric O_2 during combustion.

- Metals + $O_2 \rightarrow$ metal oxides, tiny particulate pollutants
- Sulfur + $O_2 \rightarrow$ sulfur dioxide (SO_2), a gaseous pollutant

Gasoline has little nitrogen (N_2). However, 78% of the atmospheric air in which combustion is occurring is N_2 . Most of this (>85%) is released unchanged in the car's exhaust. However, some N_2 reacts with atmospheric oxygen: $N_2 + O_2 \rightarrow$ nitrogen oxides

A natural law tells us that *matter* is neither created nor destroyed. So we know that the hydrocarbons and other substances in gasoline do not disappear. They are converted to CO_2 , water, and pollutants. The O_2 that reacted with substances in gasoline is conserved too, with most being converted to CO_2 .

Another natural law tells us that *energy* is neither created nor destroyed. As gasoline burns, only a small portion of its energy is actually transformed into mechanical energy to power the engine. The rest is "lost" as heat. But, the energy is dissipated, not "lost." Under certain circumstances, waste energy can be captured and used.

Questions 1.2

1. Assume that a gallon (3.8 liters) of gasoline weighs ~6 pounds¹⁴ (2.7 kg). How then can 20 pounds (9.1 kg) of carbon dioxide be emitted per gallon of gasoline (in the car's exhaust)?¹⁵
2. (a) How does the sulfur in gasoline end up as sulfur dioxide? (b) The metals as metal oxides?
3. With the exception of water, all the chemicals in the exhaust of your car are pollutants, more than 20 pounds (9.1 kg) of pollutants. How important is this piece of information? Explain.

around the world as natural radioactive uranium decays. But levels of radon in outside air are low. It is when radon seeps up into – and concentrates in – human structures that problems may arise. The US EPA ranks radon, associated with human lung cancer, as second only to environmental tobacco smoke as an environmental health risk. 2. *Arsenic* is natural too and previously was not a problem to people in Bangladesh and India. Their problem had been drinking surface water badly contaminated with infectious microbes. To correct this, millions of boreholes were drilled to provide clean drinking water. Unfortunately, arsenic in the rock and soil dissolves into the water in those boreholes. The result has been a massive ongoing poisoning event in which millions suffer from arsenic poisoning. 3. *Asbestos* too, is natural. But, in El Dorado County, California, population growth led to homes being built in previously unoccupied regions, including areas rich in asbestos deposits. Now asbestos exposure has become a major concern. Chronic exposure also occurs in certain regions of Turkey where naturally high levels of asbestos have led to respiratory diseases and cancer. Up until recent decades, asbestos was also a workplace pollutant.

Pollutant sources

“I am, therefore I pollute” is a statement applying to a multitude of processes: ▪ Motor vehicles including cars, buses, airplanes, ships, and off-road vehicles ▪ Chemical and petroleum refineries ▪ Manufacturing facilities ▪ Commercial operations including dry cleaners, bakeries, and garages ▪ Plants generating electric power by burning coal, oil, or natural gas ▪ Agricultural operations growing crops or raising animals ▪ Food processing operations ▪ Mining ▪ Construction and road building ▪ Military operations ▪ Forestry operations ▪ Municipal operations including drinking water and wastewater treatment, and road maintenance ▪ Activities occurring in commercial and municipal buildings, and in private dwellings including, e.g., consumer product use. See Figure 1.3.

¹⁴ A gallon (3.8 liters) of gasoline weighs between 5.8 and 6.5 lb (2.6–3 kg). The average formula of gasoline is two atoms of hydrogen for each atom of carbon (CH_2). So, by weight gasoline is ~86% carbon. The density of gasoline is ~6.1 lb/gal (0.71–0.77 g/cm³). Because gasoline is lighter than water, which has a density of 1, it floats on water.

¹⁵ See: (1) Emission facts: average carbon dioxide emissions resulting from gasoline and diesel fuel. *US EPA*, February 13, 2009. <http://www.epa.gov/oms/climate/420f05001.htm>. (2) Frequently asked global change questions. *Carbon Dioxide Information Analysis Center*. <http://cdiac.ornl.gov/pns/faq.html>. One question answered is: how much carbon dioxide is produced from the combustion of 1000 cubic feet (28.3 cubic meters) of natural gas?

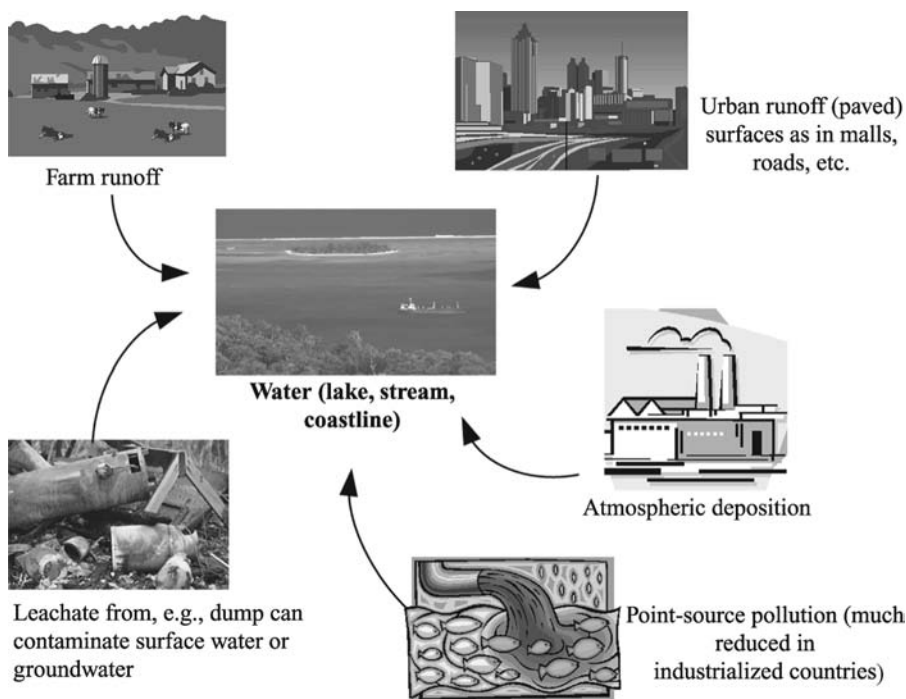


Figure 1.3

Sources of pollution to water bodies

As population grows, pollution grows. And in wealthy locales, consumption per individual typically grows over time too, and technologies become larger. Thus, without concerted effort to prevent it, pollution and other forms of environmental degradation will also grow.

Pollutant fate and transport¹⁶

Pollutants move and are transformed

Pollutants seldom stay at the point of release. ▪ Pollutants move, are transported, among air, water, soil and sediments, and often food as well. They often move *transboundary*: across state and national boundaries traveling with air or water currents. Sometimes, *biotransport* occurs meaning pollutants are carried in body tissues of migrating animals such as salmon, whales, or birds, or are found in the droppings of migratory birds. ▪ The *fate* of pollutants: a pollutant is typically transformed into end products different than the chemical form in which it was initially emitted. It may be transformed into chemicals that are no longer pollutants as when biological matter is broken down by microorganisms and incorporated

¹⁶ Ney, R E., Jr. *Where Did That Chemical Go? A Practical Guide to Chemical Fate and Transport in the Environment*. New York: Van Nostrand Reinhold, 1990.

into normal biological material within these organisms. On the other hand, a molecule such as TCDD (“dioxin”) can take years, even decades to be transformed into harmless forms.

- The process leading to the final fate can be complex. More information on the chemical fate and transport of pollutants will be presented in later chapters.

Air, soil, and water pollution is greatest at the pollutant source

Although pollutants move, their concentrations are higher near the emission source. Consider dioxins emitted as particulates from an incinerator. The highest fallout of the particulates onto vegetation, soil and water occurs near that incinerator. However, some dioxins do not fallout, but continue traveling with air currents for long distances before settling out. ▪ Wherever they fall, they may contaminate forage or grain that is then eaten by cattle and other animals – and these animals absorb these fat-soluble chemicals into their fat. Humans eating fatty meat such as hamburgers then absorb dioxins into their own fat. Chemicals such as dioxins that move into an organism’s fat may stay for years. This is a temporary “fate.” Eventually, over years the dioxins are slowly broken down and move out of the body.

Some impacts of pollutants occur far from the source

If the amount of pollutant carried in wind or water currents remains high enough, the pollutant can have effects far from where it was emitted. Examples are given below.

Water transport

In the year 2000 a Romanian mining operation spilled cyanide and hazardous metals into the Danube River, which joins the Tisza River flowing into Hungary and Yugoslavia. One Yugoslav mayor said that 80% of the fish in the Tisza near his town died. Another stated “The Tisza is a dead river. All life, from algae to trout, has been destroyed.” ▪ A few years earlier an accident at a Swiss facility washed large quantities of chemicals into the Rhine River. These were carried into France and Germany, killing fish and other aquatic life along the way.

Air transport

When a gaseous pollutant mixes evenly with the atmosphere, it can sometimes be carried worldwide. Major examples are stratospheric ozone depletion due to CFCs and global climate change due to CO₂ (Chapters 7 and 8). And, because some of these pollutants have long lives, they build up in the atmosphere over time unless their emission sources are removed. ▪ What about pollutants that change their chemical form after emission? Sulfur dioxide and nitrogen oxides (acid-deposition precursors) mix evenly in the atmosphere too. However, whereas CFCs and CO₂ are stable in the atmosphere, sulfur dioxide and nitrogen oxides are transformed from gases into tiny particles. Particles are heavier than air and don’t

mix evenly. Still, they can move hundreds, even thousands, of miles before the acid particles finish settling out onto land and water. Interestingly, although acid particles do not travel worldwide, their impact is global. This is true because acidic pollutants (most commonly emitted during the burning of fossil fuels) are released in so many places around the world.

Another characteristic of sulfur dioxide and nitrogen oxides is that they are inorganic chemicals and do not degrade in the same way as most organic pollutants do. Although only small quantities may settle out at any one spot, if emissions continue, the acids build up over time in soil and water. Acid originating in European countries harms forests and lakes in Sweden to the north. Japan's environment is damaged by coal burning in China. There are other pollutants that also travel thousands of miles, sometimes worldwide, and sometimes have impacts at a far point from the source of emissions. See Box 1.3.

Box 1.3**Pollutants can be transported in unexpected ways****The grasshopper effect**

The "*grasshopper effect*" (also called "global distillation") is a special case of pollutant fate and transport. The insecticide, *dichlorodiphenyltrichloroethane* (DDT) provides an illustration. If DDT is used in a Latin American country, it evaporates and prevailing winds blow it north.¹⁷ As DDT encounters cooler air, it condenses and comes to earth. On a warm day, it evaporates again. The process repeats itself, sometimes many times. Finally, in the far north, it is too cold for DDT to evaporate again, so it stays put – the Arctic is a *sink* for DDT and similar *persistent organic pollutants* (POPs). The POPs in the Arctic accumulate in soils and water, enter the Arctic food chain and build up in the fat of marine mammals. The Inuit, the Arctic's indigenous people eat the contaminated animals with the result that DDT builds up in their body fat to levels among the highest seen in the world. Worse, because DDT and other POPs concentrate in fat, high levels are found in the fatty portion of mother's milk. Thus, infants receive risky amounts of these pollutants as they nurse. Canada has been working to cut pollutant flow from the south and in 2008, there was good news. Canadian government studies indicate that levels of PCBs, DDT, and other POPs in the flesh of Arctic animals have either leveled off or begun to decline. This can probably be attributed to an international treaty that banned production and use of a number of POPs¹⁸ (Chapter 14).

But, if the grasshopper effect totally explained DDT accumulation in the frozen North, then DDT should be evenly distributed across the Arctic. In actuality, Canadian scientists find hotspots. Sediments in certain ponds have concentrations of DDT, 60 times higher than at nearby spots serving as controls. Investigation revealed that *contaminated droppings* of migratory seabirds (large numbers of which nest on cliffs over the ponds) were responsible for these striking observations. How did this happen? The DDT originated in southern regions where it contaminates fish in coastal waters. Seabirds eating the fish also become contaminated. Thereafter, the birds migrate to nesting sites over Arctic ponds where their

¹⁷ South of the equator, prevailing winds move the molecules toward the South Pole.

¹⁸ Scheer, R. Toxins drop in Arctic wildlife. *Emagazine.com*. July 21, 2008, <http://www.emagazine.com/view/?4292>.

DDT-contaminated droppings fall to ponds below. Those droppings are major sources of nutrition into Arctic pond ecosystems, promoting the growth of moss and plankton, which become contaminated with DDT. Insects eat the contaminated moss and plankton. They, in turn, are eaten by birds and other animals. Thus, these chemicals continue to spread in the food web and in humans. This is land-based *bioaccumulation*.¹⁹

Pollutants in sediments often don't stay buried

Sediments²⁰ are composed of soil, silt, minerals, and organic materials that have been carried in rainwater runoff from surrounding land and paved surfaces into a lake, river, or other water body. By its nature, sediment is buried by additional incoming sedimentary material. Other pollutants are often buried within the sediments too – but they are not dependably buried. ▪ Bottom-feeding organisms may take in the pollutants, thus introducing them into the food web. ▪ Riverine and coastal area sediments are sometimes dredged. When that happens, contaminants are brought back to the surface along with the sediment. ▪ Water currents, such as a strongly flowing river, also move sediments. Here, again, you see a situation where pollutants may not stay put.

Soil pollutants likewise move

Pollutants in soil also may not stay trapped. Water percolating through soil can carry pollutants down into groundwater. Rainwater can dissolve and carry off pollutants, including pesticides and fertilizers. Rainwater also erodes soil that may have pollutants absorbed within it.

The chemical fate of pollutants

Pollutants not only move. Their fate is often – as noted with acid rain precursors – to be converted into other chemicals, undergoing reactions in the atmosphere, water, and soil.

Organic pollutants²¹

Especially in moderate and warm climes, organic pollutants can be degraded in water, soil, and the atmosphere to end products that are less risky than the parent compounds. *Microorganisms*

¹⁹ Blais, J.M., Kimpe, L.E., McMahon, D. *et al.* Arctic seabirds transport marine-derived contaminants. *Science*, **309**(5733), July 15, 2005, 445.

²⁰ Erosion, sediment and runoff control for roads and highways. EPA-841-F-95-008d. *US EPA Office of Water*, December, 1995 <http://www.epa.gov/nps/education/runoff.html> [Updated February 2008].

²¹ For our purposes, it is enough to think of organic chemicals as those that contain carbon as compared to inorganic chemicals that do not contain carbon. (However, there are a limited number of inorganic carbon-containing compounds such as bicarbonate and carbonate.) Organic and inorganic compounds will be discussed in Chapter 19.

(fungi and bacteria) degrade organic wastes, including plant debris, animal remains, the organic material in trash, and also many individual organic pollutants. Microbes work in both water and soil. Microbial breakdown is a vital natural service: wastes and chemical pollutants would otherwise build up in the environment to intolerable levels. ▪ CO_2 and water are the end products of microbial metabolism when oxygen is present. An organic substance degraded all the way to CO_2 and water is said to be *mineralized*. ▪ Some microorganisms can degrade organic substances without requiring oxygen to do so. In that case, the most common end product is methane (“swamp gas”) as seen when microbial degradation occurs in the mud of rice paddies or marshes. ▪ Some synthetic organic chemicals have structures that make it very difficult for microbes to degrade them (Chapter 14). Included among these substances are polychlorinated chemicals such as dioxins, DDT, and PCBs, which sometimes persist in the environment for many years and, in very cold climates, indefinitely. ▪ Other factors contribute to degrading organic substances too. *Atmospheric oxygen* reacts with many organic substances. ▪ *Heat*: the higher the temperature, the more rapidly organic materials break down. In very cold conditions, the Arctic and Antarctic, organics may persist for many thousands of years, becoming deeply buried in snow and ice. ▪ *Sunlight*, especially the strong ultraviolet radiation of summer, contributes to the breakdown of organic pollutants. ▪ *Wave motion* in water assists degradation by bringing pollutants to the surface, exposing them to sunlight, heat, and oxygen. A chemical species, the hydroxyl radical²² contributes to the degradation of both organic and inorganic substances in the atmosphere.

Overwhelming the process

These processes provide natural services that are very effective in degrading organic substances. However, human activities also often overwhelm natural systems. Food-processors, tanneries, and paper mills are examples of facilities that, historically, released such large quantities of pollutants and wastes into rivers and lakes. Natural processes could not degrade them all, and water quality was severely degraded.

Inorganic pollutants

Inorganic chemicals are not mineralized to CO_2 and water – they are already mineral substances. Inorganic substances *do* undergo chemical reactions, but are not destroyed in the same manner as organic materials. Think about a metal. Box 1.2 noted the instance of metals burned to metal oxides. Such oxidation can also occur, albeit slowly, without combustion. You may have seen a reddish bridge: the color results from the oxidation of the iron in the bridge, that is, iron reacts with atmospheric oxygen to form reddish iron oxide. But take a sample of that iron oxide and heat it to a high enough temperature: you recover the iron while driving the oxygen back into the air. Also in Box 1.2 notice sulfur. It too reacts

²² The hydroxyl radical, composed of one oxygen atom and one hydrogen atom, has a free electron, which makes it highly reactive. It is the chief oxidizing agent in the atmosphere and is responsible for destroying organic chemicals in the atmosphere. It also can destroy inorganic chemicals (Chapters 5 and 19).

with oxygen to yield sulfur dioxide. As with iron oxide, given proper conditions, both sulfur and oxygen can be recovered.

Questions 1.3

1. Why do inorganic pollutants such as sulfur dioxide sometimes pose a greater problem in the environment than do organic pollutants such as hydrocarbons?
2. When stacks on electric power plants are built extremely high, this leads to dispersion (dilution) of sulfur dioxide and nitrogen oxide emissions. Is the dilution great enough that the emissions no longer cause environmental harm? Explain.
3. Why do organic pollutants typically degrade very slowly in groundwater as compared to surface water?
4. Why do organic pollutants typically degrade very slowly in sediments as compared to surface water?
5. Sediment contains anaerobic microorganisms (microbes that do not or cannot use oxygen). These typically produce methane as an end product. How can the methane be degraded?

Pollution that devastates

Sometimes a pollution event is so tragic that it changes our way of looking at the world. The deadly explosion that occurred in Bhopal India is one such event. Union Carbide, an American-owned factory in Bhopal, manufactured the insecticide carbaryl. The process used *methyl isocyanate* (MIC) an extremely toxic volatile liquid, which reacts violently with water. Despite this, the factory lacked stringent measures to prevent water from contacting MIC. During the night of December 2, 1984, water entered a storage tank containing 50 000 gallons (189 000 l) of MIC. ▪ The Indian government later said that improper washing of lines going into the tank caused the catastrophe. Union Carbide claimed that a disgruntled employee deliberately introduced water. ▪ In any case, 25–40 tons (23–36 tonnes) of a deadly chemical vapor settled over half this city of 800 000. About 3400 people were killed overnight, and perhaps another 15 000 died from their exposure in the following days and years. Over 40% of the women, who were pregnant at the time, had miscarriages. Tens of thousands more remained chronically ill 20-years later with respiratory infections, eye damage, neurological damage, and other ills. The catastrophe was worsened because many people lived crowded close around the factory. Moreover, poisoned residents received little medical attention at the time of the accident, at least partially because physicians didn't know what compounds were in the toxic cloud. Thus, it was difficult to know the best mode of treatment. ▪ Compensation came slowly. For many years, a Bhopal court had criminal charges pending against Union Carbide's then Chief Executive Officer, accusing him of having consciously decided to cut back on safety and alarm systems as cost-cutting measures. ▪ In 1984, Union Carbide had almost 100 000 employees, but almost went out of business and, by 1994, employed only

13 000. In 2001, Dow Chemical bought the remains of Union Carbide and, not surprisingly, found that it was now held responsible for this continuing tragedy.²³

Tiny levels of contaminants

Bhopal represents horrendous pollution. Its opposite, levels of pollutants so low that they are barely detectable presents a quandary – are such levels risky? Modern analytical chemistry is so sensitive that synthetic organic chemicals can be detected almost anywhere – in soil, water, air, food, animals, plants, and in our own bodies. As one scientist commented, “The analytical science has advanced just astronomically.” So how are we to think about such situations?

A hypothetical contaminated lake

Assume that tiny amounts of 20 different synthetic chemicals have been detected in a local lake. Each is present in an amount so tiny that it alone is highly unlikely to cause a problem, certainly not in the short run. Many of these chemicals are also found, likewise in tiny amounts in our bodies. Should we be concerned?

Possibilities that could increase your concern

1. Among the 20 contaminants are chemicals that are very similar to one another. Similar chemicals may exert toxic effects in similar ways and the levels of each, if added together, could potentially pose a problem. Organophosphate pesticides are one example. There are many different organophosphates, but each exerts toxicity in a similar way. So, if several of the contaminants are organophosphates, the total concentrations added together may cause concern.
2. Even if none of the chemicals act similarly in the body, perhaps some combination of them could exert a *synergistic* effect, that is, one chemical could magnify the effect of another chemical out of all proportion to its concentration. Testing for synergistic effects among 20 chemicals is almost impossible because we could not reasonably test them in all possible combinations.
3. Species differ widely in their sensitivity to toxicants. One species may be many times more sensitive than another. And within any individual species, including humans, there is also a range of sensitivity.

Possibilities that could decrease your concern

1. Two chemicals may be *antagonists*, i.e., one may inhibit the toxicity of another, lessening the chance of an adverse effect. Basically, one chemical acts as an *antidote* to the other.

²³ Crabb, C. Revisiting the Bhopal tragedy. *Science*, **306**(5702), December 3, 2004, 1670–1671.

2. Hundreds or thousands of chemicals are naturally present in the water; some or many may be similar chemically to the synthetic contaminants.
3. Animal and human bodies deal with contaminants using biochemical pathways that evolved over millions of years to break down natural poisons in the environment. Our bodies have no way of knowing if a given chemical is natural or synthetic.
4. A quarter century ago, chemists probably couldn't even have detected many of these chemicals. Only now with sophisticated analytical methods can we even know if there are chemicals that might be of concern.

Questions 1.4

1. 1(a) Possibilities that might increase your concern. Did any of these points increase your concern? Explain. (b) Possibilities that could decrease your concern. Did any of these points lessen your concern? Explain.
2. Even testing a few chemicals in mixtures for possible toxicity is complicated and expensive. However, it is possible to examine the effect of the contaminated water itself on aquatic life. This is called *whole effluent toxicity*.²⁴ Does whole effluent toxicity reassure you as a logical way to test toxicity? Why?
3. With which of the following conclusions do you most tend to agree and why? (a) It is alarming that many synthetic chemicals are detected. Our health, our children's health, and wildlife are likely affected. Let's find the sources of the chemicals and stop further emissions. (b) We cannot worry about every low-level contaminant. We cannot reduce emissions to zero and it would be prohibitively expensive to even reduce them to near zero. And, quite often a synthetic chemical also occurs in nature as a natural chemical. Animals and plants having evolved protective means over eons of dealing with natural poisons, and most probably can manage the chemicals in this lake too. Taking a chemical off the market could pose other problems – the chemical that replaces it in an industrial process may also pose problems that are now unknown. Let's devote our limited resources to higher risk problems.
4. Think about air pollution in an agricultural setting and ponder a situation that occurs with increasing frequency as people move into areas previously devoted to farming. New residents may complain about farm odors when farmers spread sewage sludge on their fields as a fertilizer or soil amendment. Both State and US environmental agencies support spreading carefully treated sludge. But one complaining resident said, "The human body knows when something is not good for you. Sludge must be bad. It smells so bad, it can make you nauseous." (a) Does the fact that sludge smells badly mean that airborne substances are present at a harmful level? Explain. (b) Before you can decide whether concerns are legitimate, what questions would you want answers to?
5. Another resident said, "When someone spreads sludge, you get flies in your house . . . It's awful." Do flies present a potential danger? Explain.

²⁴ Whole effluent toxicity. *US EPA*, <http://www.epa.gov/waterscience/methods/wet/> [updated July 2008].

6. If you were thinking of moving into a rural area: (a) What questions would you want to ask? (b) Should sellers be required to provide you with information on sludge-spreading or similar operations around their homes?
7. Consider that you already live in a rural setting. (a) How would you react if a large industrial farm (one with thousands of pigs, cattle, or poultry crowded into a limited space) moved into your rural neighborhood? What would your environmental and health concerns be?

SECTION III

Degradation of global environmental health

- At the Earth Summit held in Rio de Janeiro, Brazil, in 1992, the heads of 120 governments met together. Their mission was to decide how to deal with Earth's environmental problems including climate change, air and water pollution, deforestation, and loss of biodiversity (extinction of species). One result was Agenda 21, a strategy for sustainable development or, as one participant phrased it, "a blueprint for how humankind must operate in order to avoid environmental devastation."
- In 1997, 158 governments gathered for an Earth Summit+5 to discuss progress, but they found that environmental conditions were worse. A Malaysian delegate exclaimed, "Five years from Rio we face a major recession . . . a recession in spirit. We continue to consume resources, pollute, and spread and entrench poverty as though we are the last generation on Earth."
- Yet again in 2002, governments gathered for a World Summit on Sustainable Development. Despite a continuing grim environmental picture, participants took a different approach: they recognized that environmental sustainability is not possible when great numbers of people lacked even basic amenities such as safe drinking water and sanitary facilities. One major outcome was that all 191 UN member states pledged to meet eight Millennium Development Goals by 2015.²⁵ One goal was to cut extreme poverty in half while "ensuring" environmental sustainability. As you read this section, notice that gross pollution often goes hand in hand with gross poverty.

Pollution in less-developed countries

Environmental degradation in impoverished countries, often called *less-developed countries* is, according to the Asia Development Bank, "pervasive, accelerating, and unabated" (see Table 2.1). In an Atlantic Monthly article, William Langewiesche

²⁵ End poverty 2015, Millennium Development Goals. *UN Department of Public Information*, 2008, www.un.org/millenniumgoals.

describes one city, New Delhi, India, where "... the pollution ... seemed apocalyptic. The streams were dead channels trickling with sewage and bright chemicals, and the air on the street barely breathable."²⁶ Rivers in some cities are described as "open stinking sewers." ■ The World Health Organization (WHO) tells us that 2.6 billion people have no access to hygienic toilets. They use buckets, bushes, ditches or rivers; if lucky, they have latrines. More than a billion lack safe drinking water. The WHO estimates that at least 1.6-million lives are lost each year due to lack of access to sanitation and clean drinking water. Millions more are left chronically ill from the water they must drink. ■ Millions of deaths result yearly from infections resulting from eating contaminated food. ■ Just by breathing the air, children in a heavily polluted city such as New Delhi inhale the equivalent of two packs of cigarettes each day. ■ Living in rural areas may be worse: of up to 3 million deaths result worldwide each year from air pollution, about half arise from intolerable indoor air pollution. This occurs because almost 90% of impoverished households burn straw, wood, or dried manure inside their homes for cooking and often for heating, with very poor ventilation. Women and children are most affected. ■ The effects of pollution go beyond deaths to impacting people's ability to live healthy lives. One illustration: almost half the world's population, especially small children may suffer from water-borne diseases.

Pollution with worldwide impact: China²⁷

China, with its 1.3 billion people (about 20% of the world's population) will be used in this text to illustrate the environmental problems confronting rapidly developing countries. India, nearly as populous, also has severe environmental problems as it undergoes rapid industrialization and increasing consumption.²⁸

China's environment

As China works to bring its people out of poverty, its economy has been growing enormously with ever more heavy industry, cities, and coal-burning power plants. Moreover, historically, the Chinese have emphasized human dominance over nature. Animals and plants are seen as

²⁶ Langewiesche, W. The shipbreakers. *Atlantic Monthly*, **286**(2), August, 2000, 31–49.

²⁷ (1) Fu, B., Zhuang, X., Jiang, G., Shi, J., Lu, Y. Environmental problems and challenges in China. *Environmental Science and Technology*, **41**(22), November 15, 2007, 7597–7602. (2) Lorenz, A. and Wagner, W. China's boom and doom. *Der Spiegel*, February 12, 2007, http://www.salon.com/news/feature/2007/02/12/china_pollution/. (3) Global warming: China says: Et tu? *Seattle Post-Intelligencer*, November 16, 2007 http://seattlepi.nwsource.com/opinion/339989_carboned.html. (4) Yardley, J. China's turtles, emblems of a crisis (impacts of pollution, hunting, and rampant development), *New York Times*, December 5, 2007.

²⁸ Sharma, D.C. By order of the court: environmental cleanup in India. *Environmental Health Perspectives*, **113**(6), June, 2005, A394–397.

useful for medicine or food, not as important in themselves. Nearly 40% of mammal species are endangered and, for plant species, the percentage is higher still. Half of China's wetlands have been destroyed. This environmental degradation is so extreme that it is leading to social unrest,²⁹ presenting an "acute political challenge to the ruling Communist Party." The World Bank estimates that pollution has already cut China's gross national product by 8–12%.

- Air in some cities is barely breathable. By European standards, only 1% of the Chinese people breathe safe air. Observers note that "Chinese cities often seem wrapped in a toxic gray shroud."³⁰ The pollutants responsible are emitted by coal-burning power plants, smelters, and chemical factories. Emissions of sulfur dioxide and nitrogen dioxide have increased greatly in the past decade. China has an ever-increasing number of motor vehicles burning low-grade gasoline, so cars and trucks have become the leading source of the heavy haze hanging over many large cities. Burning fossil fuels is a major cause of air pollution worldwide and, not surprisingly, this is true in China too, which meets about two-thirds of its energy needs by burning coal. It already burns more coal than the United States, Europe, and Japan combined. That coal is burned inefficiently resulting in greater pollutant emissions.
- Hundreds of millions of China's 1.3 billion people lack access to safe drinking water. You can see why when you realize that less than half the cities have sewage treatment plants and a great many factories dump untreated waste into surface water. Water in about a third of China's rivers is so degraded that it cannot be used for agriculture or even industry. A State Environmental Protection Administration (SEPA) official has said that "Severe water pollution has become a threat to public health and is affecting social stability." A SEPA official referred to the Hai river as "dark green and stinking," a water body where aquatic life is extinct, demonstrating "that the traditional industrial growth mode has strained China's resources and environment to an unbearable extreme."³¹ Pollution has led to whole villages being designated "cancer villages," and pollution is now blamed as a leading cause of death in China.
- Gross pollution goes beyond harming people. The air pollutant ozone damages crops and other vegetation. As do sulfur dioxide and nitrogen oxides emitted from coal-fired power plants; these are converted in the atmosphere to acidic pollutants which, after falling to earth, damage aquatic life and terrestrial vegetation. The haze gives rise to a phenomenon known as "*global dimming*," meaning a decrease in the amount of sunlight reaching Earth. This means less light for photosynthesis, thus a lowered yield of crops and other plants. Dimming is observed in other places around the planet too, not just China.
- Transboundary transport of pollutants: Air pollutant particles formed in one locale are often chemically distinctive; they have a specific chemical signature: it is often possible to discover the sources of pollutants by chemical analysis. Thus, we can see that China's

²⁹ Buckley, C. China environment chief says pollution fuelling unrest. *Reuters*, July 5, 2007, <http://www.alertnet.org/thenews/newsdesk/SP250873.htm>.

³⁰ Kahn, J. and Yardley, J. As China roars, pollution reaches deadly extremes. *New York Times*, August 26, 2007, http://www.nytimes.com/2007/08/26/world/asia/26china.html?_r=2&oref=slogin&oref=slogin.

³¹ Lorenz, A. Interview with China's Deputy Minister of the Environment. *Spiegel Online*, March 7, 2005, <http://service.spiegel.de/cache/international/spiegel/0,1518,345694,00.html>.

pollution spreads far beyond its borders. Polluted air is wind-blown to South Korea and Japan where it is felt as irritated eyes and throats, so much so that now some cities issue warnings about the health danger. In Europe, a brown haze traced to China stretches from Germany to the Mediterranean Sea. Soot particles in increasing amounts are carried across the Pacific Ocean to far away California. The US EPA reports days when up to 25% of the particulate matter in the skies above Los Angeles can be traced to China.³²

▪ Water also transports pollutants across boundaries: the sewage from 65 million people living along the Songhua River has greatly contaminated that river. This is carried into far eastern Russia where “the river has been stinking since 1997” and where impacts are felt by the 4 million inhabitants on the Russian side. They report: “For the past 12 years, the fish have smelled like chemicals.” A much publicized incident occurred in November 2005 when a chemical plant exploded on the Chinese side spilling large quantities of benzene into the Songhua River. First the benzene impacted the local city of Harbin, which had to cut off water supplies to its 9 million inhabitants for four days, then moved on into Russia slowly being diluted as it traveled.

China’s economic growth and the environment

Economic growth is tremendously important to China. Unfortunately, studies show that when economic growth rates are adjusted for the economic damage caused by pollution, they fell to almost zero in some provinces. Deputy Minister of the Environment, Pan Yue believes that severe environmental degradation will bring the country’s economic miracle to an end. He notes that “acid rain is falling on one-third of Chinese territory, half the water in our seven largest rivers is completely useless, while one-quarter of our citizens do not have access to clean drinking water. One-third of the urban population is breathing polluted air, and less than 20% of the trash in cities is treated and processed in an environmentally sustainable manner.” Yue also pointed out that China has five of the ten most polluted cities in the world. China’s SEPA has a limited number of employees to serve a country of 1.3 billion.

The difficulty in being optimistic

Optimists believe that it is still possible to build a “green economy,” even avoid some of the historical bad experiences of industrialized countries. Steps that China is taking include working to rein in motor vehicle emissions; requiring new buildings to halve the energy used for heating, lighting, and air conditioning; and to halve the energy needed to generate each unit of Gross Domestic Product (GDP). Although China is largely fueled by coal now, it is committed to renewable energy, and is making major investments in renewable energy projects. Still, there is pessimism because of the tremendous environmental destruction already evident, and because local officials often ignore environmental mandates coming

³² Herro, A. Chinese air pollution crosses Pacific, reaches Western United States. *Eye on Earth* (a joint project of the Worldwatch Institute and the Blue Moon Fund) March 26, 2007, <http://www.worldwatch.org/node/4985>.

from the national government. Also, as one Chinese environmental scientist said, “The whole idea of ecology and ecosystems is a new thing in the culture.” Other efforts that China is making will be noted throughout this text.

Poverty and the environment

Although poverty need not be closely associated with a degraded environment, it often is (Figure 1.4). Good governance by an honest dedicated government can accomplish much. An example is Curitiba, Brazil, described as a first-world city in a third-world country. Less dramatic is the Indian state of Kerala where very poor people have better environmental health than do many in more prosperous Indian states. However, in these cases, one is speaking of a low population as compared to China’s 1.3 billion people. However, there too, there is room for individual provinces and cities to lead the way. ■ Remember, also that pollution still occurs in wealthy countries. In the US cities of Houston and Los Angeles, air pollution levels often rise above healthy levels. Moreover, consider food contamination: the US Center for Disease Control and Prevention says that millions of Americans each year suffer diarrhea attributed to contamination of foods by infectious organisms.



Figure 1.4

Poverty and pollution: child and baby on trash heap in Kenyan slum. Credit: Joseph Kinyua, student photographer. Reproduced with kind permission of the Mwelu Foundation

SECTION IV

Root causes³³

“If current predictions of population growth prove accurate and patterns of human activity on the planet remain unchanged, science and technology may not be able to prevent either irreversible degradation of the environment or continued poverty for much of the world” (Joint Statement of the US National Academy of Sciences and the Royal Society of London, 1992). One member commented, “Scientists . . . do a lot more talking about [pollution] than about the basic forces driving those things.” Toward the end of the first decade of the twenty-first century, this statement continues to apply. ♦ But, what is driving pollution? The equation, $I = PAT$ (Impact = Population × Affluence × Technology) is often used as a simple term to describe the environmental impact of humans: 1. Population: the Earth’s increasing population places increasing pressure on our environment. 2. Affluence: disproportionate levels of consumption occur among the wealthy. 3. Technology: our large-scale technologies often have destructive environmental impacts.

Population growth³⁴

Twentieth-century population growth was phenomenal (Figure 1.5). In 1998, a National Geographic article noted, “Of all the issues we face [in] the new millennium, none is more

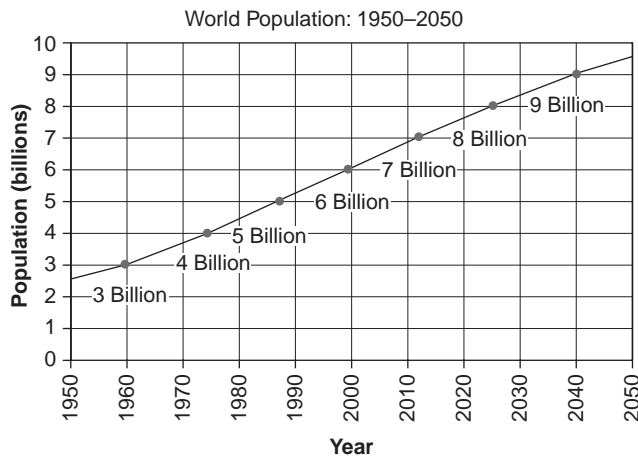


Figure 1.5

World population growth from 1950 and beyond. Credit: US Census Bureau

³³ Palmer, M., Bernhardt, E., Chomesky, E. *et al.* Ecology for a Crowded Planet. *Science*, 304(5675), May 28, 2004, 1251–1252

³⁴ (1) Katner, JUN issues “final wake-up call” on population and environment. *International Herald Tribune*, October 25, 2007 <http://www.iht.com/articles/2007/10/25/europe/enviro.php> (2) Data Finders. *Population Reference Bureau*, 2009. <http://www.prb.org/Datafinder.aspx> (3) US and World Population Clocks. *US Census Bureau*, November 22, 2006. <http://www.census.gov/main/www/popclock.html>

important than population growth.” In 2008, a UN report marking World Population Day estimated that world population will grow from 6.7 billion to 9.2 billion by 2050. Today, with some exceptions, parents around the world are having fewer children. Diseases – AIDS most prominently – have lowered populations in some countries. Because of AIDS, a number of countries in sub-Saharan Africa have an average life span less than 40 years. Populations in Western European countries have stabilized; some are decreasing. However, US population is increasing rapidly, especially through immigration, and the fact that immigrants have more children than natives. US population may double in the next half-century. And, as a 2007 UN report warned us, even if world population growth ceased today, the current population is not environmentally sustainable without major changes in how we live. See Box 1.4.

Box 1.4**Mega-cities**

Almost all population growth is occurring in “explosively growing” cities. By 2015, according to UN estimates, the world will have 23 mega-cities, those with populations greater than 10 million; all but four are in less-developed countries. These include Bombay, Lagos, Dhaka, Sao Paulo, Karachi, and Mexico City. Already, half or more of the world’s people live in cities, which grow much faster than a country’s overall population. Many have very young populations. Harvard biologist Edward Wilson observed, “The people . . . are far younger than those in the industrial countries . . . The streets of Lagos, Manaus, Karachi, and other cities in the developing world are a sea of children. To an observer fresh from Europe or North America, the crowds give the feel of a gigantic school just let out.”³⁵ ▪ Just one garbage dump, Payatas in Manila, a Philippine city of ten million receives 3000 tons (2722 tonnes) of garbage a day. Dumps get trash off the streets, but most poor cities cannot pick up all their trash, leaving streets littered with paper, plastic, bottles, and scraps of all kinds. The common practice of open burning of trash fouls city air. ▪ Only a small percentage of residents in less-developed countries own motor vehicles, but their uncontrolled emissions make the air difficult to breathe. ▪ Cities can hurt the health of their own people and, moreover, “Modern high density settlements appropriate the ecological output and life support functions of distant regions through trade and commerce, the generation and disposal of wastes, and the alteration of nature’s cycles.” As cities become ever larger, according to a Johns Hopkins report they become “black holes” soaking up the ecological output of entire regions³⁶. At the same time, cities have environmental benefits including a smaller per capita consumption than is the case with less dense settlements.³⁷

³⁵ Sloan, J.D. The bottleneck (excerpt from Wilson, E.O., *The Future of Life*, UK: Alfred A. Knopf with Little, Brown). *Scientific American*, February 2002, http://www.mnforustain.org/wilson_e_o_bottleneck.htm.

³⁶ Hinrichsen, D., Blackburn, R., and Robey, B. Cities will determine living standards for mankind. *Population Reports* (Special Istanbul+5 edition), June, 2001.

³⁷ Diamond, J. What’s your consumption factor? *New York Times*. January 2, 2008. http://www.nytimes.com/2008/01/02/opinion/02diamond.html?_r=1&oref=slogin

Questions 1.5

1. Being blamed for the large amounts of pollution that they produce irritates the Chinese. They point out that much of the pollution produced in China occurs as it manufactures products for export to Europe and the United States. Often, in fact, the polluting factories have been subcontracted by, or are owned by, foreigners. And foreign investment continues to rise. Whom shall we blame? What word might be more descriptive than blame? How can we respond to this issue?
2. Students in prosperous societies, upon learning that AIDS may reduce population in badly affected countries sometimes respond. It's all very sad, but the decreased population may be good. Aside from the moral implications of allowing these deaths, history tells us that a population reduced by disease (such as Europe's medieval plagues) quickly rebounds. And, unlike other infectious diseases, which infect all portions of the population, AIDS primarily kills young adults. Sub-Saharan Africa has about 15-million orphans, a number expected to continue to grow in coming years (See Brown and Halweil in Further reading). (a) How likely is it that a country with large numbers of uncared-for orphans, one that is also losing the most productive portion of their population, will avoid social unrest? (b) How could social unrest affect a country's environment?

Our consumption

Less than 1.5 billion individuals live in wealthy countries. They sometimes blame environmental degradation on the huge and growing populations in poor countries. Less-developed countries resent this, and blame high levels of consumption in wealthy societies for world environmental degradation and resource depletion. Individuals in North America, Western Europe, Japan, and Australia do consume, on average about 32 times more resources than poorer individuals around the globe, and produce proportionately more waste and pollutants. Even in China, individuals consume about 11 times more per capita than the impoverished. ■ The rich also impact environments distant from where they live. This happens when they buy products produced in countries with poor environmental protection. Citizens of wealthier countries are slow to confront these issues. Meanwhile, those in less-developed countries desire standards of living equal to those of developed countries.

Technology

Large-scale technologies can be environmentally devastating. A case in point is "mountaintop removal" mining described by one reporter as "mountain-range removal" that leaves "flat moonlike expanses of land." Coal-mining companies in the US Appalachian states blast away as much as 700 feet (213 m) of mountaintops, to reach coal seams. Then 20-story high machines (draglines) shovel away rocky debris at 130 tons (118 tonnes) a bite. Debris is dumped into valleys below, burying hundreds of miles of mountain streams. Streams not completely buried are left highly polluted with silt and chemicals. Companies claim it is too expensive to handle

their waste any other way. ▪ A 1977 US law forbade this practice, but mining companies evade enforcement. In fact, the administration of President Bush changed one word in a regulation – the word “waste” was changed to “fill” – thus coal companies legally dump “fill.” The noise, dust, truck traffic, and sometimes flying rocks, effectively destroy nearby communities driving people away. Companies are required by law to restore a mountain’s contour after mining. This seldom happens. ▪ Another waste resulting from mountaintop mining is “spoil” (slurries of coal dust and polluted liquids). Hundreds of impoundments have been built to contain it. In the year 2000, one impoundment atop a Kentucky mountain broke through into an underground coal mine beneath it. From there about 300 million gallons (1135 million liters) of a “molasses-like” sludge spilled into the Big Sandy River and tributaries, smothering about 1.6 million fish and wiping out local snakes, turtles, amphibians, and mussels. In the town of Inez, Kentucky, it buried lawns to depths as great as 7 feet (2.1 m), polluted public water supplies, clogged water treatment plants, and led to the shutdown of schools, restaurants, laundries, and power generation facilities.³⁸

Consider, too, wastes produced by other types of mining. ▪ Only 2.5% of the lead ore taken from US mines is lead. The other 97.5% is waste. ▪ Gold is much worse: only 0.00033% of the gold ore mined (7 235 000 000 tons or 6 500 000 000 tonnes) is gold. The other 99.99976% is waste – this happens because even ores with tiny amounts of gold are worth mining because of gold’s value. ▪ Modifying technology to lessen the environmental damage of mining and other large-scale technologies is a major challenge.

SECTION V

Our actions have consequences

Each of us impacts our environment

Consider a car. We are responsible for more than just the running of a car once we buy it. We are responsible for the environmental impact of recovering the resources used to make the car, and the impacts of manufacturing it. The car itself then produces pollution as we drive it, and has other impacts as we use and maintain it. At the end of its life, it has further impacts as its parts are disposed of or recycled. ▪ When we buy a car or any product, we accept its environmental impacts, but don’t ordinarily know what those impacts are. ▪ Our ignorance extends to food products. We don’t know the conditions under which they were grown, or processed, and, we may not even know how waste from that food is disposed of.

Think about a few of these: ▪ Affluent individuals often buy flowers in winter, unaware that the less-developed countries growing those flowers use more dangerous pesticides or larger quantities of pesticides than would be allowed in wealthy countries. Moreover, those pesticides often pollute the water in the countries growing the flowers, and workers

³⁸ Warrick, J. Appalachia is paying price for White House rule change (impacts of mountaintop removal mining). *Washington Post*, August 17, 2004, A01.

may be heavily exposed. ▪ Coffee drinkers typically don't know that they are drinking "sun coffee." Growing coffee in full sun enhances bean yields. However, "sun plantation" coffee lacks the tree canopy around shaded trees, so fewer insect-eating birds and spiders find shelter among them. Thus, more pesticides must be used to destroy insects. And lacking a tree canopy, less tree litter is produced so more synthetic fertilizer is needed. ▪ Most of the shrimp eaten in North America is imported so diners don't see the pollution and environmental degradation produced by shrimp farms in the less-developed world. ▪ Even when agricultural products are grown within a wealthy country, buyers often don't know how they are produced. Think about the excreta produced by the animals we eat. The US Senate sponsored a study that showed that the United States produces 130 times more animal waste each year than human waste. But there are no sewage treatment plants for animal waste. Instead facilities housing, for instance, thousands of pigs store their urine and feces in open air lagoons, and later spray the waste onto fields. When amounts sprayed are greater than the soil can absorb, rain washes those pollutants into nearby water bodies.

Evaluating life cycle impacts

There is a method to evaluate the environmental impacts of products including agricultural products. It is *life-cycle assessment* (LCA). LCA evaluates a product's impact at each stage of its life including the pollution and waste produced and energy used in: ▪ Recovering, processing and transporting the resources used to make it. ▪ Manufacturing, use, and maintenance. ▪ Recycling, reusing or disposing of it. We will come back to LCA later.

The "tyranny of small decisions"

You and I impact our environment in many ways. "One of the more intimate ways . . . is taking a pill or washing (your) hair." Breakdown products of medicines leave the body in urine and feces and enter the sewage system. Also going down the drain are shampoos, cosmetics, toiletry products, laundry detergents, and other household chemicals. ▪ Because wastewater treatment plants do not remove all these substances, some enter rivers and their sediment, and groundwater. Many pharmaceuticals including antibiotics are detected in rivers. Some are detected in drinking water although at very low levels. ▪ Wildlife has the highest exposure to the substances from toilets, laundry rooms, and kitchens, especially fish and other aquatic life living below the effluent pipes of municipal and other wastewater treatment plants.

Antibiotics and hormones

Although present at low concentrations, some chemical wastes from households pose real concerns. ▪ Exposing aquatic life and bacteria to even low levels of antibiotics can promote the development of resistance. Resistance means bacteria develop means to "fight back," to fend off the antibiotics used to treat humans and animal disease. ▪ Hormones, such as those

Box 1.5

Our actions do have impact

▪ “More and more we realize that a large part of remaining environmental problems comes from the cumulative impacts of our individual actions. These impacts are far more subtle and ... harder to manage than the single smokestack or wastewater discharge.” (Martha Kirkpatrick, Maine Department of Environmental Protection.) ▪ “More than half the nation’s water pollution problems spring from everyday actions.” (National Geographic Society and the Conservation Fund.) ▪ “We know that further progress on many fronts, notably air and water quality, means getting a handle on diffuse sources of pollution that result from millions of people making countless individual choices. (William Reilly, former US EPA administrator.)³⁹

Questions 1.6

1. Conservationist Wendell Berry writes “One of the primary results – and one of the primary needs – of industrialism is the separation of people and places and products from their histories.” From an environmental perspective, explain why knowing the origin of consumer products or agricultural goods matters?⁴⁰
2. What does the following statement mean to you?: “The more population grows, the more the rights of the common will impinge on the rights of the individual.”
3. Choose a product.⁴¹ Then, to the best of your ability, answer the following questions. (a) Where was it produced? (b) What are the environmental impacts of recovering the resources needed to make it? (c) Of manufacturing it? (d) Of transporting it? (e) Of using it? (f) What happens to it at the end of its useful life?
4. Corporations often spend more money on advertising than they do on environmental control. Environmentalists believe this fuels a “culture of waste” leading to heavy use of energy and other resources. People with money are enticed to buy unneeded products – more clothes, another car or TV, a new product to replace one that still works, or second homes. (a) What does the word sustainability mean to you? (b) Is consumerism compatible with sustainability? Explain.
5. Think of two ways that society might control the release of antibiotics and hormones into sewage systems. Are there ways to reduce the impacts of these substances?
6. (a) What are five decisions that you routinely make in your personal life that impact the environment? (b) How might you make those five decisions differently by taking environmental impact into account?

³⁹ Brower, M. and Lean, W. *The Consumer’s Guide to Effective Environmental Choices: Practical Advice from the Union of Concerned Scientists*. New York: Three Rivers Press, 1999.

⁴⁰ Berry, W. *Back to the Land*, in *The Best American Science and Nature Writing*, D. Quammen (ed.). Boston: Houghton Mifflin Co., 2000.

⁴¹ Ryan, J. C., and Durning, A. T. *Stuff, The Secret Lives of Everyday Things*. Seattle: Northwest Environment Watch, 1997.

found in birth control pills, are a second “intimate waste” of much concern. These can exert hormonal action on wildlife even at very low levels.

Environmental agencies in developed countries regulate an ever-increasing number of chemicals from an increasing number of sources. But can government regulate every chemical and every source of emissions? Again, think of motor vehicles, more than 200 million in the United States alone. Although these are a major source of air pollution, many people resist having to test emissions from their vehicles, or maintaining them in a manner that minimizes emissions. Could federal, state, and local environmental agencies realistically monitor every small business, every home, and every vehicle? What are other ways to deal with pollution and environmental degradation? Chapter 2 will begin to address these questions.

Delving deeper

1. Examine “How Reducing Greenhouse Gas Emissions Will Affect the US Economy” at www.climate.yale.edu/seeforyourself. Go through this exercise, making sure that you understand the points being made, and come to your own conclusions. Be prepared to discuss your findings.
2. Read Dombeck, M. The forgotten forest product: water. *New York Times*, January 3, 2003, http://www.uwsp.edu/cnr/gem/md%20pubs/NYT_3jan2003.htm. Think about Dombeck’s statements. Then relate them to the following question: if trees are planted in an area with limited water resources, are they still environmentally helpful? Explain.
3. Pose questions to yourself about the American dustbowl. Does it still have relevance to the United States or to the country in which you live? Find answers on the internet, in the library or by interviews.
4. Five billion poor individuals in the world desire higher living standards. Is it possible for us all to be wealthy? Write a brief essay on the subject. If your thesis is that wealth is more than material goods or money, then apply that principle to yourself too. Read Diamond, J., What’s Your Consumption Factor? *New York Times*. January 2, 2008, http://www.nytimes.com/2008/01/02/opinion/02diamond.html?_r=1&oref=slogin.

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“We aren’t passengers on Spaceship Earth; we’re the crew. We aren’t residents of this planet; we’re citizens. The difference in both cases is responsibility.”

Astronaut Rusty Schweikart

Some pollution problems are daunting; others less so. So this chapter begins with a brief overview as to how we can separate the “trivial” from the serious, whether the risk of a chemical or of a broader environmental problem. The chapter emphasis is on preventing or controlling pollution. Also introduced are the tools that assist us in moving toward sustainable societies. Section I introduces risk assessment concepts, how to evaluate the magnitude of a given risk, chemical risk assessment, and comparative risk assessment. Section II asks, how do we reduce, even eliminate, pollution’s risks? Legislation is important. Many laws stress trapping pollutants already produced. The pollution prevention (P^2) paradigm, also called source reduction is more effective. P^2 involves changing a process so that it produces less pollution or, sometimes none at all. Section III introduces industrial ecology (IE), which goes beyond P^2 . IE examines pollution holistically, searching for means to mesh the human enterprise into the natural environment. Some tools of IE are briefly examined including life-cycle assessment and design for the environment.

SECTION I

Risk assessment

For many years, society has struggled with the problem of how to evaluate environmental risks. Risk assessment tools have been developed over decades, and continue to be refined. ■ *Chemical risk assessment* examines the risk of individual chemicals. ■ *Comparative risk assessment* is more holistic: it compares a number of environmental risks, not all of which are pollution risks.

Chemical risk assessment

Chemical risk assessment is used to evaluate the risk¹ of individual chemicals. Members of the US National Academy of Sciences and other scientists have struggled for many years to

¹ Hazard and risk: A hazardous chemical is one with the potential to cause human illness or injury. It can be toxic, corrosive, reactive, flammable, radioactive, or infectious, or some combination of these. A substance, no matter how hazardous cannot cause harm unless there is exposure to it. If there is exposure, then we evaluate *risk*, the

develop chemical risk assessment into a useful tool. ▪ Let's consider a hazardous waste site in which a number of chemicals have been identified: we need to know the *hazard* of each chemical present, i.e., what is the potential for the chemical to cause illness or injury.² ▪ But *hazard is different than risk*. For there to be a risk, there must be exposure to the chemical. Thus, we analyze the site for evidence as to whether there is now, or in the future may be, *exposure* to the chemical. If there is exposure to one or more chemicals, then we need to know which of the chemicals pose the greatest risks, and we must concentrate on the high-risk chemicals. ▪ In Chapter 4 we will see that risk assessment raises questions that science alone cannot answer: scientists may rate a chemical as being a low risk. But a risk that is acceptable to one person may be unacceptable to another. However, applied consistently, chemical risk assessment is trusted within its limitations.

Certain characteristics of a chemical can warn us that chemical may pose a problem.

1. Does the chemical *persist* in the environment and within living creatures? Metals are chemicals that cannot be broken down, they are persistent. But some synthetic organic chemicals are persistent too because microbes, plants or animals have difficulty degrading them. Among such chemicals are dioxins and DDT.
2. Does the chemical *bioaccumulate*, build up in plants and animals to concentrations higher than in the environment? Again, dioxins and DDT are examples of chemicals that bioaccumulate.
3. Is the chemical *toxic*?

If the answer to all three questions is yes, then we refer to the chemical as *persistent*, *bioaccumulative*, and *toxic* (PBT). Even a low level of a PBT chemical warns us to treat it respectfully. Chapter 14 will address organic chemicals that are PBTs; Chapter 15 deals with metals, including PBT metals.

Comparative risk assessment

Comparative risk assessment is used to compare environmental problems. It aims to distinguish high-priority risks from medium- and low-priority risks. It can compare one complicated environmental issue such as acid deposition to another such as stratospheric ozone depletion (Tables 2.1 and 2.2). It can also be used to compare a pollution issue to a non-pollution issue. ▪ Even imperfect answers help us decide which issues will receive more attention and resources. ▪ Comparative risk assessment is often used in making environmental policy: are we spending more dollars on high risk than low risk problems? At the same time, a criticism of comparative risk assessment is that “low risk” problems may be dealt with inadequately or not at all. If you think about this criticism, you can see that comparative risk assessment, like chemical risk assessment goes beyond questions that

probability of harm. The risk can range from low to high. Many questions are asked during an evaluation, such as: how much exposure occurred? How did exposure occur – through air, water, soil, food?

² The US EPA uses an exhaustive procedure to analyze a site for the chemicals it contains and whether it poses a high enough risk to place it on the National Priority List (NPL). NPL sites receive federal attention, whereas individual states are left to clean up less risky sites.

Table 2.1 Global high-risk problems (assessed by comparative risk assessment)**High risk pollution issues¹**

Fresh water pollution and scarcity
 Air pollution (especially ozone, fine particles)
 Global warming
 Acid deposition
 Municipal solid waste generation
 Hazardous waste generation
 Increasing energy use
 Insufficient knowledge of chemicals in use
 Nitrogen-fertilizer and heavy-metal pollution

Other high-risk environmental threats²

Human population growth
 Land degradation
 Deforestation and loss of forest quality
 Marine fisheries over-fishing
 Wildlife habitat loss
 Extinction of plant and animal species
 Loss of biodiversity

High-risk threats to human health³

Drinking-water pollution
 Heavy air pollution, outdoors and indoors
 Untreated human waste and lack of basic sanitation (resulting in exposure to pathogenic microorganisms)

¹ The OECD (Organization for Economic Cooperation and Development) has 29 member states, mostly developed nations including the United States, the UK, and other western European countries, Australia and New Zealand, and Japan. The conclusions of these two organizations were very similar.

² Information from (1) UNEP report: Global Environment Outlook 2000, and the OECD Environmental Outlook report.

³ From the World Health Organization (WHO)

science can answer. ■ It includes evaluations of community values, quality-of-life and economic issues: how important to us is the corrosion of city monuments caused by acid haze or a haze hanging over a national park? How important is an unattractive algal bloom at a popular lake?

A summary of steps that may be used in comparative risk assessment follows.

Choosing issues to compare

Assume you are part of a group comparing environmental risks. You find that you must make judgments at the very beginning: which among the dozens, hundreds of environmental issues will you compare? Look at Table 2.1, and the issues evaluated. For simplicity's sake only high risk problems are shown, all of which are worldwide problems. ■ The issues you

Table 2.2 Analyzing Environmental Risks

CRITERION AND EXPLANATION	EXAMPLES
What is the scope of the effect?	
1. How large an area is exposed to pollutant?	1. Part of a state? The whole nation? The whole world?
2. How many people are exposed?	2. Ten thousand? Millions?
3. For a resource, how much is exposed? ^a	3. A small percentage of a nation's forests? All of them?
How likely is an adverse effect?	
1. Among those exposed to the pollutant?	1. A small chance of a few people suffering asthma? Or, thousands or millions developing asthma?
2. On an exposed resource?	2. The acid rain is neutralized by an alkaline soil? Or, acid rain falling on an already acidic soil?
If an effect occurs, how severe would it be?	
1. Among exposed people?	1. Suffer no obvious ill effect from a site containing lead? Or will exposed children suffer a lowered IQ?
2. On an exposed resource?	2. Fish in a polluted lake have stunted growth for one season? Or millions are killed?
What are the trends for a specified pollutant?	
1. Is its concentration in the environment increasing, decreasing, or staying the same?	1. Carbon dioxide with an ever-increasing level? Or, dioxins with falling levels in developed countries?
2. What is the pollutant's life span?	2. Ground-level methane, which can degrade in a few days? Or, a metal, which does not degrade?
3. Does its bioaccumulate?	3. A chemical easily eliminated from the body? Or, one such as dioxins or lead that accumulates?
What is the trend?	
1. Does a resource continue to be degraded, or has the situation stabilized?	1. A nation's wetlands (forests, fishing grounds, etc.) continue to be degraded? Or is the loss curbed?
	2. Coastal waters support fish spawning and growth? Or do they support growth poorly?
What is the recovery time?	
1. Can the environment recover from this stress? Or is permanent damage likely?	1. Recover in ten years, as from certain oil spills? Or, a hundred years or more for excess atmospheric CO ₂ ?

^a The word "resource" refers to a natural resource – such as a wetland, lake, forest, fish or other wildlife, soil, etc.

compare may be specific to your city, state or province. If you focus on a city, you would likely examine issues immediately relevant to that city such as local hazardous waste sites or local water pollution problems. Nonetheless, even when doing local evaluations, you may need to look at how global issues such as climate change or acid deposition may be impacting your local environment.

Getting technical assistance

To arrive at meaningful answers, your group needs expert information on each issue. Group members must agree on *which* experts to include: whom do you trust to provide objective

information? Among the questions that you might expect experts to evaluate are those in Table 2.2. Also, what is the quality of the information? What are the information gaps? However, regardless of how well informed your experts and their ability to evaluate the issues, there are always information gaps and uncertainties. Typically no further research is done during the risk assessment process to fill in such gaps.

Making decisions

Having finished dealing with the chosen experts, your group examines and discusses what you have learned. And, *how can you compare risks that seem to have no relationship to one another?* How, for instance, do you compare “habitat alteration and destruction” to “stratospheric ozone depletion”? How do you compare air pollution to ground water pollution? Look at Table 2.2 for some approaches to these questions. Given even the best expert opinion, judgments must be made. And because members of your group probably represent many backgrounds, industry, environmental organizations, government, and academic institutions, each of you may interpret exactly the same information differently. Moreover, even as you make judgments, you recognize that what you choose as most important is not absolute, and that others may revisit your work in the future. Nonetheless, many continue to find these exercises worthwhile.

SECTION II

Using legislation to protect nature’s services

Laws in the United States

Environmental laws existed before 1970, but none controlled pollution and hazardous chemicals comprehensively. The 1970s saw a dramatic change in the United States. Major laws enacted include the following. ▪ The *Clean Air Act* (CAA) in 1970, the *Clean Water Act* (CWA) in 1972, and the *Safe Drinking Water Act* (SDWA) in 1974. Legislators then turned to land pollution and passed the *Resource Conservation and Recovery Act* (RCRA, pronounced “rick-rah”) in 1976 to control the management and disposal of solid waste, including municipal and hazardous waste. ▪ The late 1970s revealed many abandoned hazardous waste sites around the United States. Congress responded by passing the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA or Superfund) to clean up such sites. ▪ Toxic chemical laws were also passed. The *Federal Insecticide, Fungicide, and Rodenticide Act* (FIFRA) in 1972, and the *Toxic Substances Control Act* (TSCA, pronounced “tosca”) in 1976 regulate chemicals not already regulated under the laws passed earlier. For example, TSCA mandated controls on polychlorinated biphenyls (PCBs), chemicals not covered by other legislation. A major TSCA mandate was to develop an inventory of all commercial chemicals used in the United States.

Subsequently, any chemical not on the inventory would be subject to scrutiny by the EPA before it could be used commercially or imported. ▪ Passing TSCA was an attempt to “close the circle,” to ensure that all chemical issues were addressed. However, the 1984 tragedy in Bhopal, India resulted in the “right-to-know” legislation, the *Emergency Planning and Community Right-to-Know Act* (EPCRA) in 1986. ▪ Important international treaties have been passed too. TSCA comes up again in Chapter 4 (Section VI).

End-of-pipe regulations

The laws just noted produced many so-called *command-and-control* and *end-of-pipe* regulations, which can be very effective when applied to large facilities. The Clean Water Act can illustrate this. ▪ When passed in 1972, only 30% of American waters were judged fishable and swimmable. By 1994, this figure was about 60%. *Fishable* means that fish from the water are safe to eat or that the quality of the water is good enough for fish to live in it. *Swimmable* means the water can be used for swimming without fear that infectious organisms or other contaminants are present at levels potentially harmful to health. ▪ After passage of the CWA, many treatment plants were built by industries and cities to recover hazardous components from their wastewater before the water was released into a receiving body: those pollutants were removed *end-of-pipe*. ▪ In response to the Clean Air Act, air emissions were trapped end-of-pipe. End-of-pipe controls were also placed on motor vehicle emissions. ▪ Hazardous wastes were treated before disposal. ▪ Municipalities and industries designed and built secure landfills to replace old leaking uncovered dumps. End-of-pipe accomplished a lot.

Laws in less-developed countries

Less-developed countries may have excellent environmental laws on the books, but often enforce laws poorly. This happens because governments are weak or corrupt, or because governments lack money or power to enforce them.

Controlling pollution by command-and-control

End-of-pipe refers to capturing pollutants after they are formed, but before release. ▪ Consider sulfur dioxide, a major pollutant produced by burning coal in electric power plants. A power plant may capture much of that sulfur dioxide from its stack to prevent it from entering the air. ▪ Or consider chromium, a metal often found in the wastewater of metal plating firms. Chromium is removed from the wastewater to prevent its release into a river. ▪ In both these instances, the pollutant still exists, but it has been captured so that it can be disposed or reused responsibly.

Box 2.1

The struggle to reduce pollution in China³

China has excellent laws on its books nationally, but has been unable to get local officials to enforce them. Local officials are more eager to generate revenue and jobs than to control pollution. In 1983, China included environmental protection as a basic national policy, but pollution and environmental degradation continued. In 1994, China developed a strategy to achieve sustainable development. Nonetheless, as factories, mines, power and industrial plants continued their “frantic growth,” the situation continued to worsen. Consider one illustration: China tried to reduce sulfur dioxide emissions between 2001 and 2005; instead emissions increased 28%.

China has environmental organizations and activists. However, although the government approves of environmental advocacy, it is hostile to “political agitation.” So, despite China’s dire environmental problems, some environmental organizers are prosecuted. “Pollution has reached epidemic proportions in China, in part because the ruling Communist Party still treats environmental advocates as bigger threats than the degradation of air, water, and soil that prompts them to speak out.” However, activists continue to emerge. One is Ma Jun, whose observations led him to believe that the reason companies in developed countries pollute less than those in China is because corporations are sensitive to public pressure. In developed countries, the people can publicly criticize poorly performing companies in a number of ways and, if necessary, boycott companies. So Ma Jun decided that pressure must be exerted on Chinese companies too. He and other knowledgeable volunteers formed a non-governmental organization (NGO), the *Institute of Public and Environmental Affairs*. This institute finds needed information by examining reports on major polluters put out by municipal, provincial, and national environmental agencies. They also follow news reports of interviews with environmental officials. They have details on 8000 companies officially cited for exceeding discharge standards into China’s rivers and lakes. (The Institute’s database shows which companies are polluting rivers and lakes and which ones. They place the information on the China Water Pollution Map Web site (<http://www.ipe.org.cn>) an online Chinese-language searchable database. It discloses details of about 10 000 water violations, about a quarter of them by foreign firms. More recently, it developed the China Air Pollution Map (<http://air.ipe.org.cn>).

People are paying attention. Fifty companies have asked to have their names removed from the list. For this to happen, they must show compliance with standards as shown by a third-party audit. The Chinese media also pays attention to the database. The media has become sharply critical of the fact that the government, notwithstanding its promises to clean up highly polluted air and water, has not done so. Moreover, above and beyond the already bad everyday emissions, major spills also continue to occur.

Ma Jun is working to gain the attention of foreigners who buy Chinese goods. His NGO wants to push for improved environmental performance of multinational corporations (MNC) that

³ China Environment Forum. *Woodrow Wilson International Center*, 2009. http://www.wilsoncenter.org/index.cfm?topic/id=1421&fuseaction=topics.documents&doc/id=496229&group_id=233293.

operate in China. The Institute has found several hundred multinational corporations (MNC) violating water and air pollution laws. Some are well-known corporations such as Pepsi, Dupont, and 3M, which have good environmental records in developed countries. Why do they behave less well in China? Fines for violations are *very* low compared to the costs of controlling emissions; local governments often shield MNCs because they provide employment, pay taxes, and contribute to local growth; and the public is often unaware of the violations. So although better performance would be expected, it's very easy for MNCs to violate laws. Ma Jun's organization has begun work to name and shame them.

A positive project of the Institute is the *Green Choice Initiative*, undertaken cooperatively with 20 other NGOs. Its purpose is to inform the public about environmentally responsible products. At the same time, it provides consumers with the names of companies cited for violations of environmental laws. These malefactors are major consumer-goods companies, about half of them foreign.

As "traditional industrial growth ... strains China's resources and environment to an unbearable extreme," the government is struggling to get away from economic growth regardless of environmental costs. It is spending many billions to control water and air pollution, and solid waste. And, very importantly, in 2007 government officials rejected the building of factories that would have been worth billions of dollars because they failed to meet standards. The national government too has begun using the "name and shame" technique on major polluters.⁴

Limitations of command-and-control⁵

End-of-pipe controls cannot recover 100% of a pollutant. An industry or electric utility may remove the first 80% from a waste stream efficiently and cost-effectively. Removing the last 20% may cost 10 times more than the first 80%, and yet a small amount of the pollutant still remains.

A specially designed incinerator may destroy 99.99% of the hazardous materials that it burns. For pollutants of special concern, a more costly technologically sophisticated incinerator can destroy 99.9999%. But the incinerator cannot destroy that last tiny amount. Even

⁴ Further Reading on China: (1) Buckley, C. China environment chief says pollution fuelling unrest. *Reuters*, July 5, 2007, <http://www.alertnet.org/thenews/newsdesk/SP250873.htm>. (2) China punishes cities for polluting rivers. *Reuters*, July 4, 2007. (3) Kahn, J. Choking on growth. Part III. In China, a lake's champion imperils himself. *New York Times*, October 14, 2007, http://www.nytimes.com/2007/10/14/world/asia/14china.html?_r=1&oref=slogin. (4) Liu, Y. Stronger regulation needed to improve corporate pollution record in China. *Eye on Earth (Worldwatch Institute and Blue Moon Fund)*, February 6, 2008. <http://www.worldwatch.org/node/5601>. (5) Nakanishi, N. Chinese group says to name-and-shame air polluters. *Reuters*, December 13, 2007. (6) Vidal, J. The looming food crisis. *Guardian*, August 29, 2007, http://www.polarisinstitute.org/the_looming_food_crisis. (7) Tremblay, J. F. China releases new cleanup plan. *Chemical & Engineering News*, **85**(49), December 2, 2007, 12. (8) Tremblay, J. F. Talks with Ma Jun, tireless environmental activist seeks to nurture China's environmental conscience. *Chemical & Engineering News*, **85**(40), October 1, 2007, 26. (9) Tremblay, J. F. Free trade or fair trade. *Chemical & Engineering News*, **86**(1) January 7, 2008, 16.

⁵ (1) Greening industry, new ideas in pollution regulation. *The World Bank*, 2009. <http://go.worldbank.org/TFGRCF3JJ0>. (2) What is green engineering. *US EPA*, September 13, 2007, http://www.epa.gov_oppt_greenengineering_pubs_whats_ge.html (this paper shows a figure, "Proliferation of environmental laws and regulations," which is worth examining).

to capture the amount they were designed to remove takes careful monitoring and ongoing equipment maintenance.

- Another problem with end-of-pipe is what to do with the pollutants recovered? The recovered pollutants must sometimes be treated themselves. An organic waste may need to be incinerated. A metal waste, if not recyclable, may need burial in a hazardous waste landfill. Moreover, the cost of pollution control – recovering, treating, and disposing of recovered wastes – continues to rise as do the costs of managing municipal wastes and sewage.
- Another limitation of command-and-control regulations that industry very much dislikes is “*one size fits all*.” A regulation tells industrial facilities not only to limit the release of specific pollutants, but also tells them exactly how they must accomplish that reduction: all facilities must reduce emissions in the same way. But no two facilities are identical, and frequently there is more than one way to reach the same end. ■ Years ago, a *Wall Street Journal* article told the following story. The AMOCO refinery of Yorktown, Virginia, was required to install a \$41 million system using a specific (one size fits all) technology to capture benzene emissions. However, AMOCO, working with the EPA, found another method that could capture five times more benzene for only \$11 million. But, the law was inflexible so the EPA could not modify the requirements. Thus, a greater amount of money was spent to capture less pollutant. ■ Recounting another such instance, in 1995, a *Scientific American* article described regulations intended to ensure the safe handling of hazardous wastes. The automotive industry produced a sludge containing zinc. In earlier years, factories sent the sludge to smelters to recover and reuse the zinc. However, in the 1980s, the zinc sludge was listed as a hazardous waste, so smelters no longer accepted it. Instead, now deemed hazardous the sludge had to be treated and disposed of in accordance with strict regulations. Clearly, in both the examples just given, the results were *unintended consequences*. Most agree that such problems arise because we try to deal with environmental problems one at a time – bit by bit – instead of looking at issues holistically. ■ Given the huge number of detailed regulations that have resulted from complex environmental laws, some counterproductive results are inevitable. The US EPA has been working to develop regulations that take these problems into account, and to find ways to modify “one-size-fits-all” when it is logical to do so. Nevertheless, the EPA must exercise flexibility within the constraints of the laws.
- Complicating the situation further is that some believe that the only acceptable amount of a pollutant is zero. This gives rise to the problem of the *vanishing zero*. Analytical chemists devise ever more sensitive methods to detect a pollutant. So, even if essentially all a pollutant has seemingly been removed, newer more-sensitive detection methods may detect it again. Thus, a chemical undetected and unregulated in one year could be detected and regulated the next.

A right-to-know law⁶

The world reacted with horror to the Bhopal disaster described in Chapter 1. Then, US citizens discovered that a Union Carbide plant in Institute, West Virginia, used the same

⁶ ScoreCard, the pollution locator. *Environmental Defense*, 2005, <http://www.scorecard.org/env-releases/us-map.tcl>.

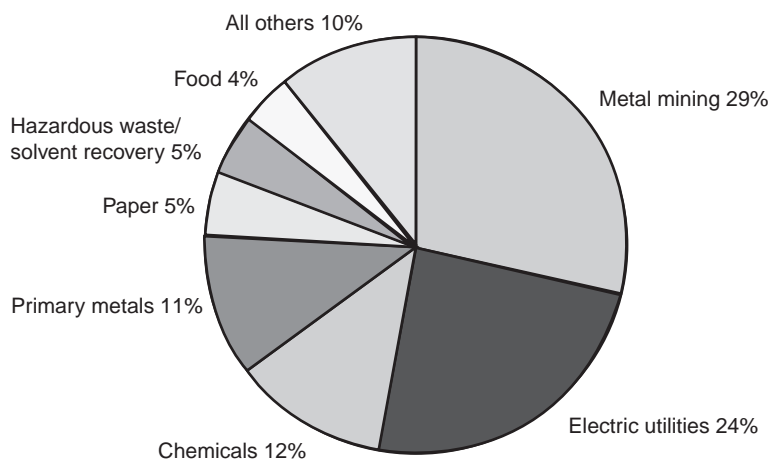


Figure 2.1

Industries accounting for TRI disposals or other releases in 2006. Credit: US EPA

highly reactive chemical, methyl isocyanate (MIC). This plant also lacked adequate means to keep water away from the MIC. The plant was quickly redesigned. More generally, an aftermath of Bhopal was the realization that such disasters could happen anywhere. After recognizing this, the US Congress passed the Emergency Planning and Community Right-to-Know Act (EPCRA). ▪ The legislation requires industries and communities to prepare emergency plans to minimize harm in case of an accidental chemical release from a factory, or from a truck or train transiting a community.⁷ ▪ The law also gave Americans easy access to information on the hazardous chemicals used in, stored in, or transported through their communities. ▪ Another section of the law, the *Toxics Release Inventory* (TRI)⁸ requires businesses to make public each year their emissions of any of about 600 chemicals such as ammonia, hydrochloric acid, methanol, toluene, acetone, and lead and cadmium (Figure 2.1).⁹ The TRI does not require that emissions be reduced only reported. However, resulting public pressure on industries and municipalities has led to a halving of releases of TRI chemicals to air, surface water, and underground injection wells. ▪ An editorial in the journal, *Environmental Health Perspectives*, stated, “This legislation may yet prove to be one of the most important events in the history of environmental health because it instigated the idea that people had the right to know about hazardous agents being manufactured, used, or stored in or around their communities. In a free and open society, the concept of “right to know” of possible risks to their health seems fundamental.”¹⁰

⁷ Emergency Planning. *US EPA*, May, 2008, <http://www.epa.gov/oem/content/epcra/index.htm>.

⁸ Browse TRI Topics. *US EPA*, <http://www.epa.gov/tri/topics/topics.htm>.

⁹ (1) Toxic Release Inventory Program. *US EPA*, March 5, 2009, <http://www.epa.gov/tri/index.htm>. (2) Consolidated List of Chemicals Subject to the Emergency Planning and Community Right to Know Act and Section 112(r) of the Clean Air Act. *US EPA*, October, 2006, http://www.epa.gov/tri/chemical/reg_requirements/Oct_2006%20Title%20III%20List%20fo%20Lists.pdf.

¹⁰ Hook, G. E. R. and Lucier, G. W. The right to know is for everyone. *Environmental Health Perspectives*, **108**(4), April 2000, <http://www.ehponline.org/docs/2000/108-4/editorial.html>.

Criticisms of the TRI

▪ A major criticism of TRI is that it merely reports the amount of a chemical released. It does not tell us how toxic the chemical is nor whether humans and wildlife are actually exposed to it. That is, TRI tells us the hazard of a chemical emission, but not its *risk*. ▪ Environmental Defense, an environmental organization points out that TRI emissions¹¹ only account for 4% of the total cancer risk nationwide. It is emissions from mobile sources such as cars and trucks that contribute 88% of the cancer risk. Diesel exhaust poses an especially high risk. Nonetheless, motor vehicle emissions are not reported. Thus, the question is raised: would a different form of disclosure provide more useful information? A recent approach may be able to do this.¹² ▪ Other critics note that TRI releases tell us very little about a facility's overall environmental performance.

TRI laws in other countries

- Europeans, too, see disclosures as a powerful and low-cost means of informing the public, which may then pressure companies to reduce emissions. The European Union (EU) version of "right-to-know" legislation is the EPER (European Pollutant Emission Register). It registers releases of 50 pollutants which, in aggregate, account for 90% of total chemical emissions from about 10 000 industrial facilities. Categories include heavy metals, pesticides, industrial chemicals, and dioxins. Unlike the US version, it also includes greenhouse gases such as carbon dioxide.¹³
- Egypt, the Czech Republic, and Mexico have similar programs too, but only for chemicals deemed especially hazardous. China, until 2008, had no TRI at all. How does this affect pollution? Take Hong Kong, which suffers from air pollution coming across the border from mainland China's Guangdong province where companies didn't need to publicly report their emissions. Two factors made this frustrating: Guangdong's government monitors air quality and had information on the identity of the major polluters, but wouldn't expose those companies. Secondly, many Guangdong facilities known to pollute Hong Kong are owned by Hong Kong residents.

¹¹ ScoreCard, the pollution locator. *Environmental Defense*, 2005, <http://www.scorecard.org/env-releases/us-map.tcl>.

¹² This approach compares the toxicity of any chemical with that of a *reference* chemical using a Toxic Equivalency Potential (TEP). There are two reference chemicals in the TEP approach. If "Chemical X" is a carcinogen, the reference chemical is the carcinogen, benzene. If "Chemical X" is a non-carcinogen the reference chemical is toluene. This allows us to compare release of "Chemical X" pound for pound with the reference chemical. ▪ Using toxicity equivalencies, it was found that, among the carcinogens emitted to air those that pose the greatest hazard to human health are carbon tetrachloride and lead (and lead compounds). This is true although, e.g., styrene and acetaldehyde are released in the greatest amounts. ▪ For non-carcinogens, toluene and carbon disulfide are released to the air in the largest quantities. However, although lower amounts of mercury and lead compounds are released, it is they that pose the greatest hazards; in particular, they pose major concerns because they can adversely affect human development and reproduction. *Commission for Environmental Cooperation*, Report profiles data on industrial releases and children's health, May 17, 2006, <http://www.cec.org/news/details/index.cfm?varlan=ENGLISH&ID=2704>.

¹³ What is EPER, the European pollutant emission register? European Environment Agency, 2003 <http://eper.eea.europa.eu/eper/introduction.asp?i=>.

Can we completely control pollution?

TRI requires industrial facilities to report many legal chemical emissions. In 1988, the first year TRI emissions were divulged, people were concerned to learn that industry had released nearly 2.6 billion pounds (1.2 billion kg) of chemicals into the air the previous year. But this was only the beginning of the story: at about the same time a nationwide study was done on all volatile organic chemical (VOC) emissions into air. The study concluded that 47 billion pounds (21.3 billion kg) of VOCs were released to the air each year – 18-times greater than 2.6 billion. Where did these VOCs come from? ▪ A portion came from industries not then required to report TRI emissions including mining operations, sewage treatment plants, landfills, and hundreds of thousands of small businesses such as dry cleaners, printers, painters, shops maintaining motor vehicles, and even bakeries and food-processing operations.¹⁴ ▪ But the striking point was: half of the 47 billion pounds (21.3 billion kg) came from motor vehicles, driven billions of miles a year. And, remember, motor vehicle emissions may pose a much greater risk than TRI chemicals. A new car pollutes much less than one made in 1970, but each year more people drive more vehicles more miles. And many drivers do not maintain their vehicles to run as cleanly as they were designed to run.

You and I, on a smaller scale, also contribute VOC emissions when using paints, pesticides, and other aerosol sprays. Emissions for which one person is responsible are small. However, multiply yourself by hundreds of millions of people and some of these emissions become significant. ▪ Environmental agencies regulate an increasing number of chemicals from a great many sources. But can government regulate each and every emission? Again, remember motor vehicles are a major source of air pollution. Yet many people resist testing, and reducing emissions from personal vehicles, or do so only under duress. Could federal, state, and local environmental agencies monitor every small business operation, every home, and every vehicle? What other approaches are available?

The waste management hierarchy (WMH)¹⁵

End-of-pipe control means capturing the pollutant after it is formed, but before its release into the environment. End-of-pipe control has been called first-generation thinking, very important but limited. ▪ A second-generation concept is *pollution prevention* (P²), which means producing less of the pollutant or waste in the first place or, sometimes eliminating it. P² is at the top of a waste management hierarchy (WMH) (Table 2.3). Valuable as they are, reuse and recycling are a step below P² on the WMH. ▪ Treatment, the third step is used when a material can no longer be reused or recycled. The purpose of treatment is to reduce

¹⁴ As one example, about 44 million pounds (20 million kg) of the VOC hexane are released into US air each year. The largest source of hexane releases is from its use as an organic solvent to extract millions of tons a year of food oil from soybeans, and to extract millions of tons more from other seeds and grains.

¹⁵ Pollution prevention and recycling links. *California Department of Environmental Control* <http://www.dtsc.ca.gov/InformationResources/resources.cfm#PPR>.

Table 2.3 Ranking preference in waste management**The waste management hierarchy (WMH)**

Pollution prevention
Reuse/recycle
Treatment
Disposal

the volume or toxicity of the waste. ▪ At the bottom of the hierarchy is disposal. The individual steps of the WMH are described below.

Steps in the waste management hierarchy

Pollution prevention¹⁶

P² is decreasing or eliminating the amount of pollution produced. Developing steps to reduce pollutant emissions when a product is manufactured is P². As is finding less noxious chemicals to use in a process where previously hazardous chemicals were used. Using less energy also means P² because pollutant emissions are reduced – emissions that result from generating and using energy. Likewise, using less water is P². ▪ You may have gathered from this short description that P² can save its practitioners money – using less material, less energy, less water, fewer controls to protect workers, and less pollution that needs to be expensively captured.

The first step a company often takes in a P² program is to evaluate its housekeeping practices. ▪ When a toxic substance is spilled, it becomes hazardous waste and the materials used to clean it up also becomes hazardous waste. So, minimizing spills is P². Even if the spilled substance is not toxic, it still takes materials – that would otherwise not be used – to clean up the spill. ▪ To make P² work, top management must commit itself to its success. At the same time employees are the ones who regularly work with a process. They are often best informed as to where and how to modify a process to decrease pollution. Some companies – 3M Corporation is a prominent example – offer bonuses to employees to develop workable P² ideas. After many years of implementing P², the employees of 3M continue to generate ideas: P² is an ongoing process. See Tables 2.4 and 2.5.

For a company to improve housekeeping may not be difficult. Likewise, P² practices, such as changing from a hazardous solvent to an equally effective, but less hazardous solvent may not be difficult. Even changing one step in a production process may be implemented without great difficulty. But, to consider changing a whole production process, the rate of return must be high because the risk is much greater – more money is spent without assurance that the new process will work properly. ▪ In the United States, the only law addressing P² is the 1990 Pollution Prevention Act. It does not mandate P². Rather it uses the TRI to encourage it: when a business reports TRI emissions, it must also describe

¹⁶ Pollution prevention, basic information. *US EPA*, January 10, 2008, <http://www.epa.gov/p2/pubs/basic.htm>.

Table 2.4 Industrial Use of P²

Previous action and result	Change that lessened pollution
Using trichloroethane (ozone-depleting and toxic organic solvent) to clean metal. When dirty, it is a hazardous waste. ¹	Replaced trichloroethane with a water-based solvent, which works just as well.
Painting steel joists by dipping them into open vats of paint; large amounts of fumes are released.	Layered paint vats with ping-pong balls. These cut emissions while not interfering with dipping the joists.
Using inefficient motors, which waste energy.	As each old motor broke down, purchased a more energy-efficient motor.
Packaging detergent in a box too large for its contents. The packaging is thrown away.	Used a smaller box. Redesigned packaging to use less material.
Manufacturing plastic beverage bottles.	Redesigned bottle to use less plastic, but remained equally strong.
A coal-burning electric power plant captures the sulfur dioxide that forms as coal is burned.	Switch to a source of coal with lower-sulfur content.

¹ Substitutes in metal cleaning. *US EPA*, January 2, 2009, <http://www.epa.gov/ozone/snap/solvents/lists/metals.html>.

Table 2.5 P² in the motor vehicle industry

A manufacturer designs a vehicle that:	The result is:
Has reduced tailpipe emissions	Less air pollution is produced
Has better fuel mileage or is of lighter weight but is still safe	Less air pollution is produced Gasoline is conserved
Uses less-toxic chemicals in manufacturing the vehicle	Worker exposure to chemicals is reduced. Hazardous waste generation is reduced.
Can be disassembled at the end of its life	Some component parts can be reused. Others are recycled. Materials are conserved. Less pollution is produced

Notice that these examples could also be used to illustrate Design for the Environment.

what it is doing to reduce emissions. ■ The EPA and state governments also collaborate with industry to stimulate P². In one EPA effort called the *33/50 Program*, 1150 participating companies reduced emissions of 17 chemicals that are very toxic or emitted in especially large amounts, first by at least 33% and later by at least 50%. In the *Green Lights Program*, both the EPA and the US Department of Energy, work with businesses and institutions to reduce the energy used in lighting. There are also programs to reduce energy use by other appliances and, in industry, to reduce energy use by industrial motors. But, remember that it's not only industry that can benefit from P² – so can government agencies, municipalities, institutions, and individuals; see Table 2.6. ■ At its most effective, P² is part of a broader

Table 2.6 Individual examples of using P²How is each of the following an example of P²? You:

Purchase a car with better fuel economy than your former car had. Maintain the car so that its fuel economy remains high

Avoid buying disposable batteries for trivial purposes

Buy energy-efficient appliances, electronics, and light bulbs and turn them off when not in use

Turn down the thermostat at night

Practice water conservation in your home and yard

Purchase durable consumer goods

Repair appliances and electronics rather than buying new ones

Buy products with as little packaging as possible

Drink tap water or beverages prepared at home

Eat less meat: this means less land, energy, water, pesticides, and fertilizers are used because grain is eaten directly rather than fed to livestock

concept – *Design for the Environment* (DfE). In DfE, from the moment that a new product is conceived, designers work to make its environmental impact as low as possible. DfE aims for a product with a longer life, fewer environmentally harmful effects, and a product that can be easily disassembled at the end of its life for reuse or recycling. We will see examples of DfE in later chapters.

Other forms of P²

▪ Another term with similar meaning to P² is *source reduction*, using less of a raw material when making a product; the result is less waste produced. This can involve a change in the design, manufacture, purchase, or use of a material or product (including packaging).

▪ Reuse of a product or material is also source reduction (as is conservation). So is using less energy because less energy, a resource is being wasted.

▪ Reducing worker exposure to toxic chemicals during product manufacture has another term, *toxics use reduction*, also a form of P².

Recycling and reuse¹⁷

Most people are familiar with *recycling* common materials such as paper, glass, and aluminum cans.

▪ Aluminum recycling offers dramatic advantages. Recycling saves 95% of energy as compared to mining aluminum from scratch and then making new containers; it also reduces air and water pollution by 95%. Recycling also conserves aluminum resources (source reduction).

▪ Recycling other metals offers savings in energy, resources, and pollution although less dramatically than for aluminum.

▪ *Reusing* a product is often closely related to P² – fewer resources are needed and less pollution is produced. As an illustration,

¹⁷ Reduce, reuse, and recycle. *US EPA*, February 18, 2009, <http://www.epa.gov/epawaste/conservation/rrr/index.htm>.

Table 2.7 Examples of industrial recycling and reuse**Reuse**

A welding plant returns empty wire spools to the supplier, who reuses them

Parts from auto engines are refurbished and reused (this is remanufacturing)

Recycle and reuse

An oil refinery refines motor vehicle oil for reuse

A paint manufacturer reprocesses waste household paint for reuse

A factory cleans a metal with a solvent, *reusing* the solvent several times. When it becomes dirty, it purifies and reuses it – it doesn't become waste

A factory recovers and reuses water used in manufacturing its product

Recycle

A paper manufacturer uses post-consumer paper – paper already once used by consumers – to make more paper.

A manufacturer produces products from used glass, metal or plastic (such as bottles, cans, packaging)

A manufacturer stamps each plastic piece used as to what kind of plastic it is (so plastics can be separated after use for recycling into products)

Table 2.8 Individual recycling and reuse**You:**

Thoughtfully recycle every household item that you can

Recycle aluminum cans, and *also* clean foil and other Al items

Find an organization to use your leftover paints rather than disposing of them

Take used oil and antifreeze to a service or recycling station

Compost grass clippings and leaves rather than placing them in the trash

Reuse paper and plastic bags many times over, or, buy fabric bags

about one-third less energy is needed to clean and refill glass bottles than to recycle them. However, glass is heavy and the energy saved would be lost if the bottles were transported to a distant market so local bottling plants would need to be used – local bottlers were once typical, not unusual. See Table 2.7 for industrial recycling and reuse examples, and Table 2.8 for examples of individual efforts.

Recycling can be problematic. ▪ Recycling produces waste, sometimes a great deal. Consider paper. Coatings and fillers amount to as much as 50% of the paper's weight, and must be recovered during the recycling process. Then, because they have no practical use, they are disposed of in a landfill. ▪ And, although metal and glass can be recycled indefinitely, paper or plastic can be recycled only a few times before losing quality. ▪ For some products, if recycling is not done responsibly major problems can result as you will see in Chapter 12's discussion of computers and other electronics taken to less-developed countries for "recycling."

Treatment

When a material cannot be recycled or reused, the third step on the waste management hierarchy is treatment. *There are two important reasons to treat a pollutant or solid waste* – to reduce its volume or to reduce its toxicity (or other hazard). ▪ The major reason municipal solid waste (MSW) is burned – considered a treatment – is to reduce its volume. ▪ The major reason hazardous waste is treated is to reduce its toxicity. Other than incineration, there are many ways to treat hazardous waste. Table 12.1 provides examples. Treatment of hazardous waste is required before it can be disposed of.

Disposal

Disposal is at the bottom of the waste management hierarchy, but responsible disposal is of major importance. A municipality must dispose of its MSW and sewage sludge in ways carefully defined by law in developed societies. Both industry and municipalities sometimes produce huge amounts of waste, which makes responsible disposal especially important. Landfills are carefully regulated. ▪ But, as we will see in Chapter 11, responsible disposal is often a challenging task. Laws do not ordinarily tell individual citizens how they must dispose of their waste. However, public policy sometimes makes it costly to citizens if they do not remove recyclables first before disposing of the rest as waste. Information can be obtained from a town recycling office or library to aid disposing of household hazardous wastes like paint or oil. In the future, if society moves toward industrial ecology (defined below) at least some wastes may become resources.

Questions 2.1

1. Do the hazardous chemicals transiting your community pose a risk? How?
2. Companies are only required to report their TRI emissions, not to reduce them. Citizens do pressure them to reduce emissions. Other than using laws and regulations to require reductions, what are other possible actions that government could take?
3. (a) One company replaced the organic solvent, trichloroethane with a water-based solvent. How is this P^2 ? (b) Consider another company that used trichloroethane to clean metals, but used it only one time and then discarded it. The company discovered that it could reuse trichloroethane several times before it becomes too dirty to perform effectively. Could this reuse also be considered P^2 ? Explain.
4. Why is reuse ordinarily environmentally preferable to recycling?
5. A packaging manufacturer develops more compact packaging for its client's product, packaging that is also lighter in weight. What are three ways that this represents P^2 ?
6. (a) Unilever Corporation makes the detergent, *All*. It developed a 32-ounce bottle of *All* that washes as many loads as 100 ounces did before.¹⁸ How is this source reduction (or P^2)? (b) How is it P^2 to use a detergent that works just as well in cold water as in hot?

¹⁸ McCoy, M. Going green, the cleaning products industry embraces sustainability. *Chemical and Engineering News*, **85**(5), January 23, 2007, 13–19.

7. In addition to examples in Table 2.6, what are two P² steps that you as a vehicle owner could take?
8. After thinking about it: what are two steps that you could easily take at home?¹⁹
9. There are many more examples of individual recycling than seen in Table 2.8 – what are two of these?
10. A researcher finds a simple inexpensive means to remove arsenic from drinking water. What step in the WMH does this represent? Explain.
11. Energy is a resource too: which step in the WMH is being used in the cases below? Explain. If unsure of what a case refers to, go to the internet for an explanation. (a) Heat is recovered from sewage effluent.²⁰ (b) Heat is recovered from a power plant's air emissions. (c) Methane is collected from a landfill for use as a fuel. (d) Regenerative braking is used in a hybrid car. (e) Incandescent light bulbs are replaced with compact fluorescent bulbs.
12. Emissions from livestock are a major source, 18%, of global greenhouse gases. That's more than the transportation sector generates. (Greenhouse gases are those that contribute to global warming.) What are two ways to reduce greenhouse gases coming from livestock?

SECTION III

Pollution prevention is not enough²¹

Industrial symbiosis²²

Pollution prevention is tremendously attractive, but we cannot avoid all waste and pollution. Moreover, P² alone cannot accomplish other critical environmental aims such as preserving species biodiversity or saving land. What if we could, legitimately redefine the word, waste? Kalundborg, a city in Denmark, is a model of treating wastes as useful by-products in a process called *industrial symbiosis*: by-products, whether material, energy, or water are sold or given to nearby facilities, which use or reuse them (Figure 2.2).

- Asnaes is Kalundborg's coal-burning electric power plant. Asnaes uses the high-temperature steam obtained from burning coal to generate electricity. Lower temperature

¹⁹ Pollution prevention at home. *US EPA*, January 14, 2009, <http://www.epa.gov/p2/> [info for greening at a number of places].

²⁰ Doyle, A. Oslo's sewage heats its homes. *Reuters*, April 10, 2006, <http://www.planetark.com/dailynewsstory.cfm/newsid/35952/story.htm>.

²¹ Greening industry, new ideas in pollution regulation. *The World Bank*, 2009, <http://go.worldbank.org/TFGRCF3JJ0>.

²² Gertler, N., and Ehrenfeld, J. R. A down-to-earth approach to clean production. *Technology Review*, Feb/Mar, 1996, 50–54.

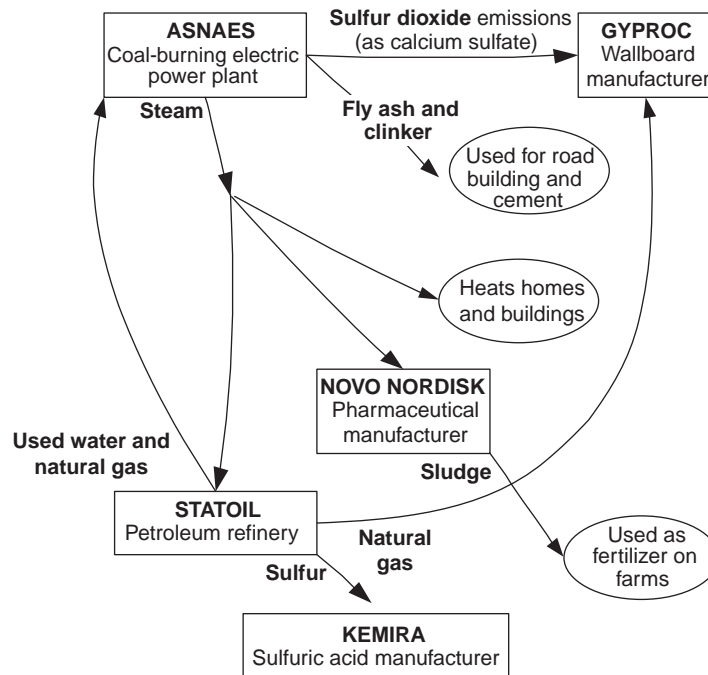


Figure 2.2

Industrial symbiosis in Kalundborg

steam, which would otherwise become thermal pollution, is piped into 5000 Kalundborg houses and buildings to provide space heating, and also into two other plants (Statoil and Novo Nordisk) to provide them with needed steam. ■ Asnaes uses a scrubber to capture the sulfur dioxide emissions resulting from burning sulfur-contaminated coal, converting them into *calcium sulfate*, which is sold to Gyproc. Gyproc uses calcium sulfate to make wallboard. Previously, Gyproc purchased calcium sulfate from Spanish mines, but now Asnaes meets most of its needs. ■ Asnaes, instead of landfilling the fly ash and clinker that results from burning coal, sells them for use in road-building and cement making.

- Statoil is a petroleum refinery. Oil refineries often burn off the natural gas found in petroleum. However, Statoil pumps its gas to Gyproc, which burns it to fire the ovens that dry wallboard. Gyproc has butane gas backup for times that Statoil is shut down for maintenance. Statoil also sells gas to Asnaes, so Asnaes burns gas as well as coal. ■ Natural gas contains sulfur too, which is removed by a process that produces hot liquid sulfur. This is shipped 50 miles (80 km) to Kemira where it is used to produce sulfuric acid. ■ Fresh water is scarce in Kalundborg. Statoil pipes its used water to Asnaes, which uses it to clean plant equipment, provide feed water to its boiler, and reduce the thermal pollution that it produces. Overall, water reuse schemes in the town have reduced demand 25%.
- Novo Nordisk is a pharmaceutical firm using microorganisms to ferment food-grade material into usable products. ■ Fermentation produces a nutrient-rich sludge. Steam – piped in from Asnaes – is used to kill surviving microorganisms. The disinfected sludge is then distributed via pipeline to a thousand nearby farms that used it for fertilizer.

Table 2.9 Pollution prevention and industrial symbiosis in action¹

Facility and problem	Action and result	Facility and problem	Action and result
1. Los Angeles Airport disposed of 19 000 tons of food waste a year	<ul style="list-style-type: none"> - Sends to sewage treatment plant. - Microbes digest waste and generate methane - An electric utility burns the methane - Saves waste disposal costs - Make money from selling methane 	4. Bell Helicopter in Fort Worth used magnesium hydroxide $Mg(OH)_2$ in electroplating. Some was lost to sewer, and ended up in wastewater sludge	<ul style="list-style-type: none"> - Pumped sludge back into process. Found could use 3–4 times before dumping - Save money by buying less $Mg(OH)_2$ - Less sludge to deal with saved money
2. ITT Industries' Virginia facility used sulfur hexafluoride SF_6 (a strong ozone depleting gas) to test tubes in night-vision devices	<ul style="list-style-type: none"> - Nitrogen was found to work as well as SF_6 without adverse environmental effect - Nitrogen is cheaper to buy than SF_6 	5. International Paper in Jay, Maine, generated steam by burning number-6 fuel oil with 1.8% sulfur and other contaminants; some became air pollutants	<ul style="list-style-type: none"> - Natural gas burning facility was built on site. Its owner sells steam to mill - Burning natural gas generates less air pollution and CO_2
3. Tennessee Valley Authority (TVA) an electric utility trapped sulfur dioxide as calcium sulfate $CaSO_4$. This was landfilled as was the fly ash and boiler slag	<ul style="list-style-type: none"> - Sells $CaSO_4$ to wallboard-maker - Sells ash and slag for use in concrete and abrasives - Eliminates landfill costs and makes money 	6. International Paper mill in Jay, Maine, found mercury Hg in its wastewater. Traced Hg to contaminated acid and alkali	<ul style="list-style-type: none"> - Found alternate suppliers to furnish uncontaminated acid and alkali. Wastewater Hg fell to levels no higher than natural levels in river

Examples 1–4 from Deutsch, C. H. Together at Last: Cutting Pollution and Making Money. *New York Times*, September 9, 2001. Examples 5–6 from Hill, M., Saviello, T., and Groves, S. The greening of a pulp and paper mill. *Journal of Industrial Ecology*, 6(1), 2002.

For additional examples, see: Environmental success stories. California Department of Environmental Control, <http://www.dtsc.ca.gov/Success/index.cfm>.

Beyond Kalundborg²³

Kalundborg provides an example of how to redefine the words, waste and pollutant. “Wastes” and “by-products” become useful products. See Table 2.9 for further examples of uses being found for what were previously wastes.

- Think about computers. What if the pollutants and wastes produced as we mine and process the raw materials that go into manufacturing computers could find uses? What if

²³ What is green engineering? *US EPA*, September 13, 2007, http://www.epa.gov/oppt/greenengineering/pubs/whats_ge.html.

the wastes and pollutants generated during computer manufacture could be used? And consider end-of-life computers and other electronics. In Chapter 12, you will see the havoc when they are improperly recycled. What if at the end of their useful lives, electronics could be efficiently disassembled and all components used again?

- Think more ambitiously. What if we could meld most human-made products, wastes and pollutants into the natural ecosystem – without harming it? For this exercise to be more than a fantasy we must make DfE a reality: develop systems in which all inorganic wastes and pollutants go back into industrial processes or, at worst, are separated for safekeeping; and in which all biological wastes (including sewage) become “food” for processes that produce useful products (or else be assimilated into ecosystems when this can be done without overloading them). In such a world human-made systems could blend into nature, not deplete nature’s ability to provide services. Chapters 11 and 18 further examines these possibilities.

Questions 2.2

1. Why is it important that facilities involved in industrial symbiosis be near one another?
2. What is a case in Table 2.9 that goes beyond P²? Explain.
3. Review Figure 2.2. Then consider industrial, municipal, or other facilities in your locale. (a) What is one possibility that exists for industrial symbiosis? (b) What factors – physical location, financial, liability, public policy – could favor such symbiosis? (c) How could waste materials produced or collected by municipal operations (recyclables, sewage) fit into the symbiosis? d. How about local agricultural wastes?
4. Many people believe that Western lifestyles are unsustainable, that per capita resource use is too high by as much as 10-fold. What is an instance where a technology evolved in a way that reduced its material input by at least 10-fold?
5. What are four products in your own life that you could reduce your consumption of two-fold without affecting your life style?
6. (a) What are five wastes that you throw away on a typical day in your home? (b) At work? (c) On trips (including travel, lodging, meals, etc.)?
7. (a) What are five wastes you generate *indirectly* when you purchase products from grocery stores, gasoline stations, auto maintenance shops, dry cleaners, doctors’ and dentists’ offices, restaurants, and retail stores? (b) What responsibility do you bear for these?

Delving deeper

1. After learning the characteristics of hazardous chemicals, contact (if possible visit) your local fire department. Ask to see a list of what hazardous chemicals are used in your community. Local facilities having hazardous chemicals will have submitted MSDSs (Material Safety Data Sheets) for them. Do you recognize the names of any of these chemicals? Are there any that surprise you? Concern you? If you are surprised, you may want to contact the facility using the chemical and ask what they use it for.



Figure 2.3

Green Screen for Safer Chemicals. Credit: US EPA

2. Recall that TRI information does not tell us the actual risk of a chemical. Nor does it tell us if the risk is high compared to other chemical risks in our environment. What public policy could you envision that would provide disclosures that would give you a greater understanding of chemical risk than provided by TRI?
3. There is major action nowadays to generate biofuels – fuels derived from corn, sugar cane, soybeans, switchgrass, and other crops – to replace petroleum fuels. (a) CO_2 is the major greenhouse gas contributing to global climate change. Grown sustainably, biofuel crops would not increase the amount of CO_2 in the atmosphere. Why? (b) Life-cycle assessment (LCA) is a process that examines all the environmental impacts that products (from computers to corn) can have: the impact of obtaining the necessary raw materials needed, and its manufacture, use, and end of life impacts (whether recycling or disposal). Diagram the factors you'd have to consider when analyzing the impacts of a biofuel. Include social impacts in your consideration. (c) What factors could contribute to preventing biological sources from being grown sustainably?
4. Think about a clothing detergent. (a) Diagram the impacts of a detergent over the four phases of its lifetime. (Your current state of knowledge will be adequate.) (b) What are four ways that the impact of using detergent could be minimized?
5. Green chemistry works to find safer chemical for industrial processes and for everyday products such as those used in cleaning (see Figure 2.3). Go to <http://www.cleanproduction.org/Greenscreen.php> and choose a subject of interest to you such as Extended Producer Responsibility. Develop a brief report on the subject you have chosen, note why it is important and how it is used.

Further reading

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For a better understanding of whether a pollutant may be harmful to living creatures, we need to understand some basic principles of toxicology. Section I introduces “the dose makes the poison,” acute and chronic toxicity, systemic and local effects, and how the body stores chemicals. We follow a chemical through the body via absorption, distribution, metabolism, and excretion. Section II examines factors affecting toxicity including gender, age, and poor nutrition and looks at how organs such as the liver, kidneys, and skin are affected by toxicants. Section III considers some of the greatest worries that people have regarding toxic substances – impacts on children and the fetus, and the ability of some chemicals to cause cancer. Environmental hormones, pollutants that mimic natural hormones, are also considered. The chapter contains boxes on topics such as bisphenol A, pesticides, and pollution’s toll on health in China.

SECTION I

All substances are toxic¹

Paracelsus, a controversial sixteenth-century physician, was faulted for treating his patients with arsenic and mercury, substances known to be toxic. Paracelsus responded with a statement still repeated 500 years later. “All substances are poisons. There is none, which is not a poison. *The right dose differentiates a poison and a remedy.*” That is to say, a “non-toxic” substance can be toxic at a high enough dose, and a very toxic substance can be safe if the dose is low enough.” The dose makes the poison” is a convenient rule (Figure 3.1). However, as we will see, there are exceptions to this rule. In any case, many factors affect toxicity in addition to dose.

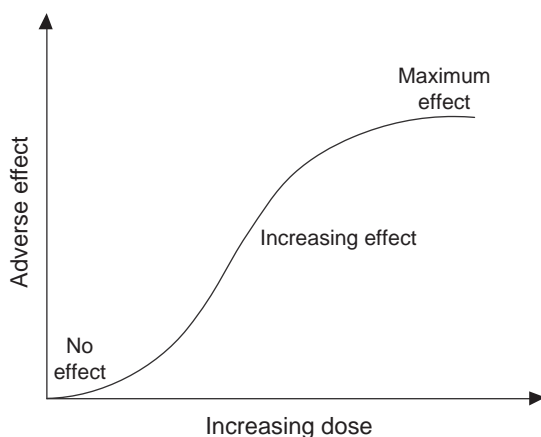
Terminology

Table 3.1 provides some definitions of words used for toxic substances. Sometimes the term “toxic chemical” is used almost as one word, but toxicity is not that straightforward

¹ Newman, C., Pick your poison: 12 toxic tales, *National Geographic*, 207(5), May, 2005, 2–31.

Table 3.1 Definitions

Toxicant	A substance causing adverse effects in a plant, animal, or human. It does so by impairing vital metabolic functions.
Toxin	A toxin is a toxicant produced by a living organism (microbe, plant, insect, spider, snake, or bird). The word is often used loosely.
Poison	A poison is a substance, which, “in small amounts is injurious to health or endangers the life of a living organism.” Poison is a synonym for toxicant, but is often used loosely.
Hazardous substance	A hazardous substance may be toxic, corrosive, reactive, flammable, radioactive, or infectious, or more than one of these. It cannot be harmful unless actual exposure to it occurs.
Xenobiotic	A chemical substance that is foreign to (not synthesized in) the body of the animal exposed to it.

**Figure 3.1**

Increasing adverse effect with increasing dose

(Box 3.1). A chemical's effects depends on many conditions including the dose given, how quickly it is given, health, age, and gender of the person or animal exposed (Table 3.2).

Acute and chronic toxicity

- *Acute toxicity* is an adverse effect seen soon after a one-time exposure to a chemical. The effect may be vomiting, diarrhea, breathing difficulties, irregular heartbeat, poor coordination, or unconsciousness. Symptoms might arise in a child who ingested a parent's prescription drug, a farm worker who sprayed a pesticide without proper protection, or a teenager who sniffed glue or gasoline vapors.
- *Chronic toxicity* results from long-term exposure to lower doses of a chemical or an adverse effect that happens long after an exposure has ended. Long term may be several

Table 3.2 Is this chemical toxic or beneficial?

Botulinum toxin	The most acutely toxic chemical known. It has caused many deaths in people eating improperly processed food In extremely tiny doses (as in Botox) it treats spasms and twitchings that respond to no other treatment. It is used cosmetically to “relax” wrinkles, but treatments must be repeated every few months
Warfarin	A synthetic chemical used as a rat poison A chemical taken to prevent strokes and heart attacks
Atropine	A “supertoxin” made by the deadly nightshade plant. An antidote for nerve gas and organophosphate pesticide poisoning
Thalidomide	A drug that caused tragic birth defects in the 1950s and 1960s Used to treat leprosy, and has potential usefulness in treating several other diseases
Curare	A natural poison employed by Amazon natives on arrow tips A chemical used to promote muscle relaxation during surgery
Nitroglycerine	A chemical used to manufacture dynamite A chemical employed to treat angina (spasms of heart arteries)
Sodium chloride (salt)	Salt has killed small children who ingested large amounts. It is implicated in high blood pressure. Too much leads to retention of body fluids. Chronic intake of highly salted foods is associated with stomach cancer A nutrient (essential to life)
Nickel and Chromium	High doses are toxic and can cause cancer Both of these metals are nutrients
Nitric oxide	A neurotransmitter produced within the body An ambient air pollutant

Box 3.1**Illustrations of paradoxical effects****Vitamin A**

▪ Worldwide, vitamin A deficiency may cause the deaths of millions of children each year, and hundreds of thousands of cases of childhood blindness. ▪ But if a pregnant woman takes large doses of vitamin A, her baby may have birth defects such as a cleft lip, cleft palate, or major heart defects. Women of childbearing age are urged not to exceed the recommended daily intake for vitamin A. Pharmaceuticals derived from vitamin A can also cause birth defects.

Aspirin

▪ Aspirin has many positive effects. It relieves pain, fever and the inflammation of arthritis. It treats and prevents heart attacks, strokes, and may prevent colon cancer. ▪ But aspirin can irritate the stomach, adversely affect children with fever and individuals with blood-clotting problems, and may cause bleeding in pregnant women. It is highly toxic to individuals hypersensitive to aspirin. Aspirin also causes birth defects in rats. Modern drugs are extensively tested before marketing. If aspirin was newly discovered, and testing demonstrated that it caused birth defects in animals, it would be suspected of doing the same in humans. It would probably only be available as a prescription drug. However, aspirin has been marketed since the nineteenth century and has not been associated with human birth defects.

Table 3.3 How do substances exert their toxic effects?

There are many ways that a toxic substance can exert adverse effects. Three examples follow.

Carbon monoxide. The blood protein hemoglobin picks up oxygen in the lungs, and transports it to the tissues where it releases the oxygen. When carbon monoxide (CO) is inhaled, it binds to hemoglobin much more strongly than oxygen and so blocks the oxygen binding, lowering the amount of oxygen available to the body. Too much blocking of hemoglobin by CO can lead to death. Smaller doses can cause headache, nausea, and other flu-like symptoms. Chronic exposure is implicated in the development of heart disease.

Botulinum toxin. This powerful bacterial toxin binds to nerve endings at the points where they join muscles, thereby blocking release of the neurotransmitter acetylcholine, which is ordinarily released by nerve fibers. With no stimulus, the muscles are paralyzed. Paralysis of respiratory muscles leads to death.

A nerve gas or organophosphate pesticide. These agents do not block acetylcholine release. Rather, they prevent acetylcholine from being degraded. The result is that this neurotransmitter accumulates leading to uncontrolled firing of the nerves.

weeks or 30 to 40 years. Examples are liver cirrhosis resulting from chronic alcohol ingestion, or a damaged nervous system resulting from chronic mercury exposure. ▪ A well-known chronic effect is cancer. Leukemia, a cancer of white blood cells, may result from long-term exposure to benzene. Lung cancer may result from chronic exposure to cigarette smoke. The typical latency period for cancer (the time of initial exposure to the time that cancer is diagnosed) is 15 to 25 years.

- A given substance may not cause acute effects, but may show chronic toxicity: if you break a mercury thermometer, your onetime exposure to elemental mercury vapor is unlikely to hurt you, but chronic exposure to mercury vapor in a work place can seriously affect the nervous system. ▪ Conversely, an acutely-toxic substance may not have chronic effects. The foul-smelling gas, hydrogen sulfide, is acutely toxic. However, long-term exposure to levels of hydrogen sulfide found naturally in “sulfur waters” is not known to have adverse chronic effects.

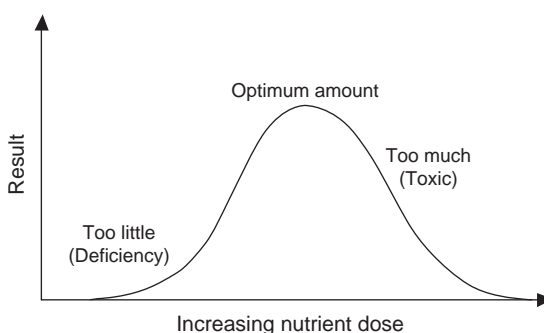
Dose

- Anything is toxic at a high enough dose. Figure 3.1 shows a dose–response curve, i.e., as the dose increases, the adverse impact increases too. Even water, drunk in very large quantities may kill people by disrupting the osmotic balance in the body’s cells. ▪ As the dose increases there are many possible toxic effects. Examples: an enzyme may suffer increasing loss of its activity, or nerves become unable to conduct impulses. Table 3.3 illustrates several mechanisms by which substances exert toxic effects.
- LD₅₀ is the dose that is lethal to half of the animals exposed to it. Determining an LD₅₀ is crude, many consider it cruel, and it provides little information as to how a chemical exerts its toxic effects. However, people continue to ask how toxic is this chemical? In 2001, an alternative test was announced that uses as few as 6 to 9 rats instead of the

Table 3.4 Comparing the toxicity of chemicals

Toxicity	LD ₅₀ *	Examples
Slightly toxic	500–5000	Aspirin, vanillin, salt
Moderately toxic	50–500	Phenobarbital, caffeine, nicotine, warfarin
Highly toxic	1–50	Sodium cyanide, vitamin D, parathion
Supertoxic	Less than 0.01–1	Atropine, nerve poisons 2,3,7,8-TCDD
Biotoxins	Much less than 0.01	<i>Botulinum</i> toxin, ricin (in castor oil beans)

* LD₅₀ is the dose killing 50% of the animals exposed to it. Here LD₅₀ is expressed as milligrams per kilogram (mg/kg) body weight. Adapted from Crone, H. D. 1986. *Chemicals and Society*, Cambridge: Cambridge University Press, p. 35.

**Figure 3.2****Dose-response curve for an increasing dose of a nutrient**

50 to 200 traditionally used, although results take longer to obtain. A European alternative uses as an endpoint, not the LD, but clear signs of toxicity. See Table 3.4.

- Figure 3.2 shows a dose–response curve for nutrients, chemicals that are essential to life such as vitamins, certain metals, and amino acids. Adverse symptoms, even death occur if you take in too little of the nutrient. As the dose increases, the animal or plant responds positively up through an optimal dose range. But as the dose gets even higher, adverse effects again occur. Serious illness or death may occur if the dose is high enough.

Dose per time

The time period over which the dose is consumed is as important as the dose. Toxicologist Alice Ottoboni has provided a number of examples.² ■ Taking one aspirin a day for 100 days may be beneficial, but taking 100 aspirins at one time can be lethal. Ingesting 1 ounce (30 ml) of hard liquor every day for 25 days is fine for most people, but drinking a fifth (25.6 ounces, 760 ml) at one sitting could be lethal. ■ The caffeine in coffee is moderately

² Ottoboni, M. A. *The Dose Makes the Poison: A Plain-Language Guide to Toxicology*, second edition. New York: Wiley, 1997, <http://www.amazon.com/Dose-Makes-Poison-Plain-Language-Toxicology/dp/0471288373>.

toxic, but to be lethal, the dose of caffeine in a cup of strong coffee would need to be 100 times higher than it is. ▪ Anyone who has chewed a piece of raw rhubarb knows the effect of *oxalic acid* (also found in spinach) on the mouth. However, you would need to eat 20 pounds (9.1 kg) of spinach or rhubarb at one sitting to ingest a lethal dose of oxalic acid. ▪ Potatoes make the insecticide, *solanine*. But to ingest a lethal dose of solanine would require eating 100 pounds (45.5 kg) of potatoes at one sitting. However, certain potato varieties – not on the market – make enough solanine to be toxic to human beings. Potato skin is a nutritious part of the potato, but pare away any green skin as green indicates exposure to sunlight and a higher amount of solanine. Bruised potatoes and potato sprouts also contain higher solanine levels. ▪ Generally, potentially toxic substances are found in anything that we eat or drink.

Does the dose always make the poison?

“The dose makes the poison” is a useful concept, but consider environmental hormones.³ Hormones are natural chemicals produced in the thyroid, ovaries or testes, pituitary, and other glands. Carried in the bloodstream to target tissues each hormone exerts specific effects. At natural levels, hormones exert actions vital to an animal’s well being. Estrogen produced in the ovaries is transported to specific target tissues where it stimulates and maintains changes that make an animal female. The estrogen exerts its effects by reacting with specific receptor molecules within target tissues. It is this hormone–receptor complex that elicits a response. *Only a tiny dose of a hormone is needed* to turn on the receptor. Up to a point the response does increase with dose. However, if the dose continues to increase, a feedback comes into play, which can turn off the effect. So what will happen if an environmental hormone (pollutant) mimics a hormone? Fortunately, pollutants ordinarily show very weak hormonal effects as compared with the real hormone. Nonetheless, wildlife is often directly exposed to such pollutants and sometimes serious effects are seen. Could human development also be affected? This question will be discussed later in this chapter.

Exposure to multiple chemicals

Persons, animals, and plants are exposed to more than one chemical at a time, in fact, often many chemicals. What is the result of multiple exposures?

- The most common effect is *additive*. This commonly happens when the chemicals in question exert their effects in a similar manner, as when a person is exposed to several organophosphate pesticides at a time: each inhibits the activity of a specific enzyme. The chemicals do not interact.
- In *synergism* the combined effect of two chemicals are greater, sometimes much greater than additive, i.e., one plus one equals much more than two ▪ Carbon tetrachloride and ethyl alcohol are both toxic to the liver, but exposure to both at the same time leads to

³ Several terms are used to describe pollutants that have hormonal activity: *environmental hormone*, *hormone mimic*, and *endocrine disrupter*. It can be confusing.

Box 3.2

One chemical at a time

Almost all of our knowledge of xenobiotics (foreign chemicals) comes from testing chemical toxicity *one chemical at a time*. This presents a problem because living creatures are exposed to mixtures of chemicals. However, we cannot routinely study chemical mixtures, nor dissect out what each chemical in the mixture is doing. ▪ One method to look at the toxicity of mixtures is to examine *whole effluent toxicity*,⁴ the toxicity of an effluent flowing from a facility into a river. The need is to see if that effluent impacts the organisms living in the water body: is the effluent, whatever its chemical composition harmful to the life forms that it contacts? ▪ However, we still typically need to understand the impacts of individual chemicals. Consider air pollution: we need to know the impact of ozone and other air pollutants individually. We learn a lot “one chemical at a time.” But remember the limitation of this approach.

much greater injury than the sum of their individual effects. ▪ Smokers, exposed to asbestos, have a magnified risk of lung cancer as compared to exposed non-smokers.

- In *antagonism* one chemical interferes with the action of another – it acts as an *antidote*. ▪ Consider a child who has ingested a household product or a person who ingested poison in a suicide attempt. Emergency-room personnel may administer *ipeccac* to induce vomiting, ridding the system of the poison, although some of the substance likely has already crossed the intestinal wall into the bloodstream. Or charcoal may be given to absorb the poison, so that it is not bioavailable. ▪ A person poisoned by methanol can be treated with ethanol to lessen the effect of the methanol. ▪ Two chemicals may react with one another to produce a less toxic product such as happens when a person poisoned with a metal is treated with dimercaprol (BAL); BAL binds to the metal ion preventing it from exerting its toxic effect.

Systemic and local effects

When speaking of toxic effects, typically *systemic effects* are being referred to – effects occurring at a point distant from where a chemical enters the body. For example, cyanide, arsenic, and other toxicants exert their poisonous effects after being absorbed into the body. ▪ However, we need to be aware of *local effects* too – effects occurring at the point of contact with skin, eyes, lungs, or gastrointestinal (GI) tract. A weak acid for instance is an irritant at the point of contact; it shows a *local* effect. A reactive gas such as formaldehyde also shows local effects such as irritating the eyes. ▪ But, absorbed into the body formaldehyde can have systemic effects too. Or, the metal nickel irritates the skin, but absorbed into the body can exert systemic effects. Some plants exert local effects at the point of contact too; consider poison ivy.

⁴ Whole effluent toxicity. *US EPA*, July 25 2008, <http://www.epa.gov/waterscience/methods/wet/>.

Absorption, distribution, metabolism, and excretion

The acronym ADME may help you to remember what happens to a chemical. A chemical normally enters the body via the lungs, the GI tract, or the skin. After entry, it may be absorbed (A) into the bloodstream, distributed (D) throughout the body, metabolized⁵ (M) by the body's tissues into different chemicals, and finally excreted (E) from the body.

Absorption

Up to this point the word exposure has been used as if you could suffer an adverse effect just by having a chemical in the environment around you. But, to have an adverse effect, you must have contact with it. For a systemic effect to occur, it must be absorbed into the body. This can happen when you inhale it into the lungs, ingest it into the digestive tract, or absorb it across the skin. ▪ Sometimes a chemical gains entry in non-ordinary ways as when injected into a vein or under the skin. Some xenobiotics are toxic only by one route of entry whereas others are toxic in two or three ways. ▪ Formaldehyde can act as a carcinogen only by inhalation. ▪ Asbestos is also a carcinogen by inhalation. ▪ However, arsenic is toxic by all three routes: skin absorption, ingestion, and inhalation.

Inhalation

Unless you deliberately inject a chemical into the body, inhalation is the fastest means by which a toxicant entering the body can exert an effect. Think about inhaling a gaseous anesthetic such as ethyl ether. Anesthesia results very rapidly after the inhaled gas passes from the lung's alveoli into the bloodstream. Many other substances can also be inhaled – consider the particulates in smoke, the aerosol droplets from a spray can, or fumes from heated metal. Because effects often occur so rapidly, exposures occurring in enclosed spaces can be especially dangerous.

Ingestion

Anything taken into the body by drinking or eating is ingested. In the digestive tract, a substance is digested into molecules, many of which may be absorbed across the wall of the small or large intestine into the bloodstream. Most absorption occurs through the small intestine and, from there a chemical enters a portal blood system that carries it directly to the liver. Because the liver is the first organ a toxicant contacts – before it has been diluted by the bloodstream – the liver receives the highest dose of an ingested toxicant.

⁵ Metabolism refers to all the biochemical processes that occur within living creatures. It includes *anabolism* (the synthesis of substances) and *catabolism* (the breakdown of substances). The term often refers to the breakdown of food and its transformation into energy.

Skin Absorption

By stopping or slowing the absorption of most chemicals, the skin protects us from the outside world. Nonetheless fat-soluble and a few other small chemicals are absorbed across the skin to varying extents, but sometimes efficiently. The pesticide *parathion* is absorbed as rapidly through the skin as when ingested or inhaled. The chemical, *dimethyl sulfoxide* (DMSO) enhances absorption of chemicals across the skin, chemicals that skin does not otherwise efficiently absorb. When thinking about skin absorption, remember:

- The larger the area of skin exposed to a chemical, the more that is absorbed.
- The longer a chemical remains in contact with skin, the more that is absorbed.
- Thin skin such as found on the abdomen or scrotum is more permeable to chemicals than the thicker skin on the soles of the hands or feet.

Chemicals such as acids, alkalis, or some metals needn't be absorbed as they can exert local effects. However, if the skin is damaged, systemic effects can also occur.

Distribution (D)

After absorption, a chemical is distributed throughout the body by the blood and taken up, to varying extents, by different organs. A specific chemical may show the most pronounced effects on one or more *target organs*. *To be toxic, a chemical must reach the most sensitive tissue at a high enough dose to exert an adverse effect* – this is the dose that is important. ▀ The nervous system is a major target organ of lead and mercury. However, these metals can affect other organs too as the dose or time of exposure increases. ▀ The petrochemical, benzene can cause acute effects, narcosis in the brain, a target organ. It also can cause chronic effects, anemia or leukemia in a different target tissue, bone marrow. ▀ Oftentimes, substances are stored in the body in ways that interfere with potential toxic effects; when this happens, they don't ordinarily show toxic effects (Box 3.3).

Metabolism (M)

To rid their bodies of an absorbed xenobiotic, animals and humans often *biotransform* it – metabolize it into chemicals that they can excrete. The liver and kidney are especially active in this process. Usually, a xenobiotic is converted into a less toxic chemical. ▀ Unfortunately, on occasion, the xenobiotic is converted into a more toxic chemical as when the liver converts the pollutant *benzene* into *benzene oxide*, a reactive chemical that damages bone marrow. ▀ The biotransformation system that evolved to deal with xenobiotics is ancient because animals have always had natural poisons in their environment. From this perspective, modern synthetic toxicants may be no worse than the toxins that living creatures have dealt with for millions of years. One major exception is those synthetic chemicals that the body has difficulty degrading such as PCBs and dioxins.

Box 3.3

More concepts: bioavailability, storage, bioaccumulation and biomagnification

Bioavailability

For a nutrient to be helpful, it must be in a physical and chemical form that the creature can access, it must be bioavailable. Likewise, to be toxic a xenobiotic must be bioavailable.

- **Physical factors** Recall the example given above of charcoal administered to a poisoning victim; the charcoal absorbs the poison making it biologically unavailable. Likewise in the environment, certain chemicals including dioxins, PCBs, and PAHs bind tightly to soil or sediment particles. The chemicals may move into, and become trapped within a particle's interior. There they are largely inaccessible, i.e., they are not *bioavailable*. An animal may ingest these particles, but the chemicals bound to them are not absorbed across the GI tract.
 - Another physical property is volatility. *Elemental mercury* (Hg^0) is volatile even at room temperature. If inhaled, about 80% can be absorbed through the lung's alveoli into the blood stream. Breathing in the vapor from a broken thermometer is unlikely to cause harm, but chronic exposure, as in some work sites in less-developed countries, can lead to serious mercury poisoning. Also, think about a person breaking a mercury thermometer and ingesting a tiny amount of elemental mercury. Because Hg^0 is not soluble, most passes through the GI tract into the feces. This makes an adverse health impact less likely.
- **Chemical factors** Think about a different chemical form of mercury, *methylmercury* (CH_3Hg^+). Methylmercury is often ingested as a fish contaminant. It is easily absorbed across the intestine into the blood stream. It is thus much more dangerous. Chronically ingested, even tiny amounts can lead to health problems especially in small children.
- **Storage** A portion of a xenobiotic distributed in the bloodstream around the body may be stored for short or long periods. As long as a chemical remains bound, it does not exert adverse effects; it is not bioavailable.⁶
 - Even blood can store chemicals by binding them to blood proteins.
 - In an animal that is chronically exposed to mercury (and certain other metals), a portion becomes bound to a protein, *metallothionin* in the kidney and is not bioavailable.
 - However, when exposure is reduced, or eliminated, the amount stored begins to decrease too. Release may be slow, but sometimes it is rapid, as demonstrated in several examples.
 - **Lead** Lead is stored in bones and teeth from which it is ordinarily, released only slowly. However, during pregnancy, a mother's bones release calcium into the blood to meet the needs of her fetus. And the stored lead is released too, exposing the fetus as the lead circulates in the blood.
 - **DDT** the bodies of animals, birds and humans have great difficulty transforming persistent fat-soluble chemicals, such as DDT into water-soluble forms. Thus, these chemicals survive stored in fat, from which they are only slowly released. To increase DDT's rate of release, an experiment was done. Laboratory rats were fed large amounts of DDT daily for 3 months. Although high levels of DDT accumulated in their fat, they suffered no ill effect. Then, their food intake was cut in half, forcing their

⁶ An exception to this protective effect is shown by radionuclides (radioactive substances). A radionuclide can undergo radioactive decay whether or not it is stored, and potentially cause harm. Consider strontium-90, a radioactive element found in the fallout of nuclear bombs tested in the atmosphere in the 1950s. Once absorbed into the body, strontium-90 is stored in bones, and increases the risk of bone cancer.

bodies to use stored fat for energy. The fat-stored DDT was rapidly released, and the rats showed visible symptoms of poisoning. ▪ Famine, hibernation and nursing Wild animals go through periods when they use stored body fat. Famine is one instance. It happens too when nursing animals use body fat for the energy needed to produce milk, as after a hibernating bear gives birth in the winter. At these times, pollutants stored in fat may be rapidly released.

Bioaccumulation

A pollutant is said to *bioaccumulate* when it reaches a concentration within a creature that is higher than found in the environment. ▪ Illustrations PCBs and dioxins bioaccumulate in fat; strontium (a metal), fluoride and lead bioaccumulate in bones; metals such as cadmium bind to proteins and bioaccumulate in the liver, kidney, and other soft tissues.

Biomagnification

When a pollutant reaches progressively higher concentrations as it moves through the food web it is said to biomagnify. ▪ Notice in Figure 3.3 that the organic pollutants, PCBs biomagnify in the Great Lakes food web. At each step the PCBs concentration grows higher: phytoplankton,⁷ one-celled plants at the base of the food chain, bioaccumulate PCBs. Zooplankton, small invertebrate animals eat enough phytoplankton to accumulate PCBs to levels higher than those in phytoplankton. In turn, smelt (small fish) eat enough zooplankton to raise their PCBs level above that of zooplankton. Lake trout eating the smelt have higher levels still. The eggs of herring gulls that eat the fish have a PCB concentration higher than lake trout, and dramatically greater than in the phytoplankton. Not only gulls, but other predators including humans may eat the contaminated fish, and also show very high PCB levels in their fatty tissues. ▪ DDT and dioxins are other well-known examples of chemicals that undergo biomagnification. ▪ Methylmercury provides an important illustration of biomagnification (Chapter 15). Bacteria in sediment convert elemental mercury to methylmercury, which then strongly biomagnifies through the food web. Methylmercury can biomagnify a million-fold in birds and mammals (eagles, gulls, seals, minks).

Excretion (E)

After exposure decreases or ceases, the concentration of an absorbed xenobiotic can begin to decrease. The rate of excretion depends on a number of factors including how it has been stored in the body (Box 3.3). Chemicals are excreted in a number of ways.

- Urine Water-soluble chemicals such as salt or sodium cyanide are largely excreted in urine. If a xenobiotic is not already water soluble, the body attempts to transform it into one that is.

⁷ Phytoplankton are tiny, often microscopic, organisms found drifting near the surface of freshwater and salt water. Zooplankton are tiny animals that include corals, rotifers, sea anemones, and jellyfish.

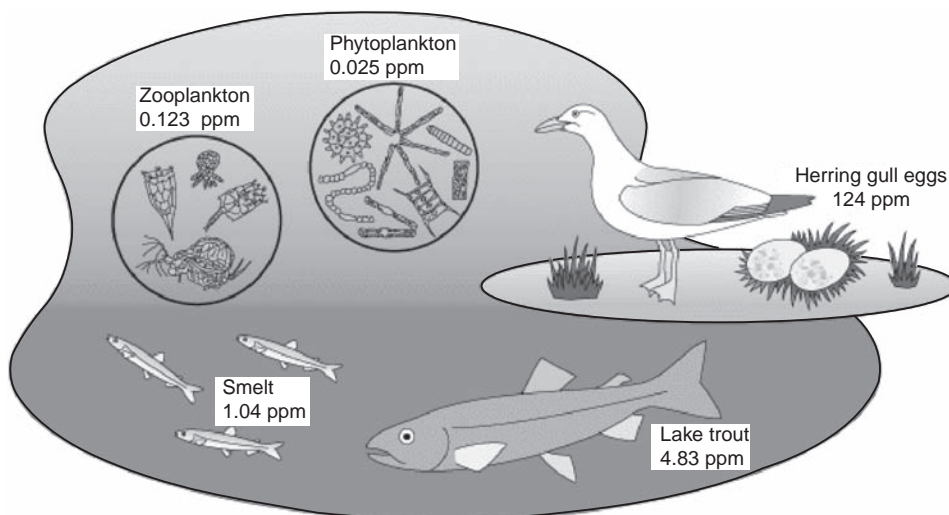


Figure 3.3

Biomagnification of polychlorinated biphenyls. Credit: US EPA

- Feces Some chemicals cannot be transformed into water-soluble forms. The liver moves these with the bile into the intestine. From there, they exit the body in the feces.⁸
- Breath Volatile chemicals such as ethyl alcohol or acetone are partially exhaled in the breath, and their odor may be detected. Gases without an odor such as carbon monoxide are also exhaled.
- Milk The milk of a nursing mother is a vehicle for some xenobiotics to leave the body. This can significantly increase the exposure of infants to chemicals like PCBs and dioxins.
- Sweat A small amount of chemicals can be excreted in sweat.
- Skin can excrete some chemicals. One symptom of poisoning by chlorinated hydrocarbons (including dioxins) is *chloracne*, a severe acne. In a bizarre case, Ukrainian presidential candidate Victor Yushchenko developed chloracne two weeks after being poisoned with dioxin in 2004 by persons unknown. If you have access to the web, see the photographs references in footnote 9.⁹ The chloracne may be the body's attempt to rid itself of the poison.

⁸ However, a portion of the chemical excreted in bile may be reabsorbed across the intestine into the blood and carried again to the liver. It may cycle around the body a number of times before complete excretion.

⁹ Poison level 6000 times higher than normal. *Sydney Morning Herald*, December 16, 2004, <http://www.smh.com.au/news/World/Poison-level-6000-times-higher-than-normal/2004/12/16/1102787153891.html>. 2,3,7,8-TCDD (tetrachlorodiphenyldioxin) is the most potent form of dioxin. Yushchenko's blood and body tissue levels of dioxin were (at least) a thousand times higher than average levels. Any higher would probably have resulted in death. He suffered intense pain. The chloracne became worse than seen in this picture with a black patch spreading over his nose.

SECTION II

Factors affecting toxicity

Once a xenobiotic is absorbed, how toxic will it be? This depends on the chemical's intrinsic toxicity (Table 3.4), its dose, dose per time, and many other factors that affect toxicity that are introduced below. It also depends on storage as described in Box 3.3.

Variation among and within species

Variation among species

A chemical that harms one species at a given dose may not be toxic to another species. Silicosis is a lung disease that was commonly found in human miners exposed to silica dust, but their similarly exposed mules were not affected. See Table 3.5. "Dioxin" or TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) is one of the most toxic chemicals known. Although formed naturally in very tiny amounts, most is generated by human activities. Dioxin toxicity varies greatly by species. The politician Yushchenko was fortunate that humans are not as sensitive as are a number of other species.

Variation within a species

Within a given species, individuals may vary greatly in their sensitivity to a toxicant, some very sensitive, others resistant. Consider aspirin or the sulfites (widely used in wine and food preservation). Some humans are hypersensitive to these chemicals but, at levels commonly used, there is no indication of adverse effects in most people.

Table 3.5 Variation in dioxin toxicity with species

SPECIES	LD ₅₀ [*]	SPECIES	LD ₅₀ [*]
Guinea pig male	0.6	Rabbit	115
Rat (male)	22	Dog	30–300
Rat (female)	45	Monkey	70
Hamster	1160–3000	Humans (estimate)	>100

^{*} LD₅₀ is expressed here as µg /kg body weight. Information adapted from Tschirley, F. H. Dioxin, *Scientific American*, **254**(2), February, 1986, 29–35.

Gender, age and nutrition

You see below the many factors that can impact sensitivity to a pollutant or food contaminant. To guard against these variations, national health-based standards are often set to protect the “most sensitive” populations such as the very young and very old.

Gender

The sex hormones, androgens and estrogens, affect animal anatomy, physiology, and metabolism in many ways. Thus, it is not surprising that the two genders can react differently to xenobiotics. ▪ Women, for example, have less alcohol dehydrogenase (an enzyme involved in metabolizing alcohol) than do men. Thus, a woman can become intoxicated more rapidly than a man of the same weight.

Age

The immune system in babies and small children is less well developed than in adults. They often – but not always – are more sensitive to toxicants than adults. See Section III for more on children. ▪ Likewise, the immune systems of elderly persons function less efficiently than in younger adults. Thus, they may react more strongly to a drug or pollutant than younger adults.

Nutrition

Good nutrition helps to maintain a healthy immune system, which provides protection against xenobiotics and infectious (pathogenic) microorganisms. ▪ Alcoholics are an example of a poorly nourished population more likely to be affected by xenobiotics and pathogens. ▪ Other susceptible populations are people whose diets have insufficient calories or insufficient nutrients (see Questions 3.1). ▪ Overweight rats and other animals develop more cancers than do animals fed a well balanced, but low-calorie diet. Obese people have a greater risk of cardiovascular diseases and of a number of cancers. ▪ Individuals who consume high-fat diets have a greater risk of colon and skin cancer. ▪ For more examples, see the discussion questions.

Questions 3.1 Lead and cadmium: two toxic metals

1. Cadmium is not a nutrient, and can be toxic at low doses. Years ago, a poisoning occurred in Japan that affected only poor elderly women living in one locale. Most had several children. Their diet consisted primarily of rice grown in cadmium-contaminated paddies. They developed *itai itai* (pain-pain), a disease characterized by kidney damage and brittle, painful bones. Others eating the same diet were not adversely affected. What factors may have caused only these individuals to be adversely affected?
2. Lead presents special risks to small children in a contaminated environment as they are most likely to ingest contaminated soil during play or inhale contaminated dust. The US Centers for Disease Control and Prevention believes that children with blood lead levels

greater than 10 micrograms per 100 milliliters (10 $\mu\text{g}/100\text{ ml}$) are at risk of lead poisoning. As you read the following two cases, recall the term, comparative risk, from Chapter 1.

Case 1: Smuggler Mountain

The area around Smuggler Mountain, Colorado, was mined for metals until the early twentieth century. Mining operations left behind large areas contaminated with lead and cadmium. Soil tests in 1982 showed such high levels of lead that the US EPA listed Smuggler Mountain as a Superfund site – a hazardous waste site posing special risk to human health.¹⁰ The EPA proposed a \$12 million cleanup that involved excavating and removing contaminated soil. However, despite the high lead levels around them, lead levels in children's blood averaged only 2.6 $\mu\text{g}/100\text{ ml}$. ▪ Typically, communities near Superfund sites are anxious to have sites thoroughly cleaned. However, the EPA's planned excavations could destroy their community, and considering that their children had low blood levels, citizens protested the cleanup plan. An independent expert panel evaluated the situation and made recommendations. It noted that only a few hot spots in Smuggler Mountain had soil containing high lead levels. Grass in summer and snow in winter covered the most heavily contaminated areas. Residents had diets high in iron and calcium, which mitigate exposure to lead. The panel recommended a more limited remediation at a cost of only \$400 000. One panelist observed: "Lead is not lead is not lead: trying to devise a single clean-up value for soil lead is not practical to use at all sites; each site must be analyzed individually."

Case 2: Lead paint in poorly maintained old houses

Many houses in older US cities were built before the 1970s, and often leaded paint was used inside and out. ▪ Homes in older inner cities are often poorly maintained, and have peeling leaded paint. ▪ Once peeled or chipped, the paint crumbles to dust, which children inhale. ▪ Small children may eat the sweet-tasting paint chips or lick the lead-painted sills of windows. ▪ Inner city inhabitants often have low incomes and poor diets.

Think about these two cases. (a) What are the routes of exposure to lead in old lead-painted houses? Consider air, water, soil, and food. (b) What are the routes of exposure in Smuggler Mountain? (c) Which children are at greater risk? Explain.

How toxicants affect organs

Toxicants can affect any tissue or organ within the body. However, a specific toxicant often has a target organ, which is especially sensitive.

Liver

One of the liver's many vital functions is to break down xenobiotics. The liver is the first organ that a xenobiotic encounters after being absorbed into the blood from the small

¹⁰ Superfund Program, Smuggler Mountain. *US EPA*, <http://www.epa.gov/region08/superfund/co/smuggler/> [August, 2008].

intestine – thus the liver is exposed to higher toxicant levels than organs that are not reached until the bloodstream has diluted it. ▪ The liver usually detoxifies xenobiotics, but sometimes it converts a chemical into a more toxic substance as when converting benzene into benzene oxide. ▪ When exposed to large amounts of a toxicant, as after a person drinks large amounts of alcoholic beverage, the liver may be unable to detoxify it all. ▪ Chemicals toxic to the liver, hepatotoxicants, include organic solvents such as chloroform and carbon tetrachloride. ▪ Most of us are familiar with the acute effects of excessive alcohol intake. Alcohol (ethyl alcohol) has chronic effects too; it is a well-known hepatotoxicant. Chronic effects on the liver of excessive alcohol intake include cirrhosis, and cancer. ▪ Most liver cancer should be preventable but, worldwide, half a million die each year from this disease. Prevention can be very difficult (Box 3.4).

Kidneys

Like the liver, kidneys detoxify xenobiotics. However, their major function is to filter the blood, eliminating waste products into the urine while retaining water and nutrients such as glucose. Remember that kidneys concentrate waste substances before they excrete them: thus the kidneys may create their own high doses of toxicants. Nephrotoxicants include some antibiotics and metals such as mercury, cadmium, and lead.

Immune System

The immune system¹¹ recognizes the difference between self and foreign substances and works to rid itself of the latter including microorganisms, cancer cells, and xenobiotics. Immunotoxic substances can cause damage by suppressing immune activity, or by causing it to overreact. ▪ Corticosteroid drugs are among the chemicals that can suppress the immune system, damage its ability to fight infections, or to remove cancer cells. These drugs are deliberately given to people who receive organ transplants to prevent the body from rejecting the new organ. Some environmental pollutants including PCBs also suppress the immune system. Individuals with poor immune system function are particularly vulnerable to infectious microorganisms and chemicals. These include the elderly, the sick (especially people with AIDS), and those undergoing chemotherapy. ▪ You are probably familiar with immune-system overreactions – allergies. Responsible agents include tree and flower pollens. Certain chemicals cause allergy-like reactions too. Autoimmune diseases such as lupus erythematosus and rheumatoid arthritis also result from overreactions.

The central nervous system

The brain requires high levels of oxygen to function normally. Thus any substance that lowers oxygen supply is neurotoxic. Carbon monoxide is a well known neurotoxin

¹¹ The immune system is a complex system of tissues, organs, and cells, which includes bone marrow, thymus, lymph nodes, and spleen. It destroys foreign substances using cells that it produces, such as lymphocytes and macrophages.

(Table 3.3). Some pesticides including malathion and parathion, nerve gases, and many drugs (legal and illegal) are neurotoxic. As are certain metals, in particular, lead and mercury (Chapter 15), and PCBs (Chapter 14). Especially in children, neurotoxic effects may be expressed in behavior such as attention deficit disorder. Behavioral problems are studied today as a sensitive means to detect an adverse effect of a neurotoxic chemical.

Skin

Local effects

An irritant can cause local effects on eyes, mucous membranes, and skin. Many substances may irritate the skin – a weak acid, such as vinegar, a detergent or other cleaning product, nickel in jewelry, or chemicals in certain plants. The skin may redden, swell, or itch. Sunlight is a non-chemical irritant. Skin exposed to an irritating chemical may react. The irritation subsides when exposure ceases. However, an irritant that is also an allergen is more serious. When an allergic person is exposed for the first time to an allergenic chemical the skin reacts and then recovers when exposure ceases just as with a non-allergenic person. However, if the sensitive person suffers repeated exposures, the reaction grows in severity, and reactions occur with much lower doses: an allergy has developed. Formaldehyde, a chemical found in many household products, is an irritant, and also an allergen.

Systemic effects

Some chemicals affect the skin after they have been absorbed into and distributed around the body. Such indirect effects may be caused by the antibiotic neomycin, which, after ingestion, can irritate the skin, sometimes severely. Arsenic can have both local and systemic effects on the skin. Systemic effects of arsenic include skin cancer.

Lungs

Local effects

- Reactive gases such as ozone (in smog), formaldehyde, or chlorine (in household products) can directly damage the lungs and mucous membranes in the nose, and eyes.
- Airborne particles breathed in – including silica, asbestos, coal or cotton dust, and even powder applied too liberally – can directly damage the lungs, and often are not completely expelled by the lungs. Adverse effects can be acute or chronic. Dust inhalation in the short run may only irritate, but chronic exposure can damage lung function: cotton dust exposure over years may give rise to brown lung disease, coal dust to black lung disease, and silica dust to silicosis.
- A number of substances increase the risk of lung cancer. These include solid substances such as asbestos, as well as some gases such as radon. Chemicals in tobacco smoke include both solid particles and gases.
- Organic solvents

Box 3.4

Reducing liver cancer¹²

For Westerners, chronic alcohol ingestion is the biggest risk factor for liver cancer. But much higher liver cancer rates are found in many poor African and Asian countries. The major risk factors there are *aflatoxins* (potent liver carcinogens) and infection with the hepatitis B virus.

- Aflatoxins are produced by molds especially *Aspergillus flavus*, which grows on peanuts, corn, rice, and other crops.¹³ Aflatoxins contaminate the meat and milk of livestock that have eaten aflatoxin-contaminated foods. No person can completely avoid aflatoxins.
 - People eating a Western diet ingest an average 19 ng aflatoxins per day, but those eating a Far Eastern diet may consume more than 100 ng. If all foods in which aflatoxins are detected were banned, a significant portion of our food supply would disappear. So, food is removed from the market only if aflatoxins are detected above an *action level*. In India the action level is 30 parts per billion (ppb), in Canada and the United States, 15–20 ppb, and in France and the Netherlands, 4 ppb. However, if India used such stringent standards, already malnourished people would have even less food. Poor countries could reduce aflatoxins on foods by improved farming and food storage practices or by using pesticides to destroy the molds producing aflatoxins, but these can be expensive.
- Now consider a second risk factor, a synergism: The risk of liver cancer in people eating aflatoxins increases about 60-fold if they are infected with the hepatitis B virus.¹⁴ There is a vaccine for hepatitis B. Why not use it and lower liver cancer incidence? Vaccines are expensive in impoverished countries. Think about some of the implications of this story. A microorganism, in this case the hepatitis B virus can cause cancer. Aflatoxins and the hepatitis B virus have a synergistic effect on liver cancer risk. The risk is accentuated by the malnutrition from which the poor more often suffer. Malnourished persons often receive higher doses of contaminants than do better nourished individuals.

may damage the lungs. ▪ Accidental aspiration of a liquid solvent or of gasoline can severely damage lungs or cause death.

Systemic effects

Lungs can serve as the entry point for toxicants. Volatile organic chemicals that evaporate from motor-vehicle or other household products are breathed in and enter the bloodstream through the lung's alveoli. The alveoli are tiny air sacs deep within the lungs at the end of the bronchiole tubes. Their normal function is to provide for an exchange between oxygen and carbon dioxide, but other chemicals also use this route.

¹² Henry, S. H., Bosch, F. X., Troxell, T. C., and Bolger, P. M. Reducing liver cancer: global control of aflatoxin. *Science*, **286**(5449), December, 1999 2453–2454.

¹³ Oniang'o, R. The never-ending story of Africa's hunger tragedy: where lies food safety? *AJFAND online*, **9**(1), 2009, <http://www.ajfand.net/Issue22/Issue22editorial.htm>.

¹⁴ Aflatoxin and liver cancer. *National Institute of Environmental Health*, November 9, 2007, <http://www.niehs.nih.gov/health/impacts/aflatoxin.cfm>.

SECTION III

In utero and children's exposure

Toxic effects on the developing embryo or fetus, baby or tiny child are of profound concern. Quite aside from obvious birth defects, scientists express concern that even very low exposures to some chemicals may have major impacts later in life. The diethylstilbestrol example noted below is an obvious example, but many other chemicals could also affect development.¹⁵ One public health expert has said, “the vulnerability of children [is] one of the central public health problems for our time.”¹⁶ Children are often more sensitive than adults to polluted environments.

Prenatal and post-natal exposures

A *teratogen*¹⁷ is a xenobiotic, which can damage the embryo or fetus,¹⁸ resulting in birth defects like mental retardation, or deformed organs. Preventing exposure to xenobiotics is especially important for the developing embryo and fetus, and the baby. Normal development requires a multitude of precise steps carefully coordinated. Environmental health specialists comment on “the exquisite sensitivity of prenatal and postnatal periods.” Adverse effects on the embryo or fetus may not cause obvious defects at birth, but can be responsible for diseases including cancer that develop later – see account of diethylstilbestrol below. There are also concerns that an increase in testicular cancer seen in young men may be due to prenatal chemical exposures. Because environmental hormones (below) may act at extremely low concentrations, even tiny exposures in utero leave us uneasy. Although xenobiotics are not the cause of most birth defects, major concerns remain.

Timing as important as dose

A teratogen is most likely to cause damage during the first eight weeks of pregnancy when organs are forming. Most damage cannot be repaired.

¹⁵ Among the substances of concern are the pesticides DDT, atrazine, methoxychlor, and vinclozolin; the metals mercury, lead, arsenic, and organotins; bisphenol A, phthalates, and PCBs; and carbon monoxide, fine particulates, environmental tobacco smoke, and alcohol. Weinhold, R. Consensus reached on prenatal exposures. *Environmental Science & Technology*, **41**(15) August 1, 2007, 5171–5172.

¹⁶ Kiewra, K. Brain pollution (impact of chemicals on children's brains). *Harvard Public Health Review* (online), Winter, 2007, <http://www.hsph.harvard.edu/review/winter07/brain.html>.

¹⁷ Diav-Citrin, O. and Koren, G. Human teratogens: a critical evaluation. *The Motherisk Program, Hospital for Sick Children, Toronto, Ontario, Canada*, http://www.nvp-volumes.org/p2_4.htm.

¹⁸ The word, embryo, refers to the first eight weeks of pregnancy, whereas fetus refers to eight weeks until delivery.

- Think about *thalidomide*,¹⁹ a drug taken in the 1950s and 1960s by pregnant women in Europe and Canada to prevent nausea. At the dose ingested, thalidomide didn't harm the women taking it. However, those women who took thalidomide when arms and legs were beginning to form had babies born with major defects such as stumps instead of arms or legs. Taken later in pregnancy, thalidomide caused no harm. Even later in pregnancy, a teratogen may cause harm, although less obvious, e.g., rather than causing observable structural anomalies it could retard the continuing growth and function of an organ.
- Because of the embryo's sensitivity in early weeks, pregnant women are advised to avoid alcohol, tobacco, and almost all drugs. Even the nutrient, vitamin A can cause birth defects if taken in above-recommended doses. Because the sensitive development phase may have begun before a woman even realizes she is pregnant, young women are advised to avoid suspect substances whenever a pregnancy is possible. Poor health in the mother can also adversely affect fetal health; so can malnutrition.
- Exposure of fathers to certain xenobiotics can damage their germ cells. In the 1970s, the insecticide *dibromochloropropane* (a soil fumigant used as a nematocide) was found to damage sperm chromosomes and lead to sterility.²⁰ The metal lead can produce malformed sperm.

Why children's sensitivity is often greater

Babies and small children often, but not always, show greater sensitivity to a toxicant than adults. This is because their immune systems are incompletely developed, and are less well able to fend off toxic insults than those in more-mature persons. Children tend to detoxify xenobiotics more slowly than do adults. Children are also developing rapidly, and the genetic material, DNA, rapidly replicates at the same time. This gives rise to more possibilities for mutations to occur.

Why is children's exposure greater?

Children are often more highly exposed to toxicants than adults. Why? ■ They eat more food per pound of body weight. Thus, if a food is contaminated, they ingest more toxicant. Pound-for-pound they also ingest more foods such as fruits treated with pesticides. ■ Children often ingest things that adults would not, such as sweet tasting leaded paint. They ingest soil too, which may be contaminated. ■ Babies and children breathe more rapidly than adults. So if air, including the home's air is polluted, they inhale a greater volume of contaminant. And, children crawling on or playing near the floor stir up contaminants, which they breathe. Think about an infant in a city. On average each day that infant takes in 110 ng of benzo benzo[*a*]pyrene pyrene, BaP,²¹ an

¹⁹ Center for the Evaluation of Risks to Human Reproduction (CERHR), Thalidomide. <http://cerhr.niehs.nih.gov/common/thalidomide.html>.

²⁰ Glass, R. I., Lyness, R. N., Mengle, D. C., Powell, K. E. and Kahn, E. Sperm count depression in pesticide applicators exposed to dibromochloropropane. *American Journal of Epidemiology*, **109**(3), 1979, 346–351, <http://aje.oxfordjournals.org/cgi/content/abstract/109/3/346>.

²¹ B(a)P is the most toxic of a family of chemicals called PAHs (Box 7.4). PAHs are emitted during all types of combustion, outside and inside the home. Family members track PAHs and other chemicals into the home on their shoes – these can transfer onto and into carpets, sofas, chairs, and other surfaces.

amount equivalent to smoking three cigarettes each day. The small child is also exposed to metals such as lead and other contaminants in house dust. Carpets are “deep reservoirs” for chemicals, microorganisms and allergens (animal dander, dust mites, and mold). This is especially true of old carpets, even regularly vacuumed ones.²²

More generally, indoor air pollution can be much greater than outside air pollution, especially in wealthy countries where outside air pollution may be well controlled. Indoor pollution may be a cause of increased rates of childhood asthma and allergies in urban areas of developed countries, especially as children spend so much time indoors.

Children of the poor

Children in wealthy nations are at risk from environmental exposures, but the situation is often much worse for children in less-developed countries (Chapter 17). Those living in cities are often exposed to highly polluted outside air. In rural areas, cooking fuels (wood, manure, or other biomass) are often burned inside the home, with poor or no ventilation. Children and their mothers most typically have the highest exposures to smoke. ▪ They are also commonly exposed to polluted drinking water too – although the infectious microorganisms in water usually pose a greater risk than chemicals. Pesticide exposure is also an issue (Box 3.5). In less-developed, but industrialized countries such as China unregulated chemical releases *and* unregulated sewage discharges pose problems.

Box 3.5

Pesticide exposure

Children

Farmers in Mexico's Sonora Yaqui Valley applied pesticides 45 times per crop cycle, and often grew two crops a year. Many Yaqui Indian families also regularly used insecticides at home. Babies were further exposed to pesticides through their mothers' milk. Thus, it was not surprising that investigators found detectable levels of many pesticides in the blood of babies born to these families. Dr. Elizabeth Guillelte and colleagues²³ examined the behavior of 33 heavily exposed children. They compared them to 17 Yaqui children from nearby foothills, whose only major pesticide exposure was to DDT that the government sprayed to kill malarial mosquitoes. Figure 3.4 shows the astonishing difference between these two groups of small children when they were asked to draw pictures of people.

Heavily exposed children were impacted in other ways. They showed less stamina than unexposed children when asked to jump up and down as long as possible, catch balls, or perform simple tasks. Their memories were also impaired. One scientist said, the magnitude of the observed changes “is incredible . . . and may prove irreversible.” In the United States and

²² To greatly lower exposure, avoid plush and shag rugs, which trap more contaminants. If babies or small children are in the home, use wood or tile flooring. Ask people to wipe their shoes at the door. Removing shoes can reduce the lead in a carpet six-fold.

²³ (1) Guillelte, E. A. *et al.*, An anthropological approach to the evaluation of preschool children exposed to pesticides in Mexico, *Environmental Health Perspectives*, **106**(6), June 1998, 347–353. (2) Raloff, J. Picturing pesticides' impacts on kids. *Science News*, **153**(23), June 6, 1998, 358.

other industrialized countries, there is continuing concern about children's exposure to pesticides, particularly farm children and children of migrant agricultural workers. The US General Accounting Office recommends educating farm-worker parents about how agricultural pesticides can affect young children. Pesticide labels should specify the period of time that children should stay out of fields after spraying. Currently, in the United States there are also efforts to reduce or, when possible, eliminate the use of pesticides in and around schools.

Flowers

Adults can suffer also. Several South American countries grow flowers in great quantities for shipment to North America and Europe. Large numbers and quantities of pesticides are used, including many banned in the United States and Europe. Fumigants used within enclosed greenhouses are often given little time to dissipate before workers return inside. More than half have headaches, dermatitis, and irritated eyes as well as respiratory and neurological symptoms. Women of child-bearing age are among these workers. Some socially conscious farm owners are working toward growing "green" flowers. One farmer uses a quarter of the pesticides he used 20-years ago and endeavors to use biological means to control pests. Such farms attract more birds, bees, and butterflies than those heavily treated with pesticides. For these farms to be viable, consumers must accept small blemishes on the flowers they buy.²⁴

Cancer

Cancer is a group of diseases. The word cancer refers to cells growing abnormally, multiplying in the absence of the usual controls.²⁵ Liver cancer is associated with chronic alcohol ingestion and with exposure to *aflatoxins* produced by molds growing on grains. Lung cancer is often associated with smoking tobacco. Leukemia, a cancer of the white-blood cells, has been associated with chronic benzene exposure in the workplace. ■ How can a carcinogen (cancer-causing agent) lead to cancer? A chemical that reaches the cell's nucleus may react with the genetic material (DNA) causing a mutation. But, before a cancer develops, the DNA may suffer many mutations, which are normally repaired by DNA-repair enzymes. Repair enzymes are a natural defense system that evolved over eons. Enzymes do not distinguish between mutations caused by synthetic carcinogens and natural carcinogens, they just repair the mutations. Sometimes trace amounts of a carcinogen can cause cancer, but it is typically higher doses of carcinogens that overwhelm repair mechanisms. The higher the dose the greater is the likelihood of damage.

²⁴ Bergman, C., A rose is not a rose (toxicity to workers from pesticide treated flowers). *Audubon* **110**(1), 2008, 46–53.

²⁵ Cancer: The News Behind the Numbers, *Berkeley Wellness Letter*, **23**(4), January 2007, 1–2.

Drawings of a person

4 year olds

Foothills

Valley

54 months
female55 months
female54 months
female53 months
female

5 year olds

Foothills

Valley

60 months
female71 months
male71 months
female71 months
male

Figure 3.4

Picturing the impact of heavy pesticide exposure. Credit: Dr. Elizabeth A. Guillette, University of Florida, Gainesville

Cancer development (Table 3.6)

- A carcinogen that directly interacts with and mutates DNA is called an *initiator*. Theoretically, an initiator has no threshold (no safe dose) and cancer could be caused by any dose greater than zero. But remember, having a trace dose in the environment does not mean that trace will be absorbed into the body, reach a target tissue, and then reach and interact with the nucleus within a cell.
- A cancer *promoter* is a chemical that impacts the growth of a *neoplasm* that has already been initiated. A promoter does not directly interact with DNA. And it *does* have a threshold, that is, there is a dose below which it does not promote cancer.
- A *complete* carcinogen is a chemical that both initiates and promotes cancer.
- Prostate, female breast, lung, and colorectal cancers are the most common cancers in the United States.²⁶ Lung cancer is the biggest cancer killer among Americans. Cancer risk

²⁶ Top 10 Cancer Sites by Incidence, United States. *Centers for Disease Control*, February 19, 2009, <http://www.cdc.gov/features/dsTop10CancerSites/>.

Box 3.6

Causes of cancer

- Tobacco About a third of all cancers are associated with tobacco use.
- Diet Almost another third is attributed to diet. Too much fat or too little fiber increases the risk of colon cancer, and possibly skin and prostate cancer. Chronic high-level consumption of salted and pickled foods is associated with stomach cancer.
- Being overweight or obese An International Agency for Research on Cancer (IARC) report indicates that about 10% of all cancers in the United States are due to being overweight or obese.²⁷
- Alcohol use Heavy alcohol consumption increases the risk of liver, colon, and breast cancer.
- Sunlight Excessive exposure to sunlight heightens skin cancer risk.
- X-rays Medical and dental X-rays are a risk factor for leukemia.
- Viral infections The human papilloma virus (HPV) increases the risk of cervical cancer. Hepatitis B virus enhances liver cancer risk. In countries where hepatitis B infection is common, liver cancer is also common. Worldwide, hepatitis B is second only to tobacco as a carcinogen, but presents a much lower risk in developed countries.
- Sexual habits HPV is associated with cervical cancer, especially in women who have had, or whose husbands have had, multiple partners.
- Bacterial infections The bacterium *Helicobacter pylori* heightens stomach cancer risk. Other associations of bacteria with specific cancers are being investigated.
- Occupational pollutants High benzene exposure is associated with leukemia, and high vinyl chloride monomer exposure with liver cancer.
- Environmental pollutants There is an association between lung cancer and very fine particles; radon, and environmental tobacco smoke; and skin cancer and arsenic exposure. Other relationships between pollutants and cancer are noted throughout this book. Some years ago, the worst case assessment of the combined risk of known environmental carcinogens was examined, which concluded that 1–3% of cancers may be due to pollution. Epidemiological studies arrived at a similar figure. However, as knowledge of cancer grows, this percentage could change.

increases with age. About one in three Americans is diagnosed with cancer by age 85. About one in five will die of cancer. The US cancer rate has been stable since 1991. Lifestyle and many other factors increase the risk of cancer (Box 3.6).

Environmental hormones

Hormones are chemicals produced within the body that are profoundly important to reproduction, sexual identity, development, and metabolism. This means that if individuals

²⁷ Rauscher, M. High number of cancers due to obesity. *Reuters*, November 1, 2005, http://www.redorbit.com/news/health/291927/high_number_of_cancers_due_to_obesity_study/.

Box 3.7

Pollution's toll on China's environmental health²⁸

China's environmental degradation is exacting a mounting toll on its citizens.

- Air China burns coal for about two-thirds of its energy, often with little control on emissions. An OECD report estimated that air levels of fine particulates resulting from burning coal result in 50 000 premature deaths and 500 000 new cases of chronic bronchitis each year. The World Bank has a much higher estimate. The problem is growing: a Chinese report predicts that deaths due to outdoor air pollution will reach several hundred thousand a year in the near future without pollution controls. In 2006, Beijing's average particulate level was 141 $\mu\text{g}/\text{m}^3$ of air whereas in the EU, the health-based standard is 40 $\mu\text{g}/\text{m}^3$.
- Water Those monitoring China's waters say that a third of its rivers and most of its large lakes have water so polluted that it is unfit for industrial, *let alone* agricultural use. About 300 million people lack access to safe drinking water although that figure may be improving. Many thousands of premature deaths a year result from drinking polluted water, mostly in rural areas. The causes of death are severe diarrhea, for which microbial contamination can be blamed.
- Cancer Moreover, dozens of "cancer villages"²⁹ exist, so-called because they have such high numbers of cancer deaths as compared to less polluted parts of China. The Ministry of Health says that, due to pollution, stomach, liver and bladder cancers are China's leading causes of death.
- Pollution's toll Using Chinese information, the World Health Organization (WHO) and the World Bank estimate total yearly deaths due to water and air pollution at 750 000 a year. Moreover, heavy metal (cadmium, lead and copper) contamination of food³⁰ and soil has been reported. Due to fears of social unrest, the government bans or downplays public reporting of statistics on pollution's adverse health effects; however, much unrest is occurring anyway. Meanwhile, health care costs continue to climb. China is, however, making a continuing effort to clean up its environment.³¹

are exposed to hormone-mimicking pollutants in the environment—*environmental hormones* – damage could ensue.³² Some industrial pollutants and some pharmaceuticals have hormonal activity. Moreover, natural environmental hormones exist too: some plants produce *phytoestrogens*, which mimic human female hormones. Environmental hormones may be active at very low doses. Worse, if harm occurs, it may not be apparent until many years later at which time it is very difficult to trace back to causes.

²⁸ (1) Kahn, J. and Yardley, J. As china roars, pollution reaches deadly extremes. *New York Times*, August 26, 2007, http://www.nytimes.com/2007/08/26/world/asia/26china.html?_r=2&oref=slogin&oref=slogin. (2) McGregor, R. 750,000 a year killed by Chinese pollution. *The Financial Times Limited*, July 2, 2007, <http://www.ft.com/cms/s/0/8f40e248-28c7-11dc-af78-000b5df10621.html>.

²⁹ Tremblay, J. -F. China's cancer villages. *Chemical & Engineering News*, **85**(44), October 23, 2007, 1821.

³⁰ Zamiska, N. and Spencer, J., China faces a new worry: heavy metals in the food. *Wall Street Journal*, July 2, 2007.

³¹ Tremblay, J. -F., China releases new cleanup plan. *Chemical & Engineering News*, **85**(49), 3 December, 2007, 12.

³² Environmental hormones are also called hormonally active agents, endocrine disruptors, or hormone-mimics.

Table 3.6 Cancer development**Cancer initiation–inducing mutation**

An *initiator* – benzopyrene is an example – reaches the DNA within a cell

It forms an adduct with DNA, i.e., becomes chemically bonded with the DNA

It is genotoxic, i.e., damages the DNA

For a tumor to grow, a number of mutations are necessary

Many mutations are repaired by DNA-repair enzymes

But if not repaired then, when the cell divides, the mutation replicates too

The US EPA treats a cancer initiator as having no threshold: no safe dose. European agencies may assume the carcinogen does have a threshold

Cancer promotion

Not all mutations are repaired. The tumor (neoplasm) grows from the cells containing these mutations

A *promoter* – chloroform is an example – enhances tumor growth, but does not damage DNA

A complete carcinogen can both initiate and promote tumor growth

Cancer progression

As the tumor grows, there are additional changes in the DNA

If the tumor is benign, it does not invade other tissues

If the tumor is malignant, it may spread (metastasize) to other tissues

Impacts on fish and other wildlife

Only animals are *known* to have suffered harm from environmental hormones. Wildlife, both animals and plants, actually lives within the environment where such pollutants are found, and several are known to have harmed wildlife reproduction and development.

▪ A notorious example is the impact of the once widely used insecticide, DDT. Because DDT persists in the environment, its concentration built up over the years that it continued in use. Eagles, osprey, and other birds exposed to DDT produced thin eggshells, often crushed before they could hatch. This greatly reduced the populations of these birds by the 1960s. ▪ In a different way, DDT led to a major population drop in Western seagulls: the gulls laid eggs that produced sterile males, or else male birds with feminized reproductive tracts or other feminine characteristics. ▪ Another infamous case resulted from a large spill of the pesticide *dicofol* into Florida's Lake Apopka in 1980. The dicofol was found to contain 15% DDT. Later observation showed that, compared to a normal hatch rate of 70–80%, only 5% of Lake Apopka's alligator eggs were hatching, and many of these died within weeks. Many survivors had feminine characteristics. These effects were traced to *p,p'*-DDE, a breakdown product of DDT. Although other lakes had not suffered a spill, many were found with high levels of DDT and other organochlorine pesticides (chlordane, toxaphene, dieldrin) due to agricultural runoff. In these lakes too, fewer alligator eggs were hatching. After two decades the hatching rate has much improved to about 50%, much better but alligator reproduction is still affected. Moreover, scientists fear that not only alligators, but turtles and frogs are also being

affected.³³ ■ Industrialized countries banned DDT in the 1970s, and many bird populations slowly recovered as these chemicals have slowly degraded.³⁴

Millions of women deliberately take estrogenic pharmaceuticals – birth control pills and hormone replacement therapy (although the number in this latter group has much decreased). These women excrete a portion of the hormones and their metabolites into toilets. Sewage treatment plants do not remove them so the estrogens are found in concentrations up to about 10 parts per trillion (ppt) in plant effluent. This is an extremely low concentration, but fish can be affected by human estrogens at levels as low as 1 ppt. ■ In one instance, male fish beneath the outflow of a wastewater treatment plant emptying into Boulder Creek, Colorado, underwent a sex change into female fish. The same thing could be observed experimentally by exposing male fish contained in tanks to water from the plant outflow. The fish most likely to be affected were those closest to the outflow of the plant ■ In cases occurring elsewhere, males don't undergo a complete change in gender, but do exhibit female sexual traits such as having immature eggs in their testes. One of the places that these "intersex fish" have been observed is in the Potomac River in the Eastern United States. Female fish were not affected in any obvious way.³⁵

Impacts on humans

The potent synthetic estrogen, *diethylstilbestrol* (*DES*) was a pharmaceutical prescribed to pregnant women in the first trimester of pregnancy (the embryo phase) between 1948 and 1971 to prevent miscarriages. DES caused no harm to the women taking it. But, 15 to 25 years later, an epidemic of a rare cancer of the vagina occurred among young women. Because so much time had passed, it was difficult to discern the cause but the epidemic was eventually traced to the women's mothers who had taken DES when pregnant. Somewhat less than one in 1000 daughters developed cancer. This was a major and disturbing finding: cancer in adults could develop as a result of in utero exposure many years before. ■ However, remember that DES is *more* potent than natural human estrogens, whereas environmental hormones are typically very weak. And DES is a pharmaceutical deliberately taken in large doses as compared to typically very low exposures to environmental hormones.

Is human health being harmed by exposure to bisphenol A?

It is reasonable to hypothesize that environmental hormones may be affecting humans. There is much concern now that the chemical, bisphenol A (BPA) – which is structurally

³³ Chatterjee, R. Florida gators battle pesticides, the poor survival rates of alligator eggs are linked to lingering toxic chemicals in lakes. *Environmental Science & Technology*, **41**(15), June 27, 2007, 5173–5174.

³⁴ DDT is still used to "paint" the insides of homes in malaria-prone areas in Africa and elsewhere, and also to treat bed nets. In both cases, mosquitoes are repelled or killed by the DDT.

³⁵ (1) Dickinson, B. and Neff, T. Effluent changes gender of fish. *Scripps Howard News Service*, December 12, 2006. <http://www.trib.com/articles/2006/12/12/news/regional/87a0a21fccb3d8a587257241006d1666.txt>. (2) Barakat, M. More "Intersex Fish" Found in Potomac, Associated Press, September 07, 2006. <http://lists.dep.state.fl.us/pipermail/pharmwaste/2006-September/000624.html>

similar to DES – may also have insidious effects.³⁶ Billions of pounds are produced each year, used to make polycarbonate plastic baby bottles, sippy cups, and sports drink containers, and BPA-based resin is used to line many food cans.³⁷ BPA is found in human blood and urine at levels known to adversely impact mice. BPA is also very controversial: when a hazard assessment of BPA was done, two very different conclusions emerged.³⁸

- High concern One group of 38 scientists, studying research on the issue concluded that, in rodents, low doses of BPA cause breast cancer, enlarged prostates, penis abnormalities, reduced sperm counts, early onset of puberty in females, type 2 diabetes, and neurological effects.³⁹ They pointed out that human exposure is within the range that brings about negative effects in lab animals, and expressed concern about human exposure to BPA. These scientists examined all animal studies no matter whether BPA administration was by mouth, skin absorption or injection.
- Low concern Another group of scientists expressed fairly low concern about BPA. However, they discounted all studies except for those in which BPA was given by mouth. They justified this by saying that injecting BPA under the skin or into the bloodstream is invalid because, for exact doses to be determined, oral administration was necessary.
- Clarifying the controversy? Recently scientists in the high concern category carried out a study concluding that the route of administration made no difference in fetuses and newborn mice: exposure by any means can cause adverse effects. Thus all the studies, regardless of the route by which BPA was administered needed to be considered.
- The US Food and Drug Administration (FDA) considers BPA to be safe for use in food and beverage containers. However, several members of the US Congress have expressed concern. They asked the FDA what studies it used to determine that BPA is not a health risk to children or adults and also urged the FDA to reconsider its decision on BPA safety. Further, some members of Congress have requested that four manufacturers voluntarily remove BPA from infant bottles and related products.⁴⁰

³⁶ Hileman, B. Bisphenol A safety: research results may call into question conclusions of a federal report. *Chemical & Engineering News*, **86**(05), February 4, 2008, 9.

³⁷ Bisphenol A (BPA) is a monomer used to make the polymer, polycarbonate. However, reactions are not 100% efficient, so not all the BPA is incorporated into polycarbonate. Some BPA remains free, able to leach out during use especially when heated, as when warming a baby's bottle of milk.

³⁸ (1) Hileman, B. Bisphenol A Safety, Research results may call into question conclusions of a federal report. *Chemical & Engineering News* **86**(05), February 4, 2008, 9. (2) Hileman, B. Bisphenol A vexations, two government-convened panels reach nearly opposite conclusions on compound's health risks. *Chemical & Engineering News* **85**(36), September 3, 2007, 31–33.

³⁹ (1) Murray, T. J. *et al.* Induction of mammary gland ductal hyperplasia and carcinoma in situ following fetal bisphenol A exposure. *Reproductive Toxicology*, **23**(3), April/May, 2007, 383–390. (2) Thacker, P. D. Plastics chemical alters female brains. *Environmental Science & Technology*, **40**(13), July 1, 2006, 4044.

⁴⁰ Congress Urges Removal Of BPA From Packaging. *Chemical & Engineering News*, **86**(19) May 12, 2008, 30.

Questions 3.2

1. Should regulatory action be taken to limit human exposure to BPA? Why?
2. What would the precautionary principle recommend? Explain.
3. Some recommend going back to glass baby bottles or else that a different plastic be used. What would you want to know about an alternative plastic before deciding whether it was a good replacement?

Is human health being harmed by exposure to phthalates?⁴¹

Another category of synthetic chemicals posing much concern as to possible impacts on humans is the phthalate family. Well over a billion pounds of phthalates are manufactured worldwide every year. Phthalates are used as plasticizers (softening agents) in children's polyvinyl chloride toys and teething rings, in medical products, in paints and varnishes, and in many cosmetic and toiletry products including nail polish, soaps, shampoos, and perfumes.

- Human exposure Depending on the product being considered, and the particular phthalate it contains, people ingest phthalates that leach from plastic products into food, inhale phthalates that become airborne, or absorb phthalates across the skin. The US Centers for Disease Control (CDC) confirmed that phthalates do get into the body. The CDC found phthalates and their metabolites in human blood and urine. It is believed that most do not pose a health threat, but two phthalates were detected at levels higher than would be expected on the basis of their production volume.⁴²
- Animal studies Recent work indicates that when pregnant rats are exposed to even tiny amounts of certain phthalates,⁴³ their male pups suffer adverse effects. Sperm-producing cells develop poorly in the pups and, at puberty, many are infertile. The higher the dose given to the dams, the greater the adverse effects observed in the pups.
- Human concerns The abnormalities seen in rats are relevant to how human testicular cancer is thought to develop. The question is asked, do phthalates in the blood of human mothers affect their embryos?⁴⁴ Moreover, it has been demonstrated that nursing babies receive phthalates from their mothers' milk.⁴⁵ Whether these are impacting health is still not definite, but the European Union and the US State of California has banned phthalates from toys.

⁴¹ ATSDR ToxFaq. Oregon Health & Science University, 2001–2009, <http://www.ohsu.edu/xd/research/centers-institutes/croet/outreach/toxfaq.cfm>. This site offers short summaries of three phthalates: diethyl phthalate, di-n-butyl phthalate, and di-n-octylphthalate (DNOP).

⁴² Erickson, B. Risk from phthalates. *Chemical & Engineering News*, **86**(51) December 22, 2008, 9.

⁴³ Not all individual chemicals in the phthalate family are equally problematic. A California law bans the manufacture, sale, and distribution of – not all phthalates – but of any toy or child care product that contains more than 0.1% of di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), or benzyl butyl phthalate (BBP).

⁴⁴ Hileman, B. Chemical exposures: unusual cross-disciplinary meeting explores effects of environmental compounds on human development and reproduction. *Chemical & Engineering News*, **85**(11) March 12 2007, 29–32.

⁴⁵ Lubick, N. Plasticizers go from breast milk to baby. *Environmental Science & Technology*, **40**(17) September 1, 2006, 5166–5167.

Other hormone mimics

Estrogen mimics are the best known environmental hormones, but there are others.

- In addition to human-produced pollutants that mimic estrogens, humans are exposed to phytoestrogens, natural plant estrogens. Phytoestrogens are found in soy-based baby formula used to feed infants unable to tolerate milk. These infants are exposed to doses of *isoflavones* 6 to 11 times greater than levels known to show hormonal effects in adults. Effects may not be adverse, but soy-based infant formula is under suspicion and being studied for possible long-term effects especially because as many as 20% of infants are fed the soy formula. It is now recommended that soy be used only as a last resort.
- Many young men deliberately take androgens (male sex hormones) to accentuate their physiques and athletic abilities.
- In addition to estrogens and androgens, other pharmaceutical hormones are widely used. A major one is synthetic thyroid hormone.
- Thus millions of people deliberately take hormones. This makes it difficult to sort out how industrial environmental hormones may fit into the picture.

Are environmental hormones impacting humans?

We know that animals have been affected by chemicals in the environment with hormonal properties. It is hard to say at this point if humans are being affected. However, as you saw above for phthalates and bisphenol A, many are seriously worried as to whether humans are being harmed.^{46,47} The University of Florida's Louis J. Guillette Jr., who did much of the work that exposed DDT's effects on alligators, warns that we must also look carefully for impacts on humans.

Delving deeper

1. Look at the list of ingredients in liquid hand soaps (and an increasing number of other products found in US stores). You will find a chemical called *triclocarban*. It is used as an antiseptic. Most of this triclocarban ends up going down our sewers and is not destroyed by sewage treatment plants, so it ends up contaminating water bodies. And because treated sewage sludge is often spread on farmland, triclocarban is found on farm fields. Go to the Internet and examine issues associated with triclocarban. Does it serve a useful purpose? Do we really need it? What problems could it cause? What does Dr. Stuart Levy of Tufts University think of the way we use this chemical?

⁴⁶ Colborn, T., Dumanoski, D. and Myers, J. P. *Our Stolen Future*. New York: Plume/Penguin, 1996.

⁴⁷ Collins, T. J. Persuasive communication about matters of great urgency: endocrine disruption. *Environmental Science & Technology*, **42**(20) October 15, 2008, 7555–7558.

2. Smuggler Mountain may not have left a “toxic legacy” to the children there. However, lead may be having a much more serious impact in an African town. Examine the following Reuter’s article: Shacinda, S. Mining leaves toxic legacy in Zambian town. Jun 21, 2007, <http://www.reuters.com/article/latestCrisis/idUSL19513545> Write or present a brief report on your findings and conclusions.

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“Ordinary risk analysis asks, How much environmental damage will be allowed?
But the precautionary principle asks, “How little damage is possible?”

Thomas Prugh, WorldWatch Institute

How can we decide what is or is not safe? How much ozone should we allow in the air that we breathe? How much arsenic in drinking water is safe? What level of dioxin in soil or food is acceptable? These and similar questions regularly arise. Because we seldom have the luxury of answering “zero,” we must determine what level above zero is safe or essentially safe. The useful albeit imperfect tool of chemical risk assessment assists us in this effort.

Section I of this chapter points out that a chemical cannot be a risk unless there is exposure to it. Also discussed are body burdens. Section II reviews epidemiological studies – investigations designed to detect relationships between exposure to a chemical and adverse health effects. Section III introduces the four steps of chemical risk assessment, both for chemicals that do not cause cancer and for carcinogenic chemicals. Section IV briefly examines risk assessment for non-humans and in less-developed countries. Section V explores what practices are used to reduce a chemical’s risk, risk management. These include non-regulatory as well as regulatory approaches. Section VI looks at how chemical risk assessment is changing and how the regulation of chemicals may also be changed.

SECTION I

A hazardous chemical is only a potential risk. It becomes a risk only if you are exposed to it. So, no matter how hazardous a chemical is, it is not a risk without exposure.

$$\text{Risk} = \text{Hazard} \times \text{Exposure}$$

If there is exposure, we need to evaluate both the hazard of the chemical (its inherent toxicity) and how much exposure there is.

Exposure^{1,2}

There are thousands of hazardous chemicals. Many could pose a risk. To determine if there is risk, ask yourself – is there exposure to it? If so, to what amounts? What is the route of

¹ Evaluating Exposure Pathways. Chapter 6: Exposure Evaluation. *ATSDR. Public Health Assessment Guidance Manual* <http://www.atsdr.cdc.gov/HAC/PHAManual/ch6.html>.

² EPA’s report on the environment: human exposure and health. *US EPA*, January 21, 2009, <http://oaspub.epa.gov/hd/home#26>.

exposure – is it through air, water, soil, or food (or more than one of these)? You have already seen illustrations of exposures to hazardous chemicals: ▪ Exposure of children to lead at Smuggler Mountain and in houses with crumbling lead paint. ▪ Exposure of babies to benzo[a]pyrene through contaminated carpets. ▪ Exposure of Yaqui Indian children to pesticides through inhalation of sprayed pesticides, or eating food or drinking water contaminated with pesticides.

Dioxins³

Think about chemicals in the dioxin family,⁴ and how exposure to dioxins can occur. ▪ Combustion Dioxins form during poorly controlled combustion in municipal-waste incinerators and other combustion sources – they are products of incomplete combustion. Dioxin particles released into air settle onto vegetation, and are eaten by cattle and other animals. Animals concentrate dioxins in their fat. Humans receive about 90% of their total exposure to dioxins when they eat contaminated fatty meat such as hamburgers and fatty dairy products. ▪ Chlorine-using processes A pulp mill using elemental chlorine to bleach pulp releases trace amounts of dioxins into their effluent. Released into a river, most dioxin is not soluble; most attaches to sediment particles. Bottom-feeding creatures ingest dioxins as they eat the tiny organisms living there. From there, dioxins biomagnify in the food web (Figure 3.3). Fish that eat the contaminated organisms concentrate dioxin in their fat and larger fish concentrate still more. Birds of prey, large mammals and humans are exposed when they eat these fish. Several other industrial processes can produce dioxins as unintended by-products including the manufacture of chlorinated pesticides. Both the pulp bleaching process and the making of chlorinated pesticides have been modified to prevent the formation of chlorinated dioxins – P².

Questions 4.1

Exposure to a substance can occur through air, water, soil, and food.

- 1 In thinking about how you can be exposed to pesticides, explain how exposure could happen through each of these.
- 2 (a) People living in homes with peeling lead paint could be exposed to lead in what ways? (b) If there was lead in the plumbing how would exposure occur?
- 3 What is a likely way that a baby or small child could be exposed to chemicals in toys?
- 4 When you use cosmetics or toiletry items, are you exposed to synthetic chemicals? Explain.
- 5 Would exposures to natural chemicals necessarily be safer? Explain.

³ Toxicity assessment (non-cancer and cancer effects for dioxins and PCBs). *Region 8 US EPA*, August 20, 2008. http://www.epa.gov/region8/r8risk/hh_toxicity.html.

⁴ Dioxins and furans are a family of chemicals. The most toxic is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD, often just called dioxin). The largest releases of dioxins today come from the open burning of household trash, municipal trash, landfill fires, and agricultural and forest fires. See 2,3,7,8-tetrachlorodibenzo-p-dioxin. *US EPA*, <http://www.epa.gov/ttn/atw/hlthef/dioxin.html> [November 2007].

Body burden

Humans are exposed to chemicals in air, water, food, and soil. But what does exposure actually mean? Remember that, unless a chemical can act directly on skin or mucous membranes, it must be absorbed into the body, become a *body burden*, before it can exert a toxic effect (Chapter 3). One health scientist gave the example: “What you really want to know is *not* whether asbestos is in the environment, but whether it’s in your lungs. If it didn’t get into your body, you don’t need to worry about health effects.” Once it *is* in your body, a chemical or its metabolites may be measured in blood samples; it can also be measured in urine or feces after excretion. Such measuring is referred to as *biomonitoring*. In 2005 the US Centers for Disease Control and Prevention (CDC) released its third *National Report on Human Exposure to Environmental Chemicals* with results from biomonitoring 145 chemicals in human blood and urine.⁵ ▪ Many of these chemicals were being monitored for the first time in this study, whereas others had been studied in earlier years too. Personnel doing the CDC study traveled in a convoy of tractor-trailers to 30 locations around the United States. They interviewed 2500 adults and children and took samples of blood and urine. People monitored were selected as being representative of the entire US population including age, gender, race, and ethnicity. Box 4.1 summarizes the results for some chemicals. CDC will continue to collect new samples in upcoming years and to test for additional chemicals not yet examined.

Box 4.1

Some of the chemicals that CDC found in our bodies

- Cotinine is a nicotine metabolite.⁶ If found in blood or urine, it indicates exposure to tobacco smoke. Compared to the early 1990s, the body burden of cotinine dropped 75% in adults, probably due to regulations restricting smoking. It dropped only 58% in children and cotinine levels were twice as high in children as in adults, probably because no regulations apply to smoking at home.
- Pesticide metabolites⁷ ▪ CDC detected metabolites of the organophosphate pesticides, *chlorpyrifos* and *diazinon* in urine. This is a concern because, although these metabolites have short lives in the body, almost every person tested had them. This means people were exposed shortly before testing, and indicates too that exposures are probably frequent. Children had greater body burdens than adults perhaps because they metabolize these pesticides differently than adults or because, pound per pound they take in more when breathing, eating, and drinking. These two pesticides have been banned for household use,

⁵ Third National Report on Human Exposure to Environmental Chemicals. CDC, 2005, <http://www.cdc.gov/exposurereport>.

⁶ The word metabolite refers to a substance produced when a living organisms converts a chemical into some other chemical(s).

⁷ The US EPA is following CDC’s work. For EPA the problem is that the disciplines of toxicology and epidemiology are not nearly as advanced as is biomonitoring. So, whether one should be concerned or not is truly not known. However, a very ambitious study is addressing this concern. The National Children’s Study is following 100 000 American children as they grow up. It monitors levels of environmental chemicals and looks for any associations with disease. However, it will be a long time before the results are in.

and the CDC will, in future studies, watch to see if levels in urine go down. • DDE (the major metabolite of DDT) had declined compared to pre-1990. This was expected because DDT production was banned in 1973. However, even people born after DDT was banned retained small body burdens. Because of its long life, DDT persists in the environment, and may also be entering the United States in imported food. Blood levels of DDE were about three times higher in Mexican-American immigrants than in other immigrants, but it is not known whether they were exposed in Mexico or in the United States.

- Phthalate metabolites⁸ Phthalates are chemicals used in plastic products such as children's toys to make them more flexible. They are also used in cosmetics, toiletry items, and industrial solvents. Seven phthalate metabolites were found in urine. Investigators were surprised that the metabolites found in the highest amounts did not come from the phthalates *used* in the highest amounts. One phthalate found at higher than expected amounts was *diethyl phthalate* used in soaps, perfumes, and shampoos. The CDC hypothesized that direct skin contact with these products may explain this, if absorption across the skin occurs. See discussion of phthalates in Chapter 3.
- Dioxins The CDC was encouraged to see that blood levels of dioxins, furans, and PCBs were below detection limits. These chemicals were detectable in studies done in the 1980s. Emissions from industrial sources have fallen about 80% since then, so decreased body burdens are probably due to a fall in environmental levels.
- Twelve hazardous metals • Because one of these metals, *lead* (Pb) has long been a major children's health concern, blood levels have been measured for decades. In 1990 (compared to the late 1970s) children's levels had dropped significantly, presumably because Pb was banned from gasoline. In 1991–94, only 4.4% of children aged one to five still had elevated blood lead levels. This has fallen to 2.2%. Children living in old lead-painted homes are still at risk. The CDC believes blood levels of Pb greater than 10 µg /100 ml presents an unacceptable health risk. • Body burdens of *cadmium* (Cd) have remained steady. Even very low levels may be associated with subtle kidney injury and increased risk of low bone mineral density, and 5% of people aged 20 years or older had urinary Cd levels in their urine near the level of concern. Cigarette smoking is considered the most likely source. More research is needed into possible health effects of exposure to low levels of Cd. • *Mercury* (Hg) can adversely affect neurodevelopment in the developing fetus. Tests on women of childbearing age showed all had blood levels of Hg below 5.8 ppb (5.8 µg/L) – the level associated with adverse effects on the fetus. This could be considered good news *except* 5.7% of the women had levels within a factor of 10 of those associated with adverse effects on the fetus; another report says up to 10% were in this category. Thus, close monitoring of Hg is needed because we still don't know what level of Hg can be considered safe. Eating mercury-contaminated fish, primarily large fish, is the primary source of exposure. To lower Hg levels in fish, the CDC recommends that society make more effort to lower Hg emissions from electric power plants, waste incinerators, and chlorine production facilities. • *Other hazardous metals* detected by the CDC included cobalt, tungsten, and uranium.

⁸ Spotlight on phthalates, CDC's Third National Report on Human Exposure to Environmental Chemicals. CDC, July, 2005, http://www.bhsj.org/eh/EnvHaz/factsheet_phthalates.pdf.

Should we be concerned about the chemicals detected in our bodies?

Richard J. Jackson, who directs the CDC's National Center for Environmental Health, stated that "just because a chemical can be measured in blood or urine doesn't mean it causes illness or disease." CDC says we must know what happens to it within living cells. Industrial organizations say the levels detected are mostly very low and thus unlikely to affect health. Environmental organizations express concern, even alarm, that so many xenobiotics are in our bodies. Jackson noted that the CDC is undertaking dozens of additional studies to address potential health concerns of these body burdens, and to see what levels of certain chemicals are safe or unsafe. Other countries are planning to do similar studies.

Of what use are the CDC studies?

A CDC official said the studies presented "a giant step forward for us in exposure information and will make big differences in our ability to identify and prevent disease." How? First recognize that not just any chemicals, but chemicals already posing concerns were measured.

- For chemicals already studied over many years, some results are encouraging: Levels of the highly toxic dioxins and of the metal lead in people's bodies have decreased over time; this means that measures taken to reduce dioxins and lead in the environment are working.
- On the other hand, the metal mercury (a risk to fetal development) was often present at levels of concern in women of childbearing age. This tells us we need to do more to reduce exposure.
- What about chemicals not previously measured? Results provide us with a baseline against which to compare future increases or decreases in body levels. And if, in the future CDC finds levels that are increasing, studies will be made of potential detrimental effects.
- Several phthalates were found at surprisingly high levels. For chemicals such as these, we can investigate why they are high, and if we should take special efforts to reduce them.

SECTION II

Epidemiological studies

Epidemiology is the study of the causes of disease, its distribution in human populations, and the factors influencing distribution. You saw the results of one study showing the association between vaginal cancers in young women and the DES taken by their mothers when pregnant with them (Chapter 3). Epidemiological studies are important because they look directly at *human* risk. They examine exposure to a chemical or other agent, and look for a connection to adverse health effects. There is strong interest, for instance, in doing epidemiologic studies to see if there are links between phthalates and negative health impacts in human.

- Historically, epidemiology was used to trace infectious disease outbreaks caused by exposure to pathogenic microorganisms – as when outbreaks of cholera or typhoid fever were traced to a contaminated water supply.

Epidemiology applied to chemical exposures

It is usually more difficult to link a disease to a chemical exposure.

- In the first successful case the English physician Percival Pott, in 1775 noted that scrotal cancers were common in boys who worked as chimney sweeps. Observing their intensive exposure to coal dust and tar, especially as they worked within chimneys without clothing, he correctly recommended that the boys should regularly bathe to remove soot.
- Before modern work place safety controls were instituted in industrial societies, a number of diseases were traced to occupational exposures. *Asbestos* exposure was linked to asbestosis, lung cancer, and mesothelioma. High-level exposure to *benzene* was linked to blood abnormalities and leukemia. Exposure to *radon* at the high levels found in uranium mines was associated with lung cancer. Note the word *association* in the preceding sentences. An association is a relationship between two situations. It is not proof that one caused the other.
- Strong associations The best epidemiological studies examine large numbers of people, preferably exposed to high concentrations of the suspect substance. This is how an association between cigarette smoking and lung cancer was made allowing us to attribute about 30% of all American cancers to tobacco use. Likewise, because so many millions of people drink alcohol, it was possible to link excess drinking to liver cancer.
- Small populations Although more difficult, good studies can be done on small populations especially if the adverse effect is unusual and all affected individuals are known to share a particular exposure. ▀ One successful linkage involved only about 100 individuals. Each had an uncommon liver cancer, and each had suffered workplace exposure to the chemical *vinyl chloride*. ▀ Another clear link that involved small numbers of individuals was the association of vaginal cancer in young women with mothers who took DES.

Difficulties in doing epidemiological studies

Confounding factors

A major reason that chemical epidemiological studies can be frustrating is *confounding factors*. These are factors which may influence study results independently of the exposure being studied. If a person smokes tobacco or drinks alcohol, this can influence their susceptibility to a disease quite aside from the exposure in question. So can gender and age, malnutrition, and a number of other factors.

Exposure

Even more difficult than assessing confounding factors is the problem of accurately evaluating exposure to the agent under study. One author of a *Science* article said, "Of all the biases that plague the epidemiological study of risk factors, the most pernicious is the difficulty of assessing exposure to a particular risk factor." The reason for this is that exposure information typically relies on human memories, which may be faulty and selective.

Community studies

So-called community studies are usually very unsatisfying. These are carried out in communities that appear to have an excessive rate or *cluster* of a particular disease. Almost any community, by chance, will have excess rates of some diseases, but people may suspect that the disease results from a common exposure, perhaps a drinking-water contaminant, chemicals in a community hazardous waste site, or air emissions from a manufacturing facility. To follow up on community concerns, epidemiologists must first determine if there is indeed a cluster. This is difficult. For instance, how do they decide on a boundary around the area where the suspect disease occurs? If the cluster appears real or, sometimes even if it doesn't, epidemiologists look for an exposure shared by the individuals who have the disease. However, the population is usually too small to make successful statistical connections. It's especially difficult to evaluate exposure if individuals know why they are being studied – bias creeps into the study. But community studies continue to be demanded by anxious and suspicious residents. Because it is so difficult to reach conclusions for a single community, some investigators take a multi-site approach, i.e., results from a number of similar sites are pooled (such as a number of communities with similar hazardous waste sites). The data are analyzed to see if more definitive results are obtained than for one community alone. These studies too are controversial.

Judging epidemiological studies

Harvard epidemiologist, Professor D. Trichopoulos, observed that epidemiologists can be “a nuisance to society. People don't take us seriously anymore, and when they do take us seriously, we may unintentionally do more harm than good.” This can happen if study results are reported with fanfare in the news media. This makes it difficult for the person receiving the information to judge how seriously to take it. Here are some questions to ask to help judge a study.

- Is this the first study on this agent, or have there been several studies all showing fairly consistent results? Exposure to very fine particulate matter in the air is a case in which many studies have shown that, as air levels of particulates increase, so do hospital admissions for respiratory diseases and some heart problems.
- How many people were studied – many thousands, just a few hundred, or even fewer? In one case several small studies indicated an association between a high-fat diet and increased breast cancer risk. But a careful study of 121 000 nurses followed for 20 years showed no association. However, although respected this study did not close the discussion of an association between fat intake and breast cancer as other studies continue to be performed.
- Were confounding variables, such as age, smoking, diet, or other lifestyle factors considered? In the case of the 121 000 nurses mentioned above, their backgrounds were well known. This allowed correction for confounding factors
- Is the disease rare? This may allow it to be more easily linked to a risk factor. Was it for example an increase in a specific rare cancer or a general increase in all cancers?

- How large was the risk factor? A 30% increase in risk or even a doubling may mean little, especially with only one study. But if there is a three- or four-fold increase in risk, the association carries more weight even with only one study. This is especially so if confounding factors were carefully evaluated.
- Even strong associations may raise the question: is the relationship biologically plausible? That is, can results be explained in terms of how living organisms are known to work? As noted above studies consistently indicated increased hospital admissions in people exposed to fine particulates, but it took longer to come up with a biological explanation as to why.
- If clinical work on human beings has been done, are the results consistent with the epidemiological study?
- Finally, is the story sensationalized? Even careful studies are often difficult to interpret definitively. Sensationalizing a report may yield only confusion.

The limits of epidemiology

Epidemiology cannot answer all the questions put to it, even after many well-designed studies of one particular risk factor have been. This has been the case with studies of electromagnetic fields (EMFs).⁹ Epidemiological studies have searched for connections between human cancer and exposure to EMFs for many years. Results have been inconsistent, sometimes contradictory. A US National Academy of Sciences panel, after carefully evaluating these studies reported in 1996 that at EMF levels found in human residences it found no evidence of adverse effects on animals or cells.¹⁰ They stated that If EMFs pose a risk at ordinary levels that people encounter the risk is very small. It is these possible small risks that pose a major problem for epidemiologists because so many factors could influence study outcomes.

But a small risk can be important: Hundreds of millions of people use electricity and are exposed to EMFs, so even a small risk could affect many people. This motivates researchers to continue studying EMF risks.

Despite their well-recognized problems epidemiological investigations can be tremendously useful and provide information that no other type of study can. Two studies in the 1990s were so highly regarded they resulted in major policy recommendations:

- An association was shown between excess vitamin A intake during pregnancy and an increased risk of serious birth defects. A second study strongly supported that conclusion: pregnant women taking four times the recommended daily intake of vitamin A had a much increased risk of giving birth to babies with cleft lip, cleft palate, and major heart defects. This study led to a recommendation that women of childbearing age not take Vitamin A in amounts exceeding the recommended dose.

⁹ EMF (electric and magnetic fields). *National Institute for Occupational Safety and Health*, 2005, <http://www.cdc.gov/niosh/topics/EMF/>.

¹⁰ Anon. NAS says EMFs no hazard. *Environmental Health Perspectives*, **105**(1), January, 1997, 25.

- Birth defects were also the subject of another study. In this case the problem was too little folic acid, a B vitamin, in pregnant women's diets. See Figure 3.2. A lack was strongly associated with serious birth defects, spina bifida (in which the spinal cord is not completely encased in bone) and anencephaly (in which a major part of the brain does not develop). The association was so clear that it too led to action: producers of flour and cereals began adding folic acid to assure that women of childbearing age had a sufficient intake.

Questions 4.2

- 1 Think about the sentence, "Alternative products are available to substitute for DEHP." If you were responsible for examining alternatives for this phthalate, what would you want to know? As you think about this, consider problems that can arise with alternatives as seen in the following two cases. (a) The metal, lead used for many years as an antiknock agent in gasoline, is particularly dangerous to the fetus and small child. Lead in gasoline was finally replaced by the chemical, benzene. However, benzene is a known human carcinogen. (b) An oxygen-containing chemical is added to gasoline to promote its cleaner burning. In the United States, methyl tertiary butyl ether (MTBE) was widely used for this purpose. However, MTBE proved more water soluble than expected, and became a widespread water contaminant. Now, it is being replaced, often with ethanol. So, should such cases dissuade you from looking for alternatives? Explain.
- 2 (a) In those countries that have not yet banned lead in gasoline, how could small children be exposed to the lead? (b) How do they continue to be exposed years after lead has been banned from gasoline?
- 3 Epidemiological studies of potential effects of phthalates on humans are needed, but getting good results could take many years. What action should society take now? Explain.
- 4 You read that a careful study of 121 000 nurses did not show an association between fat intake and breast cancer. Why would additional studies on this question be continuing?
- 5 A few years ago, two professors in the Chemistry Department of the University of Maine died within several years of each other of the same rare brain cancer. The situation was investigated by CDC staff to no avail. What might CDC have looked for? Why couldn't they come to a conclusion?
- 6 Examine Box 5.6, which reports on the relationship between disease and tiny particulates in the air. What criteria for successful epidemiological studies did these studies fulfill?
- 7 Studies show that about 60 of about 4000 substances in tobacco smoke are carcinogens in laboratory animals including tar, nicotine, formaldehyde, and benzene. In humans, 24 of 30 epidemiological studies support the conclusion that non-smokers exposed to secondhand smoke have a greater lung cancer risk than do unexposed people. (Secondhand smoke is the side stream smoke emitted between puffs of a cigarette plus the smoke exhaled by the smoker.) (a) Do these results indicate to you that secondhand smoke is a cancer risk? Explain. (b) What circumstances might increase the risk of developing cancer as a result of exposure to secondhand smoke?

- 8 American farmers have higher rates of non-Hodgkin's lymphoma as compared to the general population. Think about the lifestyle of farmers. What environmental exposures *other* than pesticides might contribute to their increased cancer rate?
- 9 Weigh the pros and cons of a study done to see if there was an association between nitrate levels in drinking water and bladder cancer. In the Midwestern US state of Iowa, large amounts of nitrogen fertilizer have been used on agricultural fields for many years. *Nitrate* runoff from these fields has reached the drinking water of many municipalities; it is in drinking water at greater than 5 ppm in many cases. In 2001, University of Iowa researchers reported the results of a study on 21 977 women in Iowa. The women studied had drunk from the same water supply for more than ten years, and only communities where at least 90% of the water supply came from a single source were included in the study. Each woman's nitrate exposure was estimated on the basis of the level in the water she drank. Results were adjusted for confounding factors (smoking, age, education, physical activity, and quantities of fruits and vegetables consumed). Researchers found a statistical link between nitrate in drinking water and an increased risk of bladder cancer. Women who drank water containing more than 2.5-ppm nitrate had a risk factor of 2.8 – they were almost three times more likely to develop bladder cancer than women whose drinking water contained less than 0.36-ppm. One author of the study noted that because there were only 47 cases of bladder cancer among the 21 977 women, the association must be considered moderate. Still, the authors believed that the results are biologically plausible as the body can convert nitrate into *N*-nitroso compounds, known carcinogens. The results raised concern because they associated bladder cancer with nitrate levels as low as 2.5-ppm whereas the US EPA standard for nitrate in drinking water is 10-ppm. The 10-ppm standard was set 50-years ago to avoid cases of *blue baby syndrome*.¹¹ At that time, possible chronic effects of nitrate such as cancer were not considered. Based on these results, some persons suggest that EPA should lower its drinking-water standard for nitrate. However, other epidemiologists evaluating the study did not believe that the study showed a meaningful association between nitrate at the levels studied and bladder cancer. If you had to come to a tentative conclusion as to whether there is an association between nitrate in drinking water at 2.5 ppm and bladder cancer, what would you conclude? Explain.

SECTION III

Chemical risk assessment

Risk is defined as the probability of suffering harm from a hazard. A *hazard* is the source of the risk – not the risk itself. For a hazard to pose a risk to you, you must be exposed to it. ■ To help you make the distinction, look at Questions 3.1, which compared lead at Smuggler's Mountain to lead in peeling paint in old houses. Lead is the hazard in both cases, but its risk differs in the

¹¹ Blue baby syndrome. *Wikipedia*, February 25, 2009, http://en.wikipedia.org/wiki/Blue_baby.

two situations. ▪ Similarly, think about walking into a cotton field sprayed with a hazardous insecticide. Your exposure to the insecticide, and your risk, differs if the field was sprayed 1 hour previously as compared to 24 hours previously. ▪ The word hazard goes beyond chemical hazards: infectious disease organisms are biological hazards. Ionizing radiation and hot water are examples of physical hazards. ▪ Chemical risk assessment is a process that systematically examines the nature and magnitude of a risk from a chemical. A risk has a probability from zero to one. Zero indicates no risk at all, and one indicates definite harm.

Why do we do chemical risk assessments?

Risk assessment provides answers to questions such as, what is the risk to my child's health of drinking water containing 3 parts per billion of atrazine (an herbicide). What is my risk if I eat meat containing 1 part per billion of the carcinogen, benzopyrene? What is the risk to a worker who is breathing air containing 1 ppm of the carcinogen, benzene? How much of the carcinogen, dioxin can safely be left in the soil of a hazardous-waste site, which is being cleaned up? What should be the standard (the limit) for ozone in city air? What should be the standard for arsenic in drinking water?

▪ A situation in which chemical risk assessment is often used is in analyzing the risks of hazardous waste sites. However, such sites often have too many chemicals to evaluate each chemical individually. Instead, investigators first determine which chemicals are present and in what amounts. Then they do risk assessments on *indicator chemicals*, those that might pose the greatest likelihood of risk to nearby populations. ▪ In Chapter 2 you read of comparative risk assessment, where one environmental risk is compared to another as when we ask, what is the risk of stratospheric ozone depletion as compared to the risk of acid deposition? Many environmental risks such as ozone depletion and acid deposition also involve chemicals; thus, chemical risk assessment is sometimes important in comparative risk assessment too.

• How do we decide when a risk assessment is warranted? First, we must answer the question: is there exposure? If so, then the chemicals of most concern are the most toxic ones, or the ones to which we have high exposure. Chemicals on which risk assessments are often done include: pesticides. A pesticide's purpose is to kill, and it may harm species other than those it was intended to kill. So we do a risk assessment on any new pesticide. ▪ Food additives will be ingested, so exposure will definitely occur. So risk assessment is done on new additives. ▪ However, there are many chemicals already in use that we are exposed to, but whose risk has not been systematically studied. More and more people want these subjected to risk assessments too.

The answers that chemical risk assessment provides are important. However, as you study the section below, notice that risk assessment is not, and cannot be, precise because we very seldom have enough information. Indeed, risk assessment *helps to compensate for a lack of information*. As a US Occupational Safety and Health Agency (OSHA) official stated, "People need to understand that we do risk assessment because we *don't* have conclusive scientific evidence available. Risk assessment is not science; it is a set of decision tools to help us make informed decisions in the absence of definitive scientific information." The tools of risk assessment do help us evaluate environmental risks and set priorities among

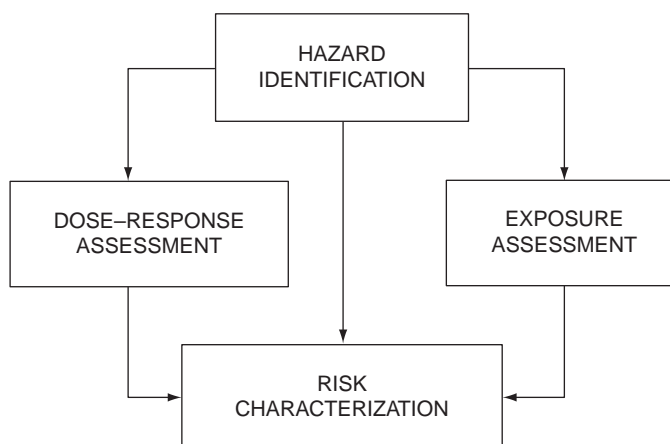


Figure 4.1

The four steps of chemical risk assessment

them. ■ Health effects evaluated by chemical risk assessment are in two categories. One is *non-cancer health effects*, i.e., any adverse effect other than cancer. The second is *cancer*. Both assessments involve the four steps shown in Figure 4.1. Be attentive to the differences between these two categories of assessment.

Non-cancer risk assessments

There are four steps in the risk assessment of a chemical (Figure 4.1).

1. *Hazard assessment* asks why is this chemical considered a hazard?
2. *Exposure assessment* asks, to what extent is there exposure to the chemical?
3. *Dose-response assessment* examines what doses are toxic to laboratory animals.
4. *Risk characterization*, the final step uses information from steps 1–3 and calculates a dose of the chemical considered safe for human exposure.

Step 1: Hazard identification¹²

How is this chemical hazardous? To answer this, we collect and analyze information available on the chemical, examining research literature, government-agency profiles, and other information. Just some of the questions needing to be answered are: what toxic effects does it cause in laboratory animals? Does it, e.g., harm the nervous system, interfere with respiration, cause birth defects, or suppress the immune system? How does it affect animals and plants? ■ How does exposure occur – by skin absorption, by ingestion, or by inhalation? Answers to these and other questions relating to the chemical are considered.

¹² ATSDR. Toxicological profile information sheet (in alphabetical order from acetone to xylene). <http://www.atsdr.cdc.gov/toxpro2.html>.

Step 2: Dose–response assessment

- Find a dose safe to laboratory animals. Expose separate groups of animals to increasing doses of the chemical. Observe the response to each dose over days, weeks, months, or longer. A control group does not receive the test chemical. A second group receives a low dose. A third group receives a larger dose. A fourth group receives a yet larger dose. ▀ The highest dose that animals tolerate without showing ill effect is the *no observed adverse effect level* (NOAEL). See Figure 3.1. But, what we really want to determine is a dose that is safe to humans exposed to it, even a lifetime of exposure. So, we divide the NOAEL by a *safety factor*.
- Determine a *safety factor*. To do this, assume a human is 10 times more sensitive than test animals. ▀ Also, assume that some humans are 10 times more sensitive than the least sensitive. This means multiplying 10 by 10 to yield a safety factor of 100. ▀ If the animal dose–response study is not of high quality, introduce another multiple of 10 to increase the safety factor to 1000. If children are exposed to the chemical, then even if the data are of good quality, increase the safety factor to 10 000 (Box 4.3).
- Determine the *reference dose*. Divide NOAEL by the safety factor. This gives the *reference dose*, RfD. The reference dose is considered to be safe for humans over a lifetime of exposure. The smaller the RfD, the more toxic is the chemical. Example: what is the RfD of a chemical with a NOAEL in rats of 1 mg/kg/day (1 milligram per kilogram of animal body weight per day), and for which the animal data is good. To calculate, divide 1 mg/kg/day by 100. This yields an RfD of 0.01 mg/kg/day. (The RfD is sometimes also called the *acceptable daily intake*, ADI.)

Box 4.2

Reducing exposure of male infants to phthalates

Chapter 3 brought up the potential dangers of chemicals capable of acting as hormones. In particular, how might such chemicals impact the rapidly developing organs of fetuses, babies, and tiny children? Think about *di(2-ethylhexyl) phthalate* (DEHP), a phthalate known to adversely affect laboratory animals. Using DEHP as a plastic softener in intravenous (IV) bags and tubing is a major issue because DEHP can leach from the bags into the fluid within them – and then directly enter the blood stream. There is concern that DEHP poses special risks to the developing reproductive tracts of critically ill male infants who sometimes have prolonged exposure through IV bags. Newborns, with developing testicles are believed to be at greatest risk. ▀ Phthalates (including DEHP) are already banned from plastic toys for children under three in Europe. Europe also banned DEHP use in cosmetics. An earlier European evaluation of DEHP for use in medical devices concluded that the benefit outweighed the risk; but, as more information accumulates, the EU's decision may change. Health Canada issued a strong warning that medical devices containing DEHP should not be used to treat infants, young boys, pregnant women, and nursing mothers. The US FDA expressed concern, saying precautions should be taken to limit exposure of the developing male. Environmental organizations call for hospitals to use alternatives, which are available.

Box 4.3

Why use factors of 10?

Sulfonamides, the first antibiotic drugs, came into use in the 1930s. In 1937 a US drug company dissolved sulfonamides in a sweet-tasting organic chemical, *diethylene glycol* (an antifreeze). Its sweet taste made it attractive to children. The drug company sold this elixir of sulfonamide–diethylene glycol without first testing the toxicity of the glycol in animals. Subsequently, about 120 people around the United States died, many of them children. This event led directly to the 1938 passage of an amended Federal Food Drug and Cosmetics Act (FFDCA) to assure that such a tragedy would not occur again.

After discovering the illnesses and deaths, US Food and Drug Administration personnel traveled the country by train collecting information on the amount of diethylene glycol that each affected individual drank. From this information, agency personnel calculated an approximate LD_{50} for human beings – the dose killing about half of the people exposed to it. They observed about a 10-fold variation in human sensitivity to the chemical. Returning to their laboratories, they tested the toxicity of diethylene glycol in animals. They found that animals too had about a 10-fold variation in sensitivity. Beginning at this time FDA began the practice of dividing a chemical's NOAEL by 100 (10×10) to provide a margin of safety for humans: humans should not be exposed to more than a hundredth of the dose that shows no adverse effects in animals. In recent years, if good information on a particular chemical is available, the US EPA determines a safety factor more specific to that chemical which may be greater than or less than 100. However, in 1996 after the US Congress passed the Food Quality Protection Act¹³ another factor of 10 was introduced for chemicals to which children are exposed, especially pesticides. This means dividing the NOAEL by 1000 (at least) to obtain a safe dose.

Although the elixir of sulfonamide provided a dreadful lesson, not everyone learned it. In the 1990s, a Chinese company shipped medicinal glycerin syrup to Haiti – it contained diethylene glycol. Eighty-six Haitian children who consumed the syrup died of kidney failure.¹⁴ More recently, yet other cases have occurred.

Human subjects Years ago human volunteers were used in chemical testing, a practice discontinued because of ethical concerns. More recently, pesticide manufacturers did 15 studies using paid adult human volunteers. The volunteers ingested doses of pesticides expected to be below the human NOAEL. Companies performed human tests with the hope of proving the pesticides safety in humans at the doses used. Having human information would allow one factor of 10 – the one used to account for differences between humans and animals – to be dropped. This would lead to higher RfD values for pesticides if humans were less sensitive than test animals. Manufacturers say that such tests are similar to those done to test the toxicity of a new pharmaceutical. The EPA sought guidance about whether to allow the use of human data. In response, a National Research Council panel called for the EPA “to set up a safety and ethics system similar to the US Food and Drug Administration’s oversight of human drug testing.” The panel concluded that such testing might be justified when there is enough known to ensure no long-term harm to participants. However, several US legislators

¹³ Food Quality Protection Act, Children and Consumers. *US EPA*, October 2000, <http://www.epa.gov/oecaagct/factsheets/epa-305-f-00-005.pdf>.

¹⁴ Diethylene glycol. *Wikipedia*, March 5, 2009, http://en.wikipedia.org/wiki/Diethylene_glycol.

and many others called any human testing immoral and illegal and asked the EPA not to allow it. Later, the US Congress passed legislation preventing EPA from relying on tests that expose pregnant women, infants, and children to pesticides as it considers permits for pesticides.¹⁵

• Thereafter the EPA issued a different type of guidelines not for the type of industry studies just noted, but for the studies of US EPA scientists who monitor exposures that occur when people are exposed to chemicals during their usual daily activities.¹⁶

Step 3: Exposure assessment¹⁷

A number of questions arise relating to human exposure to a chemical.

- Source What are sources of the chemical? Are emissions from an industrial facility? Motor vehicle exhaust? A waste dump leaching chemicals into groundwater? Are emissions to air or water?
- Route of exposure How does exposure occur?
 - If through drinking water, what is its concentration? How much does an average person drink?
 - If exposure is through food, what foods? What is the concentration in each food, and how much of each is eaten?
 - If through soil, what is its concentration, and how much soil is ingested or inhaled (as dust)?
 - If through air, what is its concentration in air, and how much is inhaled?
 - And however exposure occurs, for how long does it continue?
- Most highly exposed population
 - Some Native Americans eat large amounts of fish, with resulting high exposure to chemicals that concentrate in fish such as PCBs or methylmercury.
 - Children are most likely to ingest soil, and are at special risk from soil contaminants.
 - Small children living in houses with deteriorated lead paint have high lead exposures.
 - Urban dwellers may have the highest exposure to motor vehicle exhaust.
 - Urban people drinking disinfected water are likely to have the highest exposure to *disinfection by-products*.
 - Rural people drinking well water may have the highest exposure to radon, nitrate, and arsenic.
 - Individuals living near a hazardous waste site will likely have the highest exposures to chemicals released from that site.
- Children Give special consideration to children's exposure.
- Worst-case assumptions There is seldom enough information for a good exposure evaluation. To compensate, *worst-case assumptions* are often used. This refers to the highest possible exposure that could occur.

¹⁵ EPA's latest human pesticide testing rule called illegal, immoral. *Environment News Service*, January 25, 2006, <http://www.ens-newswire.com/ens/jan2006/2006-01-25-05.asp>. (2) Renner, R. Human pesticide testing gets qualified OK. *Environmental Science & Technology*, **38**(10), May 15, 2004, 175A–176A (3) Taylor, A. Congress banning use of data from pesticide tests on pregnant women, newborns, infants and fetuses. *Associated Press*, July 29, 2005, <http://www.ahrp.org/infomail/05/07/28.php>.

¹⁶ Exposure Research, Scientific and Ethical Approaches for Observational Exposure Studies. *US EPA*, September 8, 2008, www.epa.gov/nerl/sots/.

¹⁷ *Exposure Factors Handbook*. National Center for Environmental Assessment, US EPA, December 4, 2008, <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=12464>.

Step 4: Risk characterization

Risk characterization brings together everything learned about the chemical's hazards, dose-response data, and human exposure. This information is used to calculate its risk, its *hazard quotient*. ■ If more than one chemical is being evaluated (as when evaluating several chemicals at a hazardous waste site) the hazard quotients are added together to yield a higher risk. ■ If there are multiple pathways of exposure to a chemical (food plus water, for example) these are added together to yield a higher risk. ■ Remember from dose-response studies that an RfD is the dose considered safe over a lifetime of exposure. So, if a chemical's hazard quotient is less than its RfD, it is not considered a risk (Box 4.4).

Cancer Risk Assessment

To do a risk assessment on a chemical that may cause cancer takes four to six years, and costs several million dollars. These factors limit the number of chemicals tested. Only a chemical for which there are strong reasons to suspect that it is a carcinogen is tested. Only about 500 chemicals have been so evaluated. There are four steps of cancer risk assessment.

Step 1: Hazard identification

Hazard identification is particularly important when considering a possible carcinogen. What are the reasons to suspect the chemical is a carcinogen? For instance, is it chemically

Box 4.4

A giant risk assessment

In 1996 the US Congress passed the Food Quality Protection Act (FQPA). Congress gave the US EPA a giant task. ■ The EPA had to review all its current tolerances for 470 pesticides (many of which have more than one tolerance level depending on the particular food).¹⁸ All together the EPA had to review 9700 tolerances set in earlier years. ■ The EPA was instructed to determine not just the risks of one pesticide at a time, but to determine the *cumulative risk* from all pesticides that shared a common mechanism of toxicity. Thirty organophosphate pesticides and a dozen carbamate pesticides share a common mode of toxicity. Adding all these risks together was expected to yield a higher risk than any calculated in the past. ■ The EPA also needed to consider *all possible routes of exposure* not just exposure from food, but also drinking water, and any indoor uses. ■ And, in setting new tolerance levels, the EPA was instructed to pay particular attention to children. Without compelling evidence that children are protected, the EPA must apply an additional 10-fold safety factor. The EPA's job was to finish all these determinations by 2006. It did actually finish in 2007. Afterwards the EPA stated that, "Completing tolerance reassessment ensures that all pesticides used on food in the United States meet the FQPA's more stringent safety standard. This is an enormous milestone in US food safety and human health protection."¹⁹

¹⁸ EPA's definition of pesticide tolerance is "the amount of pesticide residue allowed by law to remain in or on a harvested crop. EPA sets these levels well below the point where the compounds might be harmful to consumers."

¹⁹ Pesticides: regulating pesticides, tolerance reassessment. *US EPA*, February 12, 2009, <http://www.epa.gov/oppsrrd1/tolerance/reassessment.htm>.

similar to a chemical known to be a carcinogen? What do other laboratory studies on animals show? Is there epidemiological information on the chemical to support the suspicion? Other important questions are: is the chemical produced in large quantities? Are large numbers of people exposed to it? If there are “yes” answers to these questions, a costly long-term study may be justified. However, if the chemical is produced only in small amounts or only used by researchers under carefully controlled conditions, it probably won’t be tested.

In an earlier era, when safety controls were poor in industrialized countries, evidence that a chemical was a carcinogen was sometimes found in the workplace. ■ Benzene, a widely used industrial chemical, was found to increase the risk of leukemia and aplastic anemia. Animal studies – indicating that benzene was a carcinogen – were unfortunately not done until later. ■ Vinyl chloride and asbestos are other chemicals whose ability to cause cancer was first observed in humans in the workplace. ■ Today, the intent is to determine a new chemical’s risk before using it. If it is dangerous, a society may choose to eliminate its use entirely. Or, if no substitute is available, it may be used under carefully controlled conditions. Unfortunately, in the poorly protected workplaces of impoverished countries this often does not happen.

Step 2: Exposure assessment for possible carcinogens

This is evaluated as described above for chemicals not suspected of being carcinogens.

Step 3: Dose–response assessment for possible carcinogens

The US National Toxicology Program recommends a special protocol for cancer dose–response studies. Rats and mice are typically the test species. In exceptional cases, as for a potent carcinogen such as 2,3,7,8-TCDD, additional species are tested too. Exposure begins immediately after weaning test animals. The suspect chemical is administered to each animal every day for 18 months to 2 years (lifetime studies).²⁰ A control group does not receive the chemical. A second group receives the *maximum tolerated dose* (MTD). The MTD is the highest dose that does not reduce the animals’ survival as a result of causes other than cancer. The MTD is determined using studies similar to those used to test chemicals that do not cause cancer except for longer time periods. A third test group receives one-half the MTD. A fourth group, receiving a lower dose is often included.

Some control animals also develop tumors over their lifetime. So toxicologists look for *excess tumors* in the animals receiving the suspected carcinogen.²¹ Look again at Figure 3.1 and see that there are low dose levels where no adverse response occurs, the No Observed Adverse Level (NOAEL). Now look at Figure 4.2: As a means of being cautious (conservative) an assumption is made: *any dose of a carcinogen greater than zero* is assumed to pose some risk, i.e., there is no safe dose. The straight line relationship (seen in the upper

²⁰ If possible, the chemical is added to food. If animals will not accept it in food, it is given through a stomach tube (a process called *gavage*). If the chemical is an airborne one, animals are exposed to it in an enclosed chamber 5 days a week for 6 hours each day. The doses administered are calculated as milligrams per kilogram of body weight (mg/kg). Each dose is tested on 100 animals (50 males and 50 females).

²¹ Researchers also look for unusual cancers or types of cancers not seen in control animals. Both benign and malignant tumors are counted.

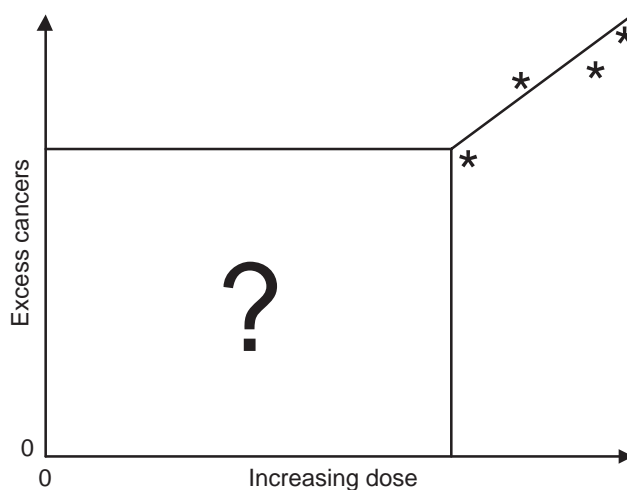


Figure 4.2

Excess cancers with increasing dose of a carcinogen

part of the line with the asterisks) goes all the way to zero. It is assumed that (unlike the dose–response curve shown in Figure 3.1) there is no NOAEL. But notice the rectangle with the question mark – the chemical is not actually tested at the low-dose levels covered by the rectangle. Even assuming no safe dose, there is ordinarily a dose–response relationship: at a higher dose, more cancers are observed. Moreover, people are not typically exposed to doses anywhere near as high as the MTD. Humans are more likely exposed to doses that are hundreds, thousands, or hundreds-of-thousands of times lower than doses tested in animals (Box 4.5).

If significantly more tumors are seen in the test group animals as compared to controls, a *cancer potency factor* is calculated (Table 4.1). The higher the cancer potency factor, the more potent is the carcinogen. Chemicals display huge differences in their potency, that is, in their ability to cause cancer. “Dioxin” (2,3,7,8-TCDD), the most potent rodent carcinogen known, is 10 million times stronger than the weakest carcinogen. The mold toxin, aflatoxin B₁ is also potent, although considerably weaker than TCDD. In turn, aflatoxin is 8500 times more potent than DDT. Chloroform, benzene, and methylene chloride are examples of weak carcinogens.

Step 4: Risk characterization for possible carcinogens

For this step, information on the chemical’s hazard identification is examined as are exposure studies, and cancer potency calculations resulting from dose–response studies are completed. Then, after further calculations, a risk statement is prepared on the probability that a given amount of exposure will result in cancer.

- Risk is expressed as the increased chance – due to the exposure – of developing cancer over a 70-year lifetime. A few illustrations, using drinking-water contaminants as examples follow. Arsenic For every additional 2 µg /l (micrograms/liter) of arsenic in

Table 4.1 Cancer potency of selected chemicals

CHEMICAL	Cancer potency factor*
2,3,7,8-TCDD	100,000
Aflatoxin B ₁	2,900
Ethylene dibromide	41
Arsenic	15
Benzo[<i>a</i>] pyrene	5.8
Cadmium	6.1
PCBs	4.34
Nickel	1.05
DDT	0.34
Chloroform	0.081
Benzene	0.029
Methylene chloride	0.014

* Expressed as mg/kg per day

Box 4.5**Making assumptions in cancer risk assessment**

To calculate the cancer risk resulting from exposure to a chemical, assumptions are made.

1. A chemical that causes cancer in animals can also cause cancer in humans.
2. It is legitimate to extrapolate from the high doses used in animal studies to the (ordinarily) much lower doses to which humans are exposed.
3. All carcinogens are initiators (Table 3.6.) although it is known that some are promoters.
4. A chemical is a carcinogen even if it promotes tumors only at MTD, or if there are excess tumors only in one sex, one species, or one strain of that species. (Rodent strains prone to develop cancer are often deliberately used.)

Trichloroethylene was classified as a carcinogen because, given at MTD to a strain of cancer-prone mice, the males showed excess tumors. Assumptions are made because regulatory agencies want to err on the safe side. A US FDA administrator said, "When science fails to provide solutions, FDA applies conservative assumptions to ensure that its decisions will not adversely affect the public health." Some countries including England, Denmark, and the Netherlands believe that safe doses (thresholds) of carcinogens do exist. They believe that the dose-response curve is as seen in Figure 3.1, not the straight line response going to zero seen in Figure 4.2

drinking water, risk increases by 1 in 100 000. That is, for every 100 000 people, two additional cases of cancer are projected. Tetrachloroethylene (TCE) For every additional 2.4 µg /l of TCE, cancer risk increases by 1 in a million. Radon Drinking water containing 300 picoCuries/liter of radon results in an increased cancer risk of 2 in 10 000.

- These numbers are specific, but *no one really knows the exact risk*. US regulatory agencies routinely add a caveat to their assessments: "These estimates represent an

upper bound of the plausible risk and are not likely to underestimate the risk. The actual risk may be lower, and in some cases, zero” (Box 4.5). In other words, a risk assessment produces a theoretical number. Compare a theoretical risk to a known risk such as driving. Each year about 40 000 Americans are killed in driving accidents. Given this number an accurate calculation can be made as to the risk of death that each person faces when driving.

SECTION IV

Risks to non-humans

Chemical risk assessment is also used to examine risks to natural resources – animals, plants, whole ecosystems, resources such as lakes, or stratospheric ozone. Many chemical risks have been identified over the years. Among these are impacts attributed to DDT in the 1960s including thinning of bird eggshells (resulting in eggs crushed before they could hatch) and other impacts on bird reproduction; damage to water life, e.g., some paper mill or municipal wastewater treatment plant effluents impair the reproductive development of downstream fish; acid rain damages aquatic creatures and forests; chlorofluorocarbons (CFCs) reduce stratospheric ozone resulting in increased ultraviolet radiation reaching the Earth; nutrients running off into water bodies causing abnormal algal growth and subsequently too little oxygen for aquatic animals; or carbon dioxide’s impacts as a greenhouse gas and as an ocean acidifier.

Risks to wildlife

It is wildlife that is typically most vulnerable to chemical pollution. Fish and other aquatic life live in, and many creatures drink from, polluted water bodies. On land, it is worms and other organisms living there that are impacted by contaminated soil.²² Laws also poorly protect wildlife. Some protections exist. ▪ In the United States and other industrialized countries, many facilities discharging into receiving streams must routinely test the toxicity of their effluents to demonstrate that aquatic life is not being harmed. ▪ Hazardous waste sites must be cleaned to specifications that include protecting wildlife. ▪ Sometimes regulations that protect humans also protect wildlife as when regulations limiting air emissions reduce animal, tree, and plant exposure as well.

²² In many less-developed countries, human beings also lack protection. Instances are children or adults exposed to high levels of pesticides on farms; exposure to high levels of lead when this metal is recovered through unsafe recycling techniques; or impure drinking water. There are, unfortunately, many other examples.

Risks in impoverished countries

“It is a truism . . . that the major predictor of ill health is poverty because poor people are the least able to obtain uncontaminated water and food . . . and obtain the knowledge necessary to avoid [the contamination].”

- Sewage Pollution of water and food with infectious agents is rampant in many impoverished countries, typically more serious than chemical contamination. More than a billion people worldwide lack access to clean drinking water. Children under five are particularly impacted. Infection leads to diarrhea which, untreated often leads to death. In Asia alone an estimated 4 million infants and small children die each year from diarrhea. Contributing to infections is a lack of toilets and other sanitary measures.
- Chemical pollutants Children in less-developed countries are often heavily exposed to chemical pollution. Consider urban motor vehicle exhaust, or surface water into which industrial waste has been dumped. High pollution levels can suppress children’s immune systems making them more susceptible to infectious diseases.
- Occupational exposure Children and adults often labor in risky occupations. Among many examples is scavenging among trash in dumps, or working unprotected in battery-recycling operations exposing them to lead-fumes as batteries are melted. Whole families often live at or near work sites, so all are exposed.

Officials may see environmental protections as a “Western agenda” not relevant to them and some suspect that such protections will lower economic opportunity for their citizens. Can the risk assessment and risk management tools developed in wealthy countries have meaning in such conditions? Pollution-limiting laws may be on the books, but lack of resources and corrupt officials often prevent enforcement. Public officials who care about the laws may lack resources to enforce them or the education to use laws knowledgeably. Workers and others may accept dangerous exposures as the way life is. But if the will exists, risk management tools can be developed and enforced even in very poor locales. The Indian state of Kerala works to protect its environment.²³ And Mexico City, where air pollution is a major problem, is implementing policies restricting when cars can be driven and mandating that new motorcycles emit 50% fewer pollutants; the same is true of Sao Paulo.²⁴

Back to the developed world

Pointing to poor conditions in less-developed countries is easy, but high exposures still occur in industrialized countries too. Nitrogen oxides pollution from heavy motor-vehicle traffic in New York, Paris, Tokyo, and Los Angeles is among the highest in the world.

²³ Kerala reassessing the environment. *India Together*, March 27, 2007, <http://indiatogether.org/2007/mar/env-keralenv.htm>.

²⁴ Barclay, E. Clearing the Smog: Fighting Air Pollution in Mexico City, Mexico, and São Paulo, Brazil. *World Bank Group*. June 23, 2007, <http://www.dcp2.org/features/47>.

Particulate pollution from motor vehicles is also often high in American and European cities. Environmental justice issues continue, as when dumps and other polluting facilities are disproportionately located in neighborhoods occupied by the poor or people of color. Roxbury, an inner city neighborhood in Boston, Massachusetts, has within its borders 80 auto repair shops in a 1.5-square-mile (388 hectare) area, trash transfer stations, heavy truck traffic (often idling as the trucks wait to take on or drop off materials), food processing facilities with bad odors, furniture stripping sites, pervasive dust arising from many sources, hazardous waste sites, and many houses with leaded paint.

SECTION V

Managing risk

Scientists carry out the four steps in a chemical risk assessment. After risk characterization, results are given to non-scientists, risk managers. It is they who decide how to lower risk. Risk managers are often employed in agencies such as the US EPA or the World Health Organization. Law makers, legislators, can be risk managers too. The goal of risk managers is to make the risk of a carcinogen *negligible*. An excess cancer risk of one in a million is considered negligible (virtually safe dose, or *de minimis*). An FDA commissioner stated, “When FDA uses the risk level of one in a million, it is confident that the risk to humans is virtually nonexistent.” Some believe that cancer risk assessment is so conservative that an excess risk of 1 in 100 000 or 10 000 is acceptable, especially if the chemical has been shown to be a carcinogen only in animals. Others are less sure. ■ The major reason for risk management is to reduce risk, but other factors must be considered. ■ Statutory requirements: what does the law require? ■ Technology: is the technology available to control the chemical or pollutant in question? ■ Cost: the cost of risk reduction is always a factor. ■ Public concerns: an aroused public can push risk reduction measures. ■ Political concerns: politics affect decision-making. ■ Although there are often many ways to lower a risk, not all will be feasible or cost effective. Laws and regulations are often the first possibility considered, but risks can be lowered in a number of ways. In addition to laws with regulatory components, legislators may appropriate money for education as one approach to risk management, or provide incentives (not just monetary), to citizens and industry to change their ways. Several of these are seen below.

Laws and regulations

Especially after Earth Day in 1970, laws were passed in many countries mandating reductions in pollutant emissions. Not just federal, but state (or province), and sometimes city laws are important in reducing emissions. Past regulations depended on facilities capturing a pollutant end-of-pipe, but other legislative tools are increasingly available. ■ *Emissions-trading* is one.

In this process, a facility which, for whatever reason, cannot or does not want to reduce its emissions so it is allowed to buy emission rights from a facility that has reduced its own emissions more than necessary. The buyer of emission rights pays less than it would cost to install or modernize their technology. The low-emitting facility makes money by selling a portion of its emission rights. ■ An emerging and important risk management tool is *take-back* laws: the EU mandates that producers take back cars and electronic equipment so these don't pollute at the end of their useful lives.

Regulating chemicals

The United States has passed a number of laws to regulate chemicals (Chapter 2). The most comprehensive was the Toxic Substances Control Act (TSCA) passed in 1976. TSCA authorized the EPA to obtain information on all new and existing – already more than 70 000 at the time – chemical substances.²⁵ TSCA's purpose was to ensure that the health and environmental effects of a new chemical was known before it was marketed, and that the US EPA had authority to control chemicals that “cause unreasonable risk to public health or the environment.” This was to include, if necessary, banning particularly risky chemicals. Unfortunately, in practice, the EPA is almost powerless to regulate problematic substances, and even has had major difficulty getting industry to furnish toxicity information on chemicals. Finally, in 2009, the US Congress has become serious about legislation to reform chemical control.²⁶ Other US laws have, over the years, been passed that partially filled in the gaps.

Meanwhile the European Union enacted a law in 2007, Registration, Evaluation and Authorization of Chemicals (REACH)²⁷ that deals with high-production chemicals – the more than 30 000 chemicals produced in a volume of greater than 1 metric tonne (1.1 tons) per year. REACH requires manufacturers to register and provide toxicological information for all such substances. A new agency has power to ban chemicals deemed to present significant health threats. And, industry will need to demonstrate the safety of their chemical products – this is an example of the use of the precautionary principle (see below). Under REACH, any chemical posing a “very high concern” will be phased out of production. Exceptions will be made for essential chemicals if good alternatives are not available. However, such chemicals would be clearly labeled, so consumers can themselves decide whether to buy the product.²⁸

■ Canada is updating its regulation of the 23 000 chemicals on its market.

Non-regulatory tools to manage risk

Described here are some approaches used to reduce risk.

- Educate the public. Let people know useful actions they can take for certain chemicals, e.g., how to reduce radon in their home, or how to safely use, or eliminate the use of pesticides.

²⁵ TSCA statute, regulations and enforcement (this site also provides information on other chemical-control laws). *US EPA*, January 2, 2009, <http://www.epa.gov/compliance/civil/tsca/tscaenfstatreq.html>.

²⁶ Hogue, C. Revisiting chemical control law *Chemical & Engineering News*, **87**(10) March 9, 2009, 24–25.

²⁷ Short, P. Kick off time for REACH. *Chemical & Engineering News*, **86**(29), July 21, 2008, 27–29.

²⁸ For an overview of REACH see Q&A: Reach chemicals legislation. *British Broadcasting Company*, November 28, 2005, <http://news.bbc.co.uk/2/hi/europe/4437304.stm>.

- Government and industry can develop agreements to, together foster emissions reductions. This often happens in Europe. ■ In some US states, environmental agencies collaborate with industry to find cost-effective ways to reduce emissions.
- There are many cases of industries voluntarily taking action, albeit often with prodding. One large action is the US EPA's High Production Volume (HPV) Challenge Program. An HPV chemical is one produced in, or imported into, the United States in quantities of 1 million pounds (~450 000 kg) or more per year. The EPA challenged chemical manufacturers and importers to make health and environmental effects data on HPV chemicals publicly available. Companies agreed to take on 2200 (out of 2400) HPV chemicals.²⁹ However, 2200 is small compared with the 30 000 chemicals in the REACH program, which *is* regulatory. Nonetheless, the EPA has information available that it also makes available to the public.
- Environmental organizations and other groups often exert pressure on industry to reduce emissions or become better environmental stewards. That is beginning to happen in China too (Box 2.1).
- Governments work together. ■ One testing program involves a cooperative effort among United States, Japanese, and European scientists to evaluate not just HPV, but all 87 000 commercial chemicals to determine which ones are environmental hormones. ■ Another joint effort among the United States, Canada, and Mexico is to develop a North American framework to manage risks of common chemicals. These countries believe this program may be even a better means of managing chemicals than the REACH program.
- Think of risk reduction in the longer term: society supports research by industry, government, and universities aimed at better understanding chemical risk and finding better ways to reduce it. One important program is to develop "green" chemicals (see Delving deeper, below) and to develop environmental technologies to control or reduce emissions.

Using the precautionary principle to lower risk³⁰

In the United States, usually a substance must first be shown to be dangerous before it can be controlled. Many believe that this approach has "failed to adequately protect human health and the environment." Compare this to the *precautionary principle*. Its premise is, "When an activity raises threats of harm to human health or the environment, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically." Later, if restrictions prove to be over strict, they can be relaxed. The principle is used in the EU more widely than the United States; see the REACH program described above. This difference has led to a quandary for retailers and manufacturers. When one region of the world requires the precautionary principle be applied to chemicals, but another does not, with which do they choose to comply? Companies increasingly choose the more restrictive rules.

²⁹ A summary of the High Production Volume Challenge is at <http://www.epa.gov/HPV/pubs/general/basicinfo.htm>.

³⁰ Müller-Herold, U., Morosini, M. and Schucht, O. Choosing chemicals for precautionary regulation: a filter series approach. *Environmental Science & Technology*, **39**(3), February 1, 2005, 683–691.

Reducing risk to children

Because babies and children are at higher risk from chemicals than adults, ongoing efforts aim to reduce that risk. ■ Pesticides: In 1996, the US Congress passed the Food Quality Protection Act (FQPA). This requires EPA to develop new standards for pesticide residues on food with an emphasis on reducing risk to children. Before the FQPA, cancer risk was the only adverse effect considered when setting a pesticide tolerance, i.e., the pesticide residue legally allowed to remain on a food. No special consideration was given to children. Now the EPA must consider a broad range of health effects, particularly those that could affect children. And when setting pesticide tolerances, if evidence to the contrary is poor, then an extra 10-fold safety factor must be added to protect children. See Box 4.3. ■ The EU testing program, REACH, likewise lowers the safety threshold to account for the special sensitivities of the fetus and young child. ■ The US EPA, citing the special risk that mercury poses to the fetus and small child, announced that coal-burning electric power plants will be required to reduce mercury emissions. ■ An increasing number of programs work to educate parents on how to better protect their children from chemical risks in the home.

Not enough protection for children?

Professors Philippe Grandjean and Philip J. Landrigan (Harvard School of Public Health and Mount Sinai Medical School) analyzed data on the toxicity of many industrial chemicals. They identified 202 that could damage developing brains. Their concern is that chemical pollution around the world has already likely harmed many children.³¹ Saying that toxic substances can disrupt the precisely regulated complex processes necessary to brain development, they express belief that even small interferences can have subclinical effects – effects that are not obvious, but are there nonetheless. One of every six children already has an obvious developmental disability, many involving the nervous system including autism, attention deficit disorder, and mental retardation. Grandjean and Landrigan concluded that more legal protection is needed for children.

SECTION VI

Changing chemical risk assessment, changing regulation of chemicals

Chemical risk assessment

Chemical risk assessment is subject to much criticism: how relevant to humans are animal tests, especially considering that human exposure is ordinarily much lower than the doses given to

³¹ Kiewra, K. Brain pollution. *Harvard Public Health Review* (online), Winter, 2007, <http://www.hsph.harvard.edu/review/winter07/brain.html>. Also see the World Health's Association's, *Principles for Evaluating Health Risks in Children Associated with Exposure to Chemicals* at http://whqlibdoc.who.int/publications/2006/924157237X_eng.pdf, released online in July, 2009.

those animals? Animal tests are time consuming and costly, which means that although some chemicals are thoroughly tested, many others are tested to a limited extent or not at all. Many also consider animal testing to be cruel. However, there have not been good alternative methods.

In 2007, the US National Research Council (NRC) outlined an approach that relies less on animal studies and more on *in vitro* methods.³² (*In vitro* methods study living cells or tissues cultured, and studied outside a living creature; such methods have advanced greatly over the years.) Cultured *human* cells and tissues may become a substitute for live animals while, at the same time, allowing information to be obtained that is directly relevant to humans, and doing so much more rapidly than can be done with whole animal studies. The toxic effects of a chemical on specific metabolic pathways in cultured cells can be studied. And the NRC recommends using rapid, automated “high-throughput assays” to test the toxicity of hundreds or thousands of chemicals, each at many concentrations. ■ Some animal testing would still be needed because cell or tissue studies, at the current stage of development, could not show us everything that a whole animal could. In addition, studies of human exposure will continue to be needed to provide that essential information. Exposures that people actually experience could then be used to select doses to be tested for toxicity. Recall the many chemicals the CDC found in small amounts in human bodies; such doses could be directly tested on specific metabolic pathways using human cells or tissues.

Questions 4.3

- 1 In many places in the Midwestern United States, the herbicide, atrazine has been discovered in drinking water at unhealthful levels. Farmers commonly use atrazine in large amounts, and it reaches surface water by rainwater runoff. What are two ways to reduce this risk? (Think of personal, school, community, state or federal action)
- 2 Now answer the same questions for a different situation: Assume that atrazine was not found in drinking water, but in local ponds and wetlands. There research indicates it may be responsible for serious developmental abnormalities in frogs.
- 3 (a) You live near a large industrial facility that uses trichloroethylene, and this organic solvent has been detected in your drinking water. How could the solvent have gotten there? (b) Although you have been told that the level is not unhealthy, you want action. What might you do?
- 4 The most toxic form of dioxin (2,3,7,8-TCDD) is found in tiny quantities in meat that you buy at the grocery store, especially in fatty hamburger meat. Assume you buy hamburgers. (a) What type of hamburger can you choose that would not contain dioxin? (b) Once the hamburger is purchased, even if it is fatty what steps could you take to reduce your exposure? (c) Is there anything you could do to reduce exposure if you buy hamburgers at fast-food restaurants?
- 5 Supporters of the precautionary principle believe that a risk assessment approach asks, “How much environmental damage will be allowed?” whereas the precautionary principle asks, “How little damage is possible?” (a) What is your immediate reaction to this statement? (b) Now, read Box 4.5. Does this change your mind in any way?

³² Fentem, J. and Westmoreland, C. Risk assessment and new technologies: opportunities to assure safety without animal testing and better protect public health? *AltTox.org*, December 6, 2007, <http://www.alttox.org/ttrc/overarching-challenges/way-forward/fentem-westmoreland/>.

Delving deeper

1. What are the ethics of testing low doses of pesticides or other chemicals in human beings? As you ponder this question, read and think through at least two of the items in footnote 00. First, ask yourself: why is testing of pharmaceuticals in humans considered acceptable? How is testing pesticides or other pollutants in humans different? Prepare a one-page closely reasoned report on your conclusions.
2. The organization, Clean Production Action has a free tool, Green Screen for Safer Chemicals. See www.cleanproduction.org/Green.Greenscreen.php to find less toxic alternatives for questionable chemicals. Examine its four benchmarks and the examples given. After you are clear that you understand the approach, write a brief essay with examples to demonstrate this tool.
3. Read the US EPA's Risk Assessment for Toxic Air Pollutants: A Citizen's Guide. *US EPA*, June 6, 2007. http://www.epa.gov/ttn/atw/3_90_024.html. Summarize this information for your class, and be prepared to answer questions.

Further reading

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2009. TSCA statute, regulations & enforcement (Site also provides information on other chemical-control laws). <http://www.epa.gov/compliance/civil/tsca/tscaenfstatreq.html> (January 2, 2009).
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“Wind, rain, and radioactivity do not stop at the border for passport control, but go where they will. Pollution? Coming soon to a place near you . . . We’re all Down-winders now.”

David Nyhan (*Boston Globe*)

The reality of outdoor air pollution is more than the words “ambient air pollution” can convey (Box 5.1). It is the eye-stinging pollution surrounding us in a city crowded with motor vehicles¹, the odor of ozone on a hot hazy day, the choking of a heavy dust storm, the smoke from wood or coal fires on a winter day, the fumes from an uncontrolled industrial facility, odor from uncontrolled sewage or an open dump. Many living in wealthy countries are spared the worst of these. Not so for the many living in less-developed countries, who are increasingly exposed.

In this chapter, Section I examines six principal air pollutants – the *criteria* (or priority) pollutants. Section II introduces Volatile Organic Chemicals (VOCs), which together with criteria pollutants account for the large majority of air pollution. Section III introduces HAPS (hazardous air pollutants, also called air toxics). HAPS are not ordinarily as pervasive as criteria pollutants, but can be very important in specific locales. Section IV describes massive movements of criteria air pollutants that can be directly observed from space – traveling combustion pollutants, major dust storms, and smoke from massive fires. Section V briefly examines pollution in less-developed countries. For each criteria pollutant, and for VOCs and HAPS, we ask the following questions: • What is this pollutant? • Why does it concern us? • What are its sources and its environmental fate? The environmental fate question was first raised in Chapter 1 and will be briefly answered for many pollutants in Chapter 5 and beyond. • How can its emissions be reduced?

SECTION I

Criteria (or principal) air pollutants²

The higher the dose of a substance to which a living creature is exposed the greater the possibility of an adverse effect. Now, apply this principle to the six criteria (or principal)

¹ Tait, R. As the crow flies: birds flee Tehran’s polluted air. *guardian.co.uk*, January 13, 2009, <http://www.guardian.co.uk/environment/2009/jan/13/crows-pollution-iran-environment-wildlife>.

² (1) Six principal pollutants (through 2006). *USEPA*, January 22, 2008, <http://www.epa.gov/air/airtrends/2007/report/sixprincipalpollutants.pdf>. (2) What are the six common air pollutants? *US EPA*, <http://www.epa.gov/air/urbanair/>.

Box 5.1

Air pollution terms

- **Ambient air pollution** is that found in the air around us (tropospheric air pollution). The troposphere is the lower layer of the atmosphere (starting at the Earth's surface).
- **Criteria air pollutants** The term criteria air pollutants originated with the US 1970 Clean Air Act.³ That law required EPA to set standards (National Ambient Air Quality Standards, NAAQS⁴) to protect human health and welfare from pollutants in ambient air. Before setting standards, the EPA had to identify the most serious pollutants. To do so it used specific *criteria* (characteristics of the pollutants, and their potential health and welfare effects). The six pollutants that the EPA identified account for the large majority of air pollution, both in the United States and worldwide. These are carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x), ozone (O₃), and particulates or particulate matter (PM₁₀). Lead (Pb), the sixth, was included at a time when it was being emitted in dangerous amounts. The US EPA now calls these pollutants, the six *principal* pollutants or six *common* pollutants.
- **Volatile organic pollutants (VOCs)** VOCs, as a group, are also emitted in large amounts, especially the hydrocarbons from mobile sources. VOCs are often grouped with criteria pollutants.⁵
- **Hazardous air pollutants (HAPS)** Legislation was the source of the term, *hazardous air pollutants* – also commonly called toxic air pollutants.

air pollutants. They are produced in large amounts. We and other living creatures are often exposed to them at levels high enough to exert adverse effects. Air pollution in Houston, Mexico City, Istanbul, and many other cities, often causes painful breathing, eye irritation, and headaches. Trees and plants are also adversely affected. Because of this, each criteria pollutant has an ambient air standard set for it, a standard that is based on its risk. Each criteria pollutant is described below. ■ Combustion, especially fossil fuel combustion produces all six of these major air pollutants. *Exhaust from motor vehicles accounts for about half of these emissions.* When you examine Table 5.1, notice the words particulate and aerosol.⁶ These words are relevant for several of the principal pollutants.

³ The plain English guide to the Clean Air Act (EPA-456/K-07-001). US EPA, April, 2007, <http://epa.gov/air/caa/peg/peg.pdf>.

⁴ *Primary standards* set limits to protect public health, including the health of the most sensitive populations including children and asthmatics. *Secondary standards* are set to protect “public welfare” such as impacts on visibility, harm to animals, crops, vegetation, and buildings and statuary. See <http://epa.gov/air/criteria.html>.

⁵ Canada, e.g., includes VOCs among its Criteria Air Contaminants, but not lead, http://www.ec.gc.ca/cleanair-airpur/Pollutants/Criteria_Air_Contaminants_and_Related_Pollutants-WS7C43740B-1_En.htm.

⁶ The gaseous pollutants sulfur dioxide and nitrogen oxides, can be chemically transformed in the atmosphere into tiny particles, which can form *aerosols*. Aerosols are a gaseous suspension of fine solid or liquid particles. A number of volatile organic pollutants also form aerosols. Metals are directly emitted as particulates, although a portion of mercury emissions are gaseous.

Table 5.1 Ambient air pollutants

Pollutant	Characteristics or examples
Criteria pollutants	Six pollutants, each of which has an ambient air standard
Ozone (O ₃)	A major component of photochemical smog formed from NO _x , VOCs, and oxygen in presence of sunlight and heat. Motor vehicles are major generators of NO _x and VOCs.
Carbon monoxide (CO)	Produced by combustion of fossil fuel and biomass. All by itself, CO represents more than 50% of air pollution. In urban areas, motor vehicles are the predominant source of CO.
Sulfur dioxide ^a (SO ₂)	SO ₂ is oxidized in air ^b to sulfuric acid under moist conditions or to sulfate in dry. Both are particulates and major components of haze. Fossil-fuel-burning power plants produce about two-thirds.
Nitrogen oxides ^a (NO _x)	NO _x are oxidized in air ^b to acid under moist conditions or to nitrate in dry. Both are particulates and components of haze. In cities, motor vehicles generate most NO _x . Coal-burning facilities produce significant quantities too.
Lead ^c (Pb)	Lead is emitted as a particulate during metal mining and processing, and during fossil fuel combustion.
Particulates (PM ₁₀ and PM _{2.5})	Tiny solid particles composed of one or several chemicals. They have many sources. Combustion is a major source of the tiniest particles. Notice that lead is emitted as a particulate and that SO ₂ and NO _x can be converted to particulates. So can some organic VOCs.
Volatile organic pollutants (VOCs)^d	Organic chemicals that evaporate easily. Some significantly contribute to smog. Motor vehicles are a major source.
Hazardous air pollutants (HAPs)	Each HAP has an emission control; not an ambient air standard. HAPs are also called toxic pollutants. About 70% are also VOCs.
Organic chemicals ^d	Examples are benzene, formaldehyde, and vinyl chloride.
Inorganic chemicals ^c	Examples are asbestos and metals such as cadmium and mercury.

^a Some SO₂ and NO_x are converted to particulate forms (aerosols).¹

^b Air contains oxygen which reacts with, *oxidizes*, sulfur dioxide.

^c Most emitted metals are already particulates.

^d Some VOCs and some organic HAPs are converted to particulates (aerosols).

Carbon monoxide (CO)⁷

CO is a colorless, odorless, flammable gas, a product of incomplete combustion produced when a carbon-containing material is burned. Only under ideal conditions, with an excess of oxygen and optimal burning conditions, is carbon completely oxidized to carbon dioxide (CO₂). See Box 5.2. Carbon monoxide (CO) is pervasive. By itself, CO accounts for more than 50% of air pollution by weight nationwide and worldwide. Worldwide, hundreds of millions of tons are emitted yearly.

⁷ Carbon monoxide. US EPA, 2007, <http://www.epa.gov/air/airtrends/2007/report/carbonmonoxide.pdf>.

Box 5.2

Don't confuse carbon *monoxide* with carbon *dioxide*. Carbon monoxide (CO) is an incomplete product of combustion, and is very toxic. Carbon dioxide (CO₂) is a complete product of combustion, and much less toxic. (Carbon dioxide will be discussed in Chapter 7.)

Why CO is of concern

Levels of CO found in city traffic are often high enough to aggravate heart problems. Carbon monoxide causes up to 11% of hospital admissions for congestive heart failure in older people. Knowing how CO works will clarify how it adversely affects the heart, and causes other adverse effects: (a) The blood protein *hemoglobin* contains an iron atom, which normally picks up oxygen in the lungs and transports it to the body's cells. There oxygen is released and exchanged for the waste gas, carbon dioxide (CO₂). (b) Hemoglobin carries CO₂ back to the lungs, releases it, and once more picks up oxygen. (c) Carbon monoxide is so toxic because it has about 250 times greater affinity for the iron atom in hemoglobin than oxygen does – so CO displaces oxygen. (d) This means less oxygen reaches the heart. Even relatively small displacements affect heart function in sensitive people. The brain too demands a steady oxygen concentration for optimum functioning, so a lowered level of oxygen can cause headache, dizziness, fatigue, and drowsiness. ▪ Higher doses of CO, such as found in enclosed spaces with improperly operating combustion appliances, may lead to coma and death (Chapter 17). ▪ The US ambient air standard for carbon monoxide is 9 ppm averaged over 8 hours; if this is exceeded more than once a year, an area is violating the standard.

Sources and environmental fate of CO

Carbon monoxide is formed anywhere that a carbon-containing material is burned. Thus, CO exposure happens anywhere that combustion is occurs. ▪ Major sources In urban areas, motor vehicles emit up to 95% of CO. Drivers stalled in traffic or driving in highly congested areas can have high CO exposure. So can traffic control personnel, mechanics working inside garages, and parking garage attendants. ▪ Lesser sources Cigarette smoke contains CO. Individuals exposed to CO on the job who also smoke, increase their risk of adverse effects. ▪ Facilities burning coal, natural gas, or biomass are CO sources. ▪ Burning biomass (wood, dried manure, other dried vegetation) for cooking, heating, and light is a CO source. These lesser sources can be significant in certain locales or situations. ▪ Environmental fate CO can persist in the atmosphere for one to two months before it is converted to CO₂ – thus CO contributes to CO₂ in the atmosphere.

Reducing CO emissions

▪ Consider what happened when oxygen-containing fuel additives were added to gasoline in 20 US cities to enhance its burning in winter, a season when engines run less efficiently.

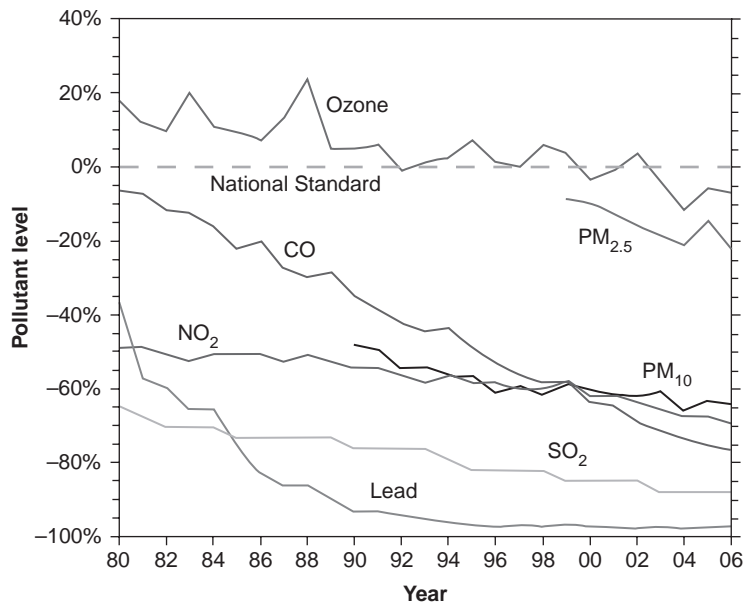


Figure 5.1

Falling levels of the six principal air pollutants (1980–2006). Credit: US EPA

In the winter of 1991 to 1992, those cities had exceeded EPA's carbon monoxide standard on 43 days. One year later, 1992 to 1993, after introducing oxygenated fuel, they exceeded the standard on only 2 days. Between 1988 and 1997 the number of times that the standard for CO was exceeded dropped 95%. EPA called this "astonishing." Western Europe also tightened CO emission standards too with similar results. ▪ In the 1950s, atmospheric levels of CO began to increase concurrent with increasing combustion. The 1970s showed a slow but steady downward trend as increasingly stringent emission controls were imposed in the United States and elsewhere: ▪ The EPA established national standards for tailpipe emissions. About half of motor vehicle CO emissions in the United States come from only 10% of the vehicles. Inspection programs attempt to find these, and work to repair or remove them from the road. ▪ Facilities burning fossil fuels or wood are required to maintain high burning efficiencies to reduce emissions. ▪ Many places prohibit open burning of trash and garbage. Figure 5.1 shows that nationwide, CO has continued to drop over the years. Between 1970 and 2005 American CO emissions dropped from 197 million tons (179 million tonnes) a year to 89 million tons (81 million tonnes).

Ground-level ozone(O₃)⁸

Unlike atmospheric oxygen (O₂), ozone (O₃) has three oxygen atoms. And, although O₂ is reactive, O₃ is more reactive. Many of us know the odor of ozone from hot summer days in the city, lightning storms, or improperly maintained electrical equipment such as a

⁸ Ground-level ozone. US EPA, 2007, <http://www.epa.gov/air/airtrends/2007/report/groundlevelozone.pdf>.

Table 5.2 Ozone levels and air quality

Concentration	Air quality
0.000–0.050 ppm	Good: No health impacts expected
0.051–0.100 ppm	Moderate: Unusually sensitive people should consider limiting prolonged exertion outdoors.
0.101–0.150 ppm	Unhealthy for sensitive groups. Active children and adults, those with respiratory problems should avoid prolonged outdoor exertion.
0.151–0.200 ppm	Unhealthy. Active children and adults, and those with respiratory disease should follow the advice for 0.101–150. Others, especially children, should limit prolonged outdoor exertion.
0.201–0.300 ppm	Very unhealthy. Active children and adults, and people with respiratory disease should avoid all outdoor exertion. Others, especially children, should limit outdoor exertion.
Alert Healthy individuals exercising outside in “unhealthy” periods should do so in early morning hours before ozone begin to climb. See www.epa.gov/airnow for a daily update on air quality.	

Box 5.3**Smog and ozone**

The word, smog refers to *photochemical smog* because sunlight plays a major role in its formation. Ozone is a major component of smog, but smog contains other photochemical oxidants too including peroxyacyl nitrates (PAN) and nitrogen dioxide. And smog contains particulate matter making it “air you can see.”⁹

Don’t confuse ground-level (tropospheric) ozone with stratospheric ozone. Ground-level ozone is a serious pollutant, but in the atmospheric layer above the troposphere (the stratosphere), ozone performs a vital function. It absorbs the sun’s harmful ultraviolet rays, thereby protecting life on Earth (Chapter 8).

photocopier. O₃ is a summer pollutant found in photochemical smog (Box 5.3). Ground-level O₃ is the same O₃ found in the stratosphere. However, ground level (tropospheric) O₃ is a pollutant whereas in the stratosphere ozone performs a major positive function. Most ground level O₃ comes from human activities. Ozone is found naturally even in areas remote from human activity, but natural levels are low, 0.02–0.05 ppm (Table 5.2).

Why O₃ is of concern

Even atmospheric oxygen, essential to life is reactive enough to sometimes harm living creatures – and O₃ is much more reactive. The EPA considers ozone the most serious and persistent air quality problem in the United States, describing O₃ as the “most . . . intractable

⁹ The word *smog* originated in London in 1905. It described the *smoke* and *fog* combination that then commonly obscured visibility. This smog resulted from the sulfur dioxide, soot, and tarry materials that came from uncontrolled burning of high-sulfur coal. This still happens today in places without the technology to capture sulfur dioxide. In the first half of the twentieth century, severe smog episodes in England and the UNITED STATES caused thousands of deaths.

air pollutant in urban air.” Moreover, O_3 is often present at levels known to have deleterious effects on health and natural life. ■ Health impacts *Acute* health effects of ozone exposure are irritation of eyes, nose, throat, and lungs and a decreased ability of the lungs to function optimally. At 0.2 ppm young adults develop inflammation of the bronchial tubes and tissue deep within the lungs. Even at the legal limit of 0.075 ppm¹⁰, O_3 adversely affects some people, including some healthy individuals. Exercising people are especially susceptible, and are advised to exercise early in the morning on days when O_3 levels are expected to become unhealthful later in the day (Table 5.2). People with asthma or bronchitis, especially children, are highly susceptible to O_3 , which can also increase susceptibility to infection. ■ *Chronic* O_3 exposure can permanently damage lungs. A recent well-regarded study analyzed data on 450 000 urban Americans over a period of 18 years. It found that those living in cities such as Houston or Los Angeles, exposed to high ozone levels, have a quarter to a third greater risk of dying from respiratory diseases, mostly pneumonia and chronic obstructive pulmonary disease (COPD).¹¹ Each additional 10 ppb of ozone was linked to a 4% increased risk of death. ■ Non-health impacts It was recognized in the Los Angeles of the 1940s that O_3 greatly damaged vegetable crops.¹² Although ozone is primarily generated in urban areas, it sometimes survives to spread over wide regions. The US Department of Agriculture reports that *ground-level ozone causes more damage to plants than all other air pollutants combined*. Crop losses in the United States may be as high as 5% to 10%. Sensitive crops are damaged by ozone at 0.05 ppm. More resistant crops withstand 0.07 ppm or higher. Many foresters consider O_3 the air pollutant most damaging to forests. ■ Worldwide, perhaps 35% of crops grow in areas where O_3 levels exceed 0.05–0.07 ppm. If trends continue, up to 75% of world crops may grow in areas with damaging O_3 levels by 2025. If the area also has acid deposition and other air pollutants, the combination may be more damaging still. ■ In addition to impacts on living creatures, O_3 reacts with and damages many surfaces such as fabrics and rubber materials.

Sources of O_3

Unlike CO, which is emitted as CO, ozone is not a *primary* pollutant. Motor vehicles are a major source of the O_3 *precursors*, VOCs and NO_x . In the summer’s heat and the sun’s strong ultraviolet rays, VOCs and NO_x react with atmospheric oxygen (via several steps) to generate O_3 (Figure 5.2). Knowing how O_3 forms, you may guess that, in a city O_3 levels

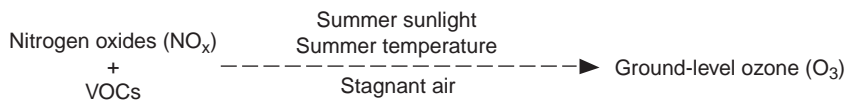


Figure 5.2

Formation of ground-level ozone

¹⁰ Ozone air quality standards. US EPA, October 14, 2008, <http://www.epa.gov/air/ozonepollution/standards.html>.

¹¹ Ozone exposure taking toll on American lives. *MedlinePlus*, March 11, 2009, <http://www.hon.ch/News/HSN/624942.html>

¹² Effects of ozone air pollution on plants. *USDA*, April 8, 2009, <http://www.ars.usda.gov/Main/docs.htm?docid=12462>.

will build up over the course of a summer day: early morning levels are low. Then vehicle exhausts from morning traffic lead to increased concentrations of NO_x and VOCs. As the day progresses, the temperature rises, and the sun's ultraviolet rays grow stronger. Thus, the level of O_3 generated increases in the course of the summer day. ▪ Other large sources of O_3 precursors include coal-burning electric power plants and industrial facilities. ▪ Also off-road motor vehicles, airplanes, construction equipment, lawn mowers, and other garden equipment emit VOCs and NO_x . ▪ Environmental fate Ozone reacts with and oxidizes many other substances; if it survives, it breaks down into O_2 .

Reducing ground-level ozone

It is probably clear to you that levels of ground-level O_3 cannot be reduced without reducing emissions of its precursors, NO_x and VOCs. Billions of dollars have been spent in efforts to do this, often with unsatisfactory results. ▪ Motor vehicles *A major reason for our inability to lower O_3 is our inability to control motor vehicles.* It is these, which, in urban areas emit more than half of NO_x and 40% of VOCs. ▪ After the 1970 US Clean Air Act was passed, motor vehicles were designed to run much more cleanly and emissions fell 90% or more per gallon of fuel burned. Unfortunately, at the same time the number of motor vehicles continued to rise as did the number of miles driven per vehicle. So NO_x and VOC emissions remain high. ▪ Poorly maintained vehicles, even if quite new, have much greater NO_x and VOC emissions than well-maintained ones: it is important to regularly inspect motor vehicles to ensure they are running cleanly. ▪ Other measures include reformulating gasoline to burn more cleanly to reduce VOCs emissions. ▪ Smaller measures include installing vapor recovery nozzles on gasoline pumps; these reduce VOCs emissions during refueling. ▪ Other sources Many countries, especially industrialized ones, have lowered NO_x emissions from power plants and industrial facilities. ▪ Technical difficulties Regulations designed to reduce VOCs or NO_x don't necessarily lead to the O_3 reductions anticipated. This happens because the reactions leading to O_3 formation are not as straightforward as Figure 5.2 might indicate. Still, efforts have paid off: researchers have found that not all VOCs contribute equally to O_3 formation. Knowing this may lead to efforts to reduce emissions of particular VOCs such as formaldehyde, which contribute most heavily to O_3 formation. Technological changes are not enough. How do we reduce fossil fuel use? What will lead to changes in the way we buy and operate vehicles? (See Chapter 13.)

Difficulties in setting and complying with O_3 standards

Recall from Chapter 4 the procedure used to set a standard has, as one step, the determination of a no observed adverse effect level (NOAEL). This is not easily done with ozone because this problematic molecule provokes a biological response right down to natural background levels. What is observed instead of a NOAEL is a continuum where the impact continues to decrease as the dose decreases. Moreover, some crops suffer at even low O_3 levels. So choosing a safe dose is very difficult. ▪ In the United States of the 1990s, the primary standard for ozone in ambient air was 0.12 ppm. However, information on ozone's adverse effects continued to accumulate – in animals

and people (including volunteers exposed to ozone in enclosed chambers) and in crops and trees. So, the EPA re-evaluated the 0.12 ppm standard, and after much controversy and legal wrangling, it began implementing a new standard of 0.084 ppm in 2002. However, a third of Americans continued living in areas out of compliance with the 0.12 ppm standard. Then, in 2008, after yet another re-evaluation, it was apparent that 0.84 ppm was also harmful and the EPA moved to a standard of 0.075 ppm¹³ However, many locales still remain out of compliance with the 0.84 ppm standard. ■ Another problem for cities attempting to comply is that the O₃ standard primarily affects – not industry – but communities with heavy traffic – people who accept restrictions on industry do not want restrictions on themselves: how much they drive, the vehicles they drive, or the condition of those vehicles.

Future ozone issues

A Massachusetts Institute of Technology study concluded that as fossil fuel burning continues to increase, so will ground-level ozone. “Even assuming that best-practice technology for controlling ozone is adopted worldwide, we see rapidly rising ozone concentrations in the coming decades.” This will lead to increasing damage to global vegetation, especially food crops. In future years, increases in temperature and in carbon dioxide could benefit vegetation in some temperate regions, but benefits may be offset by the increasing ozone levels. Crops are especially sensitive to ozone’s impacts because they are fertilized: fertilizer stimulates crops to open their stomata and bring in more air – including more ozone pollutant. Over the twenty-first century, crop yields could fall significantly.¹⁴ ■ The intractable ozone There are ozone success stories. Indeed, many American, Canadian, and Mexican cities control ozone levels or at least keep them from increasing. Cities do this in the face of ever-increasing populations and increasing numbers of motor-vehicles. In Figure 5.1 note that air concentrations of five out of six of the principal air pollutants have steadily decreased over the years. But ozone levels appear almost intractable.

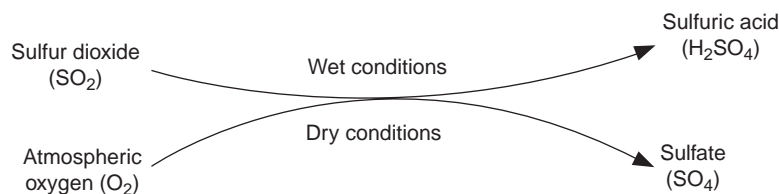
Sulfur dioxide¹⁵

Sulfur dioxide (SO₂) is a corrosive acid gas, colorless with a sharp irritating odor. It accounts for about 18% of all air pollution, making it second only to CO as the most common urban air pollutant. It is converted in the atmosphere into substances, which form aerosols (Figure 5.3). Sulfuric acid and sulfate are the major aerosols formed.

¹³ There has been much criticism of the EPA for its 0.075 ppm standard because a science advisory panel had recommended 0.06–0.07 ppm. Others criticize that 0.075 is too stringent at a time when so many locales are unable to meet the old 0.084 standard. See Wald, M. L. Environmental Agency Tightens Smog Standards, *New York Times*, March 13, 2008, <http://www.nytimes.com/2008/03/13/washington/13enviro.html?hp>.

¹⁴ Stauffer, N. Human-generated ozone will damage crops, according to MIT study. *MIT News*. October 26, 2007, <http://web.mit.edu/newsoffice/2007/ozone-1026.html>.

¹⁵ Sulfur dioxide. *US EPA*, 2007, <http://www.epa.gov/air/airtrends/2007/report/sulfurdioxide.pdf>.



Sulfuric acid and sulfate are aerosols. These wash out with rain, or slowly settle out by gravity. Both are acidic deposition.

Figure 5.3

Transforming sulfur dioxide to sulfuric acid and sulfate

Why SO₂ and its acid aerosols are of concern

Health impacts of SO₂ and its aerosols ▪ Sulfur dioxide reacts with moisture in the eyes, lungs, and other mucous membranes to form strongly irritating acid (about 90% of this conversion occurs in the upper respiratory tract). Exposure to SO₂ can trigger allergic-type reactions and asthma in sensitive individuals (as can the sulfites used in food preservation). Sulfur dioxide exposure also aggravates preexisting respiratory or heart disease. ▪ As with O₃, low SO₂ concentrations can damage plants and trees. ▪ Sulfur dioxide's atmospheric lifetime is only about a day. Thus, if the only problems resulting from SO₂ were the ones just noted, they would be manageable. ▪ However, SO₂ can be converted into tiny particles, largely liquid sulfuric acid and solid sulfate. These tiny particles form aerosols, a gaseous suspension of fine solid or liquid particles, which can remain airborne for many days. The dry particles can slowly settle out; the liquid sulfuric acid can be rained out. Such tiny aerosols, only 0.1 to 1 μm in diameter, can be deeply inhaled into the lungs and inflame them.

Environmental impacts of aerosols ▪ They form a haze that affects visibility, and reduces the amount of sunlight reaching the Earth (Box 5.4). ▪ Sulfuric acid and sulfate are a major part of the acid deposition problem (Chapter 6). ▪ Aerosols have a cooling influence on climate (Chapter 7). ▪ Sulfate particles in the stratosphere provide surfaces on which ozone-destroying reactions can occur (Chapter 8). Aerosols formed from nitrate and nitric acid contribute to these impacts; see below.

Sulfur dioxide sources¹⁶ and environmental fate

Human sources In the industrialized Northern Hemisphere, human activities produce *five times more* SO₂ than do natural sources. Worldwide, the figure is about two times as much. Sulfur is found in all raw materials – including coal, crude oil, and gas. Sulfur is converted to SO₂ when fossil fuels are burned. The EPA reports that 87% of the SO₂ released into US air is attributable to fuel combustion. In 2002, electric utilities burning fossil fuels produced about two-thirds of the anthropogenic¹⁷ SO₂ in the United States. The worst offenders are

¹⁶ Sulfur dioxide. *US EPA*, April 8, 2008, <http://www.epa.gov/air/emissions/so2.htm>.

¹⁷ Anthropogenic refers to something that originates in human activities.

Box 5.4

Food production and sulfur dioxide emissions in China

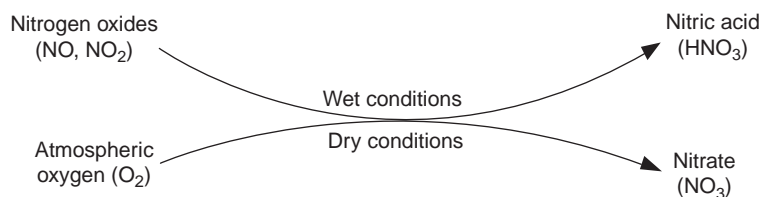
China, a nation of 1.3 billion people, generates most of its electricity by burning coal and is the world's largest emitter of SO₂. A Georgia Institute of Technology study found disturbing results: the haze resulting from sulfuric acid and sulfate aerosols is cutting agricultural production. This happens because haze partially filters out the solar energy reaching plants. Researchers estimated that the haze reduces sunlight by 5–30%. Moreover, decreased sunlight affects up to 70% of China's agricultural areas.¹⁸ With its huge and still growing population, China already has to import food. If crop production is further hindered by pollution, the situation may be worsened. ■ There *are* solutions. One is installing technology to lower SO₂ emissions. Indeed, China is making major efforts to change how it uses energy. It has closed many small inefficient industrial facilities; started to burn coals containing less sulfur; and switched many residents, who previously burned coal, to gas or electricity.

utilities burning high-sulfur coal. ■ Many metal ores including aluminum, copper, zinc, lead, and iron contain sulfur, so metal smelters emit SO₂. ■ As oil is processed into gasoline, SO₂ is also formed. However, sulfur is more readily removed from petroleum during its refining than is the case for coal; thus, motor vehicles account for a lower percentage of SO₂ emissions. (See Figure 6.4.) Other sources of SO₂ emissions include industrial facilities such as petroleum refineries and cement manufacturing operations. Natural sources Most SO₂ is anthropogenic, but many natural sources exist including sea water, marine plankton, bacteria, plants, and geothermal emissions. Erupting volcanoes are a major but periodic source. In 1991, the Filipino volcano Mt. Pinatubo ejected about 20 million tons (18.1 million tonnes) of SO₂ into the atmosphere. This huge quantity is believed to have been responsible for cooling the Earth's climate for several years thereafter. Environmental fate Two major substances into which SO₂ is converted (oxidized) are the liquid particulate, sulfuric acid and the solid particulate, sulfate. See Figure 5.3. More information is given in Chapter 6.

Reducing SO₂ emissions

Over the past 30 years many nations have mandated emission controls on sources of SO₂ including coal-burning power plants and other industrial facilities. See the Chapter 6 section on reducing emissions of acid precursors. Meanwhile, see Figure 5.1: with control and P² measures taken, sulfur dioxide emissions have continued to decrease. Separate data show that in 1970 SO₂ emissions were 31 million tons/yr (28 million tonnes/yr) in the United States, but in 2005 emissions were 15 million tons (13.6 million tonnes).

¹⁸ Chameides, W. L., Yu, W. L., Liu, H. *et al.* Case study of the effects of atmospheric aerosols and regional haze on agriculture: an opportunity to enhance crop yields in China through emission controls? *Proceedings of the National Academy of Sciences*. **96**(24), November 23, 1999, 3626–13633, <http://www.pnas.org/cgi/content/full/96/24/13626>.



Nitric acid and nitrate are aerosols and wash out with rain, or slowly settle out by gravity. They are acid deposition in both cases. Importantly, they are also plant nutrients.

Figure 5.4

Transforming NO_x gases to nitric acid and nitrate

Nitrogen oxides (NO_x)

NO_x is the word used for a group of gases, especially *nitric oxide* (NO) and *nitrogen dioxide* (NO₂). NO_x is pronounced “knocks.” Another NO_x is *nitrous oxide* (N₂O). Nitrogen oxides account for about 6% of US air pollution.

Why NO_x gases and their acid aerosols are of concern

Health impacts of NO_x and its aerosols Direct exposure to NO_x irritates the lungs, aggravates asthma, and lowers resistance to infection. Nitrogen dioxide is poisonous to plant life. ▪ As tiny aerosol particles, nitrate and nitric acid (into which NO_x can be converted in the atmosphere), they are deeply inhaled into, and inflame, the lungs. See Figure 5.4. Environmental impacts ▪ Nitric acid and nitrate are part of the haze that affects visibility (Chapter 5); and contribute to acid deposition (Chapter 6). As aerosols they have a cooling influence on climate (Chapter 7). Aerosol particles provide surfaces on which ozone-destroying reactions can occur, contributing to stratospheric-ozone depletion (Chapter 8). Also see Box 5.5.

Sources of NO_x¹⁹ and environmental fate

Human sources Nitrogen compounds occur naturally in fossil fuels in very small amounts. But NO_x gases are formed primarily from a high-temperature reaction between atmospheric nitrogen and oxygen. See Box 5.5. ▪ As is true of CO, the major source of NO_x is motor vehicles, including off-road vehicles such as construction equipment. Motor vehicles account for about 55% of US emissions overall, and a greater percentage in urban areas. ▪ Electric utilities emit another 22%, and industrial/commercial/residential facilities another 22%.

Natural sources ▪ NO_x gases are produced by lightning and volcanoes. ▪ Microbes decomposing vegetation in soil produce nitrous oxide (N₂O). If nitrogen fertilizer is added to the soil, microbes produce even larger amounts.

¹⁹ Nitrogen oxides. *US EPA*, April 8, 2008, <http://www.epa.gov/air/nitrogenoxides/>.

Table 5.3 Sulfur dioxide, nitrogen oxides, and global change

Issue	Role of sulfur dioxide
Acid deposition	Sulfur dioxide emissions are converted in the atmosphere to sulfate and sulfuric acid – major contributors to acid deposition (Chapter 6).
Stratospheric ozone depletion	Volcanic eruptions inject sulfur dioxide into the stratosphere where it is converted to particles. Analogous to ice particles at the poles, these provide surfaces on which ozone depleting reactions occur (Chapter 8)
Global climate change	Sulfur dioxide is converted to sulfate or sulfuric acid particles. These have an “anti-greenhouse” effect. They do so by absorbing part of the sun’s radiation, preventing it from reaching and warming the Earth’s surface (Chapter 7).
Issue	Role of nitrogen oxides (NO_x)
Acid rain, stratospheric ozone depletion, and climate change	NO _x emissions are converted in the atmosphere to nitrate and nitric acid, which contribute to the problems shown on the left.
Ground-level ozone	NO _x , but <i>not</i> sulfur dioxide, is converted to ground-level ozone (Chapter 5).
Nutrient pollution	NO _x is converted to nitrate and nitric acid. After deposition to earth and water, these can “over-fertilize” waters leading to eutrophication (Chapter 10)

Box 5.5**How NO_x is formed and impacts specific to NO_x****Formation of NO_x**

Atmospheric nitrogen, N₂ is a very stable chemical. However, burning fossil fuels at a high temperature promotes a reaction between atmospheric N₂ and atmospheric oxygen, O₂. It is this reaction that results in NO_x formation when fossil fuels are burned. So, nitrogen oxide gases are emitted almost anywhere that high-temperature combustion occurs. This is unfortunate because high temperatures otherwise promote *efficient combustion*, thus lowering emissions of carbon monoxide, PAHs and other incomplete products of combustion (Box 1.2). Many impacts of NO_x and its particulates are *shared* with SO₂, and with aerosols of sulfate and sulfuric acid (Table 5.3).

Impacts specific to NO_x

Nitrogen oxide gases have important impacts *not* shared with SO₂. (1) NO_x gases are precursors of ground-level ozone. (2) Deposited onto earth or into water, these nitrogen compounds serve as plant nutrients. They can benefit plant life, *but* high concentrations have adverse even devastating consequences. (3) Nitrous oxide (N₂O) is often considered a NO_x. It is a strong greenhouse gas, but fortunately emitted in fairly small quantities.

Environmental fate Two major substances into which NO_x gases are converted (oxidized) are the liquid particulate, nitric acid and the solid particulate, nitrate. See Figure 5.4. We will learn more of these in Chapter 6.

Reducing NO_x emissions

See progress to date in Figure 5.1. This issue will be discussed in Chapter 6.

Particulate matter (PM)

What is particulate matter (PM)?²⁰

Atmospheric gases (N₂, O₂, SO₂, etc.) blend into air in a homogeneous manner. *Particulate matter does not*. PM (or particle material) is solid, albeit the particles may be very fine; and is composed of liquid aerosol particles and solid aerosol particles. PM accounts for about 10% of US air pollution. PM is a confusing pollutant.

- Composition varies. Other criteria pollutants are specific chemicals, carbon monoxide, ozone, sulfur dioxide, nitrogen oxides, and lead. But, PM has no fixed composition. A particle may contain only one chemical such as sulfate, sulfuric acid, or lead oxide. Other particles may contain a number of pollutants: organic chemicals, metals, dust (with all that it can contain), tiny bits of biological matter, etc.
- Size varies greatly. PM may be as large as visible cotton dust, historically found in fabric mills. Or, PM can be submicroscopic particles, aerosols. It is these tiny particles – even at low concentrations – that pose major problems.
- Other pollutants can become PM. You have already seen that SO₂ and NO_x are oxidized in the atmosphere into the aerosols (nitrate, nitric acid, sulfate, and sulfuric acid). Also, a number of other pollutants can be converted to particulates including some organic vapors that condense into liquid particulates.
- Metals are particulates. An exception is elemental mercury, largely emitted as a vapor. Many hazardous air pollutants (see below) are metals, and emitted as particulates.

Why PM is of concern and which particles are of most concern²¹

When we inhale small amounts of dirt, dust, or pollen, we can usually cough these up from the throat, blow our nose, or sneeze. Others can be swallowed or spat out.

Health impacts The idea of a particle seems innocuous – a tiny piece or speck – nothing to inspire alarm. The reality is different. Before the advent of workplace protection laws PM took a terrible toll. Workers with chronic exposure to silica dust developed silicosis. Coal miners developed black lung disease from coal dust. Textile workers developed brown lung

²⁰ Particulate matter. *US EPA*, January 15, 2009, <http://www.epa.gov/air/particlepollution/index.html>.

²¹ Air quality guide to particle pollution. *US EPA*, August, 2003, <http://airnow.gov/index.cfm?action=static.aqguidepart>.

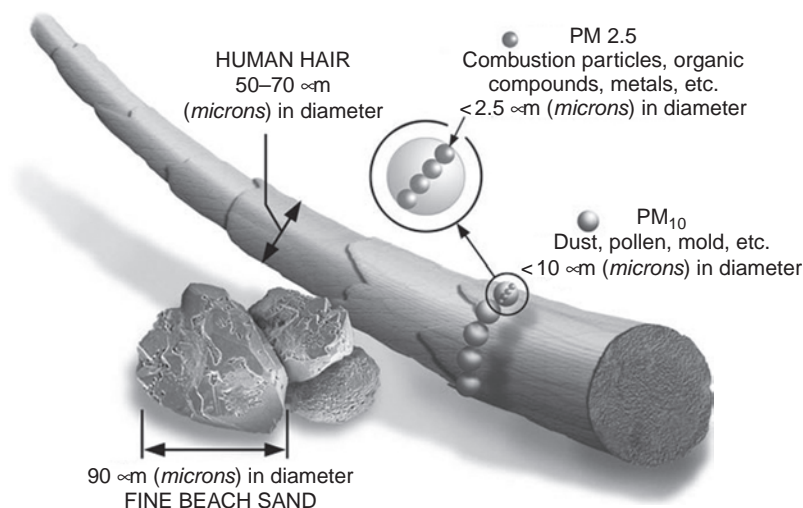


Figure 5.5

How big is particle pollution? Credit: US EPA

disease from cotton dust. Workers inhaling airborne asbestos developed asbestosis, lung cancer, or mesothelioma. All these are disabling or deadly diseases. Many workers inhaled large quantities of all sizes of particles, overwhelming their respiratory systems. ▪ In the twenty-first century, workplaces in developed countries have been cleaned up. Nonetheless, we are left with a major particulate problem – the very tiniest of particulates. The US EPA regulates particles with diameters of 10 μm or less (PM_{10}). The more dangerous category is particles with diameters of 2.5 μm or less (0.1–2.5 μm or $\text{PM}_{2.5}$), which are also regulated. See Figure 5.5. The diameter of $\text{PM}_{2.5}$ is barely one-fortieth the width of a human hair. ▪ Sulfate particles, and some soot and dust particles are as small as 0.01 μm . These particles, the ultrafines, <0.1 μm may be most dangerous. Deeply inhaled, fine and ultrafine particles can reach and inflame the lung's alveoli (tiny air sacs where oxygen is exchanged with carbon dioxide). The ultrafine may pass into the bloodstream and exert effects elsewhere in the body.²² The relationship between $\text{PM}_{2.5}$ and disease is remarkable (Box 5.6).

Environmental impacts ▪ Fine particles ($\text{PM}_{2.5}$) strongly contribute to the haze or smog seen in many cities, which often spreads far into rural areas. Sulfate and sulfuric acid aerosols in US parks illustrate this. Visibility reduced by haze in western national parks is up 50% compared to earlier years. In eastern parks, which are exposed to a greater number of emission sources, haze has reduced visibility by 80% compared to the 1940s. *Just in the 1980s, the Shenandoah and Great Smoky Mountains parks in Virginia and North Carolina saw a 40% increase in sulfate particles.* Instead of blue sky, one often sees pale white haze or gray fog composed of dilute sulfuric acid. These increases in sulfuric acid and sulfate hazes in the 1980s happened as sulfur dioxide emissions nationwide were decreasing. There is much that we don't yet understand. ▪ Particulates also contribute to a variety of other problems depending on what they contain.

²² Nel, A. Air pollution-related illness: effects of particles. *Science*, **308**(5723), May 6, 2005, 804–806.

Box 5.6

A relationship to cancer and death

Epidemiological studies continue to indicate relationships between fine-particle pollution, PM_{10} and $PM_{2.5}$ and death rates among sensitive individuals. Studies reported that more deaths from heart and lung diseases occurred in a given locale on days with high levels of fine particles in the air, even levels that were in compliance with the pre-1997 standard. The particles believed to be most responsible, $PM_{2.5}$, consist of sulfate or nitrate, soot and other chemicals resulting from burning fossil fuels in coal-burning power plants, manufacturing facilities, and motor vehicles. You are probably not surprised that inhaled PM can cause respiratory problems or lung cancer. However, reputable studies also report increases in heart disease, vascular disease, and stroke after long-term exposure to $PM_{2.5}$.

The strongest work supporting a connection to lung cancer was reported in 2002.²³ Researchers tracked 500 000 people from 1982 through 1998. They reported the causes of all the deaths that occurred in these people over these years, and looked at levels of $PM_{2.5}$ in the air of locales where those individuals had lived. They corrected results for confounding factors including occupational exposure, age, sex, race, smoking, drinking, obesity, type of diet (fat, vegetable, fruit, and fiber intake) and used improved statistical techniques. They found that every $10 \mu/m^3$ increase in airborne $PM_{2.5}$ resulted in a 6% increase in the risk of death by heart or lung disease, and an 8% increase for lung cancer. Risk was especially great in Los Angeles, but also in Chicago and New York City, and in rural areas with coal-burning power plants. The elderly were at greatest risk, as were those already suffering from heart or lung diseases such as asthma and bronchitis. One study leader commented, "This study provides the most definitive epidemiological evidence to date that long-term exposure to air pollution in the United States is associated with lung cancer."

But *how* can PM cause disease? For a long time PM epidemiologic studies were criticized because many particles contain more than one chemical, raising the question: which chemical(s) cause diseases? The same criticism was earlier made of relationships found between second-hand tobacco smoke (among people living with a smoker) and lung cancer. But, in both cases the particles contain a number of carcinogens such as PAHs (see Box 5.7) as well as toxic metals bound to the particulates. In both cases, tiny particles are trapped and retained in the lungs. However, we do need more research. What PM chemicals are most responsible for the effects observed? How do they promote lung cancer and heart disease?²⁴

Sources of PM_{10} and $PM_{2.5}$ and environmental fate

- PM_{10} The major source of PM_{10} or "coarse" particles is dust and dirt raised by vehicles or wind from farms (fertilizer, dried manure, or dried crop residues), from roads, unpaved

²³ Pope, C. A., Burnett, R. T., Thun, M. J. *et al.* Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Journal of the American Medical Association*, **287**(9), March 6, 2002, <http://jama.ama-assn.org/cgi/content/full/287/9/1132>.

²⁴ Schoor, J. L. Carol Browner's legacy: $PM_{2.5}$. *Environmental Science & Technology*, **40**(15), August 1, 2006, 4530.

Box 5.7

The ubiquitous PAHs²⁵

Benzene is both a VOC and a HAP. We spoke of benzene as near ubiquitous in the environment because of its widespread emissions. Even more widespread pollutants, classed as a HAP are the *PAHs* (polycyclic aromatic hydrocarbons). They form as particulates, as products of incomplete combustion (Box 1.2). PAHs are polycyclic (many-ringed) hydrocarbons. They cling to sediments and soil, are difficult to degrade, can bioaccumulate in fat, and are toxic.

- Toxicity Breathed into the lung as fine particulates, PAHs can cause respiratory distress. Several are known human carcinogens: among these, benzopyrene is the most potent. Recall (Chapter 4) that an excess risk of no more than one in a million is the goal for exposure to carcinogens. However, even rural soils (away from major highways) sometimes pose an excess risk close to one in a million, and PAH levels in urban soils pose a risk that is much higher. Fortunately, PAHs are often not bioavailable: they can be detected in soil, but are bound so firmly that even if the soil is ingested, absorption is limited.
- Sources More than 4 million tons (3.6 million tonnes) of PAHs are emitted into US air each year. They are found wherever any carbon-containing material is burned, wood, fossil fuel, plastic, cotton, a browned oven roast or char-grilled food. Natural sources include forest and grass fires, petroleum and volcanic eruptions. But it is coal burning and motor-vehicle exhausts that have greatly increased environmental levels. Burning of agricultural wastes and wood burning can be significant in certain locales.
- Exposure Airborne PAHs settle into water. They have very low water solubility and instead concentrate in sediment. There they are protected from the sunlight, warmth, and oxygen that could help destroy them. Airborne PAHs also settle onto soil, food crops, and other vegetation. In homes with smokers, tobacco smoke is a primary route of PAH exposure. Otherwise, foods are the route of 90% of human exposure, especially leafy vegetables and unrefined grains. We also ingest PAHs when eating charcoal-grilled foods or browned, especially very brown meats, baked goods, and toast. Smoking one or more packs of cigarettes a day can double, in some cases quintuple, a person's PAH exposure.
- Reducing emissions PAHs are particulates, so proper controls can capture a large portion of emissions from, e.g., fossil-fuel burning facilities. Using conditions that promote more complete combustion is an important P² means of lowering PAH formation. Becoming less dependent on fossil fuels is another.

and paved. Construction sites release large amounts of dust. PM₁₀ also includes pollen. Only about 6% of PM₁₀ comes from burning fossil fuels. A natural PM source found in coastal areas is sea salts, which have high levels of chloride and can corrode local buildings and statuary.

²⁵ ToxFAQs™ for polycyclic aromatic hydrocarbons. ATSDR, September, 1996, <http://www.emla.hu/prtr/chems/tfacts69.html>.

- PM_{2.5} Most PM_{2.5} and the even tinier ultrafines originate from fossil-fuel combustion, especially diesel motor vehicles, electric power plants, and industrial operations such as steel mills emitting sulfur dioxide. ▪ Power plants and other incinerators also produce *fly ash*, whose fine particles contain carbon, hydrocarbons, metal oxides, and silicon dioxide. Silicon dioxide in window glass is benign, but in fly ash or fine blowing sand, it is dangerous. Fly ash particles also trap dioxins formed during combustion. ▪ Locales with large numbers of inefficiently burning wood stoves contribute to particle levels. Rural areas generate airborne particles when burning biomass. Recall that with efficient combustion, most organic material is converted to carbon dioxide and water, with little particulate matter and soot. More particles form when combustion is inefficient.

Environmental fate There are many types of PM, so the fate depends on the particular chemical composition of the PM being considered. Those that are organic may be destroyed or transformed into other chemicals while in the atmosphere. Many others settle onto earth and water and are transformed there by microorganisms or by a number of other reactions.

Reducing PM emissions

- In 1997, the US EPA set new standards for particulates and, at the same time, for ozone. As happened with ozone, it was only in 2002 that the new PM standard withstood court appeals and its implementation allowed. ▪ The old PM₁₀ standard of 50 µg/m³ of air was retained. ▪ A new PM standard specific to PM_{2.5} was added, 15 µg/m³. Note, in Figure 5.1, that PM₁₀ measurements didn't begin until 1990 and PM_{2.5} not until 1999.
- Combustion By now you see that reducing emissions from combustion sources producing PM_{2.5} is a major need. Remember – the same is true for carbon monoxide, ozone, sulfur dioxide, and nitrogen oxides. In addition to controls, Americans need to commit to lessened dependence on fossil fuels. So do many other countries. The European Union is also focusing attention on reducing ozone and PM. When the EU adopted its Clean Air for Europe (CAFE) program in 2001, these two were targeted as “the air pollutants of greatest concern”.
- But PM_{2.5} poses quandaries as we contemplate reducing emissions. Despite excellent epidemiological information on its dangers, major questions need answers before PM_{2.5} emissions can most effectively be reduced. ▪ Example The chemical composition of PM_{2.5} differs between the East Coast and the West Coast of the United States. Moreover, although PM_{2.5} clearly has adverse health effects, we don't know *what* PM_{2.5} component is most responsible – sulfate, nitrate, elemental carbon, carbon compounds, metal oxides, or? If we determine which PM_{2.5} chemicals are most dangerous, we could design controls specific to those chemicals. This could reduce risk more efficiently than attempting to stringently control every fine-particulate source.

Lead²⁶

Lead is an important pollutant that will be more completely described in Chapter 15. In the 1970s, when EPA designated lead as a criteria air pollutant, lead was still added to gasoline in the United States, and incinerators were less well controlled than today. More generally, lead emissions were less well controlled. ▪ Since the late 1970s, lead has been eliminated from gasoline and from paint used indoors. In developed countries, lead emissions from industrial facilities have been lessened. Coal-burning power plants have been controlled, but still emit some lead along with other metals. ▪ Developed countries A major problem remains: as a metal, lead is not degraded. Thus lead mobilized into the environment many years ago, remains a significant pollutant today. Lead is found in paint of old houses, often in the soil outside those homes, and in the solder of old water pipes. It is still found in roadside soil that was contaminated from car exhaust. ▪ Less-developed countries Although leaded gasoline has been eliminated from gasoline in most countries, some still use it. Coal-burning power plants are typically poorly controlled. Recycling of lead-acid batteries in impoverished countries remains an occupational exposure even to children. Leaded tableware, sometimes unsafe to eat off of, is still made.

Questions 5.1

- 1 Think about a warm sunny summer day in an urban area. People who exercise outdoors are advised to do so early in the morning on such a day. Explain why.
- 2 Where might you personally be exposed to: (a) carbon monoxide (b) ozone (c) particulate matter (d) sulfur dioxide (e) nitric oxides? (f) lead?
- 3 How would the way you may be exposed to sulfuric acid and sulfate be different from possible exposure to sulfur dioxide?
- 4 Environmental improvements can involve cost. Assume that you want to convince your employer to conserve fossil fuels. (a) Outline your reasons for doing so. (b) What kind of changes could be done at no cost? (c) Which involve short-run costs? (d) Long run costs? (e) What benefits would your employer see?
- 5 Your highest exposure to particulate matter, including fine particles, occurs inside your home. Does this mean we can lessen our emphasis on regulating particulates in outside air? Explain.
- 6 What criteria air pollutant(s) would most concern you in the following instances? Explain in each case. (a) You are a garage attendant or a traffic officer in a large city. (b) Air pollution from a nearby urban center reaches your farm. (c) A truck is parked near an air intake of the motel where you are spending the night. Because the truck contains perishables, its motor is left idling. (d) You are a park ranger in the Great Smoky Mountain National Park.
- 7 What have you learned about ozone and particulates that made it reasonable that they would be considered together when new standards were set?
- 8 Consider: "The more the population grows, the more the rights of the common will impinge on the rights of the individual." How is this statement relevant to regulating motor vehicle emissions?

²⁶ Lead in air. *US EPA*, October 16, 2008, <http://www.epa.gov/air/lead/>.

SECTION II

Volatile organic chemicals (VOCs)²⁷

As *volatile organic chemical* implies, these are compounds of carbon,²⁸ and compounds that readily evaporates into the air. A great many organic chemicals are *volatile*.²⁹ Benzene and other volatile hydrocarbons found in gasoline are well known examples. Another is *methylene chloride*, a paint stripper. We typically like the smell of VOCs emitted inside new cars, but the odor of VOCs emitted from new carpets, clothing, or drapes may irritate eyes and noses. You can get a sense of the many types of VOCs in our environment by examining VOC sources.

Why VOCs are of concern?

Health impacts Because there are so many individual VOCs, it is hard to generalize as to their health impacts. However, many drivers and pedestrians develop headaches and other symptoms if heavily exposed to volatile hydrocarbons in motor vehicle exhausts. Sensitive individuals may react with attacks of asthma or other respiratory problems.

- Individual VOCs vary in specific health impacts. As you would expect, high concentrations of a chemical such as benzene may cause dizziness, nausea and other symptoms. Lower level exposures, over longer time periods can lead to ill health effects that depend on the particular VOC.
- Many VOCs are also hazardous air pollutants (HAPs), which will be discussed below.
- Ozone formation Remember from Figure 5.2 that VOCs play a major role in the formation of ground-level ozone.

Sources and fate of VOCs³⁰

- Combustion Hydrocarbons are the most common VOCs, and motor vehicles are the largest VOC source. These emit up to half of all VOCs in the United States. Look again at Box 1.2: internal-combustion engines burn hydrocarbon VOCs inefficiently, emitting large amounts as incomplete products of combustion. Hydrocarbons also evaporate as gas tanks are filled, and when vehicles are running, idling, or cooling. Combustion engines are pervasive, used not just in cars, trucks, and buses, but in

²⁷ Definition of Volatile Organic Chemicals (VOC). *US EPA*, November 26, 2007, http://www.epa.gov/ttn/naaqs/ozone/ozonetech/def_voc.htm.

²⁸ Excluded from the category of VOCs are carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate.

²⁹ The US EPA refers to VOCs as organic gases, <http://www.epa.gov/iaq/voc.html>.

³⁰ Volatile organic compounds. *US EPA*, October 21, 2008, <http://www.epa.gov/air/emissions/voc.htm>.

airplanes, construction, farm and forestry equipment, gasoline-powered lawn and garden equipment.

- Non-combustion Petroleum refineries, chemical plants, and electric-power plants can be important *local* sources, but less so overall as compared to the pervasive VOC emissions of motor vehicles. A great variety of facilities including gasoline stations, auto maintenance shops, paint and print shops, dry cleaners, wood-drying, or wood-painting operations emit VOCs. Restaurants and bakeries emit pleasant-smelling VOCs, but large bakeries emit large amounts of ethanol formed by the action of yeast. Sewage treatment plants and composting operations emit VOCs too, often with odors that we consider objectionable.
- Natural sources Trees and plants are a large natural source of hydrocarbons, especially in hot weather. Trees may be significant VOC sources, even in large cities. In Maine, a heavily forested state, trees produce more than 90% of the state's VOCs. The VOCs responsible for the smell of pines are terpenes which, although pleasant smelling, can contribute to ozone formation. Natural VOCs are not by themselves a problem, but must be figured into strategies to reduce ozone formation. However, trees do *not* emit the NO_x that interact with VOCs to form ozone.
- Homes and offices Although we don't produce large quantities of VOCs in our homes or offices, they can be a large source of human exposure. Sources of VOCs within the home are freshly painted walls, household solvents, charcoal broiler starters, aerosol sprays, even deodorants and cosmetics (Chapter 17).

Fate of VOCs Many break down in the atmosphere through a series of chemical reactions that start with hydroxyl radicals. The hydroxyl radical ($\bullet\text{OH}$), often referred to as an atmospheric cleanser is a highly reactive free radical.³¹ See Chapter 19.

Reducing VOC emissions

By 1985, VOC emissions had dropped about 30% compared to 1970 in the United States, presumably due to regulations enacted in the 1970 Clean Air Act (CAA) and its 1977 amendments. In 1990, CAA amendments mandated further reductions in motor vehicle emissions. ▀ Southern California was especially aggressive in reducing not just VOC emissions from motor vehicles, but all vehicle pollutants. California took measures that included switching to less polluting fuels, and mandating that motor vehicle manufacturers sell a specified numbers of low-polluting vehicles. ▀ Other locales have taken actions such as highway lanes that can be used only by vehicles carrying more than one passenger, or requiring that tolls be paid by those who drive in peak-traffic hours. Sometimes employers pay employees to take alternative forms of transportation to work. Chapter 13 has more information on reducing motor vehicle emissions. In 1970, US VOC emissions were 34 million tons (31 million tonnes), which slowly dropped over the years to 16 million tons in 2005.

³¹ A free radical is an atom or molecule that has one or more unpaired electron. See free radical. Answers.com. <http://www.answers.com/topic/free-radical>.

Questions 5.2

The EPA reports that 200 million tons (181 million tonnes) of five criteria pollutants (sulfur dioxide, nitrogen dioxide, carbon monoxide, lead, and particulate matter) plus VOCs were emitted in the United States in 1997.

- 1 Ozone is a criteria pollutant – why wasn't it on this list?
- 2 What chemical change must sulfur dioxide and nitrogen oxides undergo before either is able to deposit onto water and soil?
- 3 What criteria pollutants can deposit to water and land without chemical conversions?
- 4 Large quantities of VOCs are emitted by motor vehicles. Chemically speaking, these VOCs can be described by one word. What word?
- 5 What is the eventual fate of most VOCs in the environment?

SECTION III**Hazardous air pollutants (HAPS)^{32,33}**

HAPS are often called *toxic air pollutants* or just air toxics. Also commonly called *air toxics*, exposure to HAPS can cause serious health and environmental problems. The 1970 Clean Air Act had authorized the EPA to list and regulate HAPS emitted into air. However, the process was so slow that Congress itself chose 188 chemicals to include in the 1990 US Clean Air Act Amendments. ▪ See examples of HAPS in Table 5.4. Many additional chemicals could qualify as HAPS, but these 188 were considered as higher priority. HAPS are not unique to the United States, but occur around the world. ▪ Many VOCs are HAPS; so are many metals. Remember the Toxic Release Inventory, TRI from Chapter 2. Many of the 188 HAPS are also TRI chemicals.

Do not conclude from the fact that they are called “hazardous” or “toxic” that HAPS pose greater problems than do criteria air pollutants. Criteria pollutants are hazardous – and toxic – too, and are typically produced in much larger quantities than HAPS. Our exposure is also usually greater. However, HAPS are important in a circumstances specific to each chemical.

Why HAPS are of concern

The risk of adverse effects of a particular HAP depends upon its intrinsic toxicity and the level of exposure to it. It is not feasible to consider all HAPS here, so only a few representatives follow.

³² About air toxics. *US EPA*, January 15, 2009, <http://www.epa.gov/ttn/atw/allabout.html>.

³³ National air toxic assessment. *US EPA*, 2002, <http://www.epa.gov/ttn/atw/nata/>.

Table 5.4 Examples of 188 federally regulated HAPS in the United States*

Organic	Representative sources or uses
1. Benzene	1. Gasoline, cigarette smoke
2. Toluene	2. Gasoline, vehicle exhaust, smoking, paints
3. Ethylene glycol	3. Automobile antifreeze, brake fluid
4. Methanol	4. Windshield antifreeze, solvent
5. Chloroform	5. Formed during water chlorination
6. Methyl bromide	6. Fumigant
7. Formaldehyde	7. Particleboard and plywood, insulation, cosmetics
8. Parathion	8. Insecticide
9. Styrene	9. Manufacturing plastics, rubbers, adhesives, cushions
10. Vinyl chloride	10. Manufacture of plastics, new automobile interiors
11. PAHs	11. See Box 5.7.
Inorganic	Representative sources or uses
1. Asbestos (fibrous mineral)	1. Once widely used to fireproof materials
2. Arsenic	2. Mining and smelting operations, glass making, petroleum refining, metal alloys
3. Cadmium	3. Used in electroplating and NiCad batteries, and as a pigment & plastic stabilizer
4. Chromium	4. Used in electroplating auto parts and bathroom fixtures, and as a chemical catalyst
5. Mercury	5. Mercury measuring devices such as thermometers, as well as lamps and dental amalgams
6. Nickel	6. Electroplating, in alloys, chemical catalyst

* The original list of hazardous air pollutants. *US EPA*, November 12, 2008. <http://www.epa.gov/ttn/atw/188polls.html>

- *Benzene* is a high-production chemical with many uses. One is as an anti-knock agent in gasoline. Benzene can irritate the skin and eyes, cause headaches and dizziness. At the high levels once found in some work places, it was associated with leukemia and aplastic anemia. Benzene exposure occurs anywhere that gasoline is used, commonly motor vehicles. It is also in cigarette smoke. Because benzene is one of the most common HAPS, it is not surprising that exposure to benzene is near ubiquitous.
- *Formaldehyde* is another high-production HAP. It is released from factories that manufacture furniture or pressed wood products. Formaldehyde can irritate the eyes and lungs. At high doses it is an animal carcinogen. Some people develop severe allergies to formaldehyde.
- *Chloroform* was used as an anesthetic for 100 years before its ability to cause liver damage was appreciated. It can also be toxic to the kidneys and, at high concentrations, is an animal carcinogen. Chloroform is released from sewage treatment plants, from pulp-bleaching facilities, and other facilities that use chlorine-containing chemicals.
- *Cadmium* is a highly toxic metal. It bioaccumulates in plants, shellfish, and in the kidneys and liver. It is emitted by metal-refining facilities, and by manufacturing facilities that

make cadmium-containing products. Incinerators emit cadmium in small amounts, as do power plants and other facilities that burn fossil-fuels.

- *Mercury*, another highly-toxic metal, is a neurotoxin. Elemental mercury is the only liquid metal. It is volatile and is emitted by coal-burning power plants. It becomes especially toxic after bacteria convert it to methylmercury, which biomagnifies in the food web.

Potential for exposure

An individual HAP poses the most concern of possible exposure at or near its point of emission because that is where its concentration is the highest.³⁴ However, wind currents can carry a HAP far from its source, albeit in progressively more diluted form.

- Chloroform emissions are primarily important only near facilities that use chlorine-containing chemicals, such as municipal wastewater treatment or pulp-bleaching facilities.
- Several HAPS – benzene is a major case – are more widespread. Each benzene source may be local, but sources are ubiquitous.
- Metal HAPS pose special problems because they persist in the environment. Metals have built up in soil and sediment in certain locations. ▪ Because every motor vehicle that burns gasoline emits HAPS, there are many millions of small metal-emitting sources. On a larger scale, every fossil fuel – burning power plant, and many industrial facilities emit at least trace amounts of metals.
- In Chapter 17 you will see that the greatest source of human exposure to HAPS such as benzene, formaldehyde, and others is often in our own homes.

Reducing emissions of HAPS

Each of the six criteria pollutant has its own ambient air standard, a standard based on its risk. However, setting standards is both time consuming and costly. Moreover, once standards are set, a whole area must decide how to go about reducing emissions of those criteria pollutants. ▪ HAPS were handled by an alternative approach. The 1990 Clean Air Act Amendments mandated *maximum available control technology* (MACT) to reduce emissions of a particular HAP from individual facilities. ▪ Other ways, in addition to regulations can be used to reduce HAP emissions. ▪ Before 1990, more than 1000 companies engaged in a voluntary program to reduce emissions of 17 air toxics produced in large quantities or that posed special risks. ▪ Also, HAPS are among the chemical emissions that must be reported on the Toxic Release Inventory. Such public declarations have led many facilities to work harder to reduce them.

³⁴ US EPA, Risk Assessment for Toxic Air Pollutants, http://www.epa.gov/ttn/atw/3_90_024.html.

Questions 5.3

Before answering these questions, make sure you understand how criteria air pollutants differ from HAPS.

- 1 What actions can you take within your household to lower your PAH exposure?
- 2 (a) What if the 188 HAPS were called the risky air pollutants – how would the meaning change? Explain. (b) Consider the chemicals reported on the Toxic Release Inventory – what if it was called the Risky Chemical Release Inventory?
- 3 (a) What HAPS are likely to be emitted in your community? (b) In what ways could you personally be exposed to these?
- 4 Burning gasoline in 200 million motor vehicles is the single largest source of ambient air pollution in the United States. At the same time, motor vehicles consume over half of the petroleum used in the United States. This high consumption is a national security issue. (a) Does this knowledge increase the likelihood you might think carefully about fuel economy when you buy a motor vehicle, or affect how you drive and maintain it? Explain. (b) If knowledge alone is not enough, what *could* change your behavior? (c) Under what circumstances do you walk, take public transportation, or bike? (d) What would cause you to use these options more often?
- 5 (a) Social critics observe that the United States regulates pollutant emissions and encourages P^2 , but remains blind to the root causes of environmental damage – growing population and growing consumption. Do you agree? Explain.
- 6 VOCs along with four criteria pollutants (carbon monoxide, sulfur dioxide, nitrogen oxides, and particulates), account for about 98% of *all* air pollution. Fossil fuel combustion is a major source of all five. (a) Assume you believe that society should do more than it does now to reduce fossil fuel dependence. After reflection, note three steps that you would recommend society take. (b) How could those steps be relevant to you as an individual in terms of reducing your own dependence on fossil fuels?

Europe

European countries have the same air pollutants as the United States and show similar impacts of smog and particulates on human health, as well as ozone damage to vegetation, and acid deposition impacts on soils, trees and waters. ■ In late 1999 European countries adopted a cooperative protocol to aggressively address these pollutants under the UN Convention on Long-Range Transboundary Air Pollution. Each signatory country was assigned ceilings on its emissions of sulfur dioxide, nitrogen oxides, VOCs, and ammonia. Ceilings for each pollutant were individualized to the circumstances of each country. By 2006, sulfur dioxide emissions in 15 EU countries had declined 65%. Although NO_x fell only 30%, and VOCs only 38%, there were nonetheless fewer high ozone episodes. PM Although Europe had a cap of 40 $\mu\text{g}/\text{m}^3$ on PM₁₀, it was not until 2007 that the European Parliament approved a limit on PM_{2.5} of 25 $\mu\text{g}/\text{m}^3$.³⁵ This was part of a strategy to reduce

³⁵ Burke, M. EU contemplates first-ever limit for PM_{2.5}. *Environmental Science & Technology*, 40(1), January 1, 2006, 11.

fossil-fuel pollutants more generally along with agricultural pollutants including ammonia emissions from fertilizers and manure. Each of 15 EU countries would choose how it wanted to control emission

SECTION IV

Observing massive pollution from space

Transboundary pollution is carried by wind, water, or animals beyond the arbitrary borders set by humans. International treaties and agreements have made efforts to control transboundary pollution but, as described below, a tremendous amount remains to be done. Note that the traveling air pollutants described are criteria pollutants.

Carbon monoxide and smoke

Large dense masses of particulate matter such as generated by devastating fires or mammoth dust storms can be visually observed from space. But detecting a gas requires instrumentation.

Instrumental observation

Spacecraft can capture a picture of global air pollution: the NASA spacecraft, Terra, began taking pictures of carbon monoxide from space in 1999 using instrumentation called MOPITT (Measurements of Pollution in the Troposphere). MOPITT visualizes clouds of CO traveling across Earth's surface (Figure 5.6) 2 miles (3.2 km) above Earth's surface. From there, CO rises to yet higher altitudes and continues traveling with wind currents.

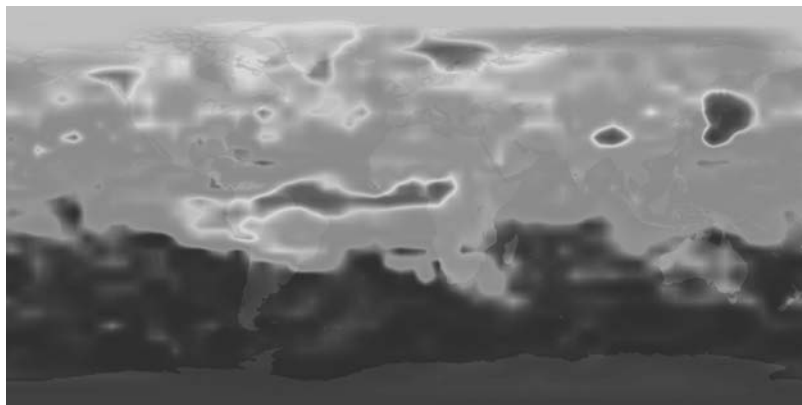


Figure 5.6

Carbon monoxide detected by instruments in space

Under different meteorological conditions CO sinks to Earth's surface and adds to ground-level pollution. Carbon monoxide is the only combustion pollutant that MOPITT can *directly* detect, but CO in turn serves as a tracer for NO_x and other combustion pollutants produced with the CO. MOPITT can observe emissions emanating from a city, but cannot precisely pinpoint the source. It can observe the enormous CO clouds produced by forest and grassland fires in Africa and South America. Such clouds of CO and other combustion pollutants travel across the Southern Hemisphere as far as Australia during the dry season. Because MOPITT can follow the pathways and determine concentrations, it is useful in mapping the distribution of CO pollution around the globe. It is expected to be helpful in setting international environmental policy.

Direct observation

Orbiting satellites can directly observe the smoke clouds resulting from heavy fires. An example was the mammoth fires in Indonesia's rain forests observed in 1997. These fires were described as a planetary disaster, "one of the most broad-ranging environmental disasters of the century." Humans deliberately set them to clear rainforests in order to plant rubber, palm oil, rice, and timber plantations. For weeks, a smoky haze fell over Indonesia, Malaysia, Singapore, Thailand, Brunei, and Australia. Smoke aggravated or caused lung and other health problems. Factories and schools closed. Shipping was disrupted. Airports closed and tourism was hard hit. Crop yields fell as a perpetual twilight haze settled over the region, a major example of global dimming. The damage was calculated at \$6 billion, quite aside from long-term environmental and health damage, and the displacement of the forests' indigenous peoples and animals. Despite the world's appalled reaction to these fires, they have been set again repeatedly. In 2006, fire impact on Indonesia and Southeast Asia was more severe than seen since 1997. Environmental ministers from affected countries have been unable to develop a strategy to attack this ongoing catastrophe. An Indonesian stated that "It is affecting the people and the economy of Indonesia much more than the other countries . . . It's a . . . shared responsibility." Non-governmental organizations have called for naming those responsible with the hope of shaming them, and also prosecuting them. They stated "There needs to be a concrete plan and political will."³⁶ Mammoth fires occur elsewhere on the globe too, often in the Amazon rain forests.

Investigating observations

The ability to observe carbon monoxide, smoke, and dust from space is impressive. However, it sometimes takes major efforts to trace traveling pollutant clouds, their origins, routes of travel, and environmental impacts. ▪ One problem was to trace the origin of pollutants, especially NO_x which lead to smog in the New England States. Much was traced back to the US Midwest where there is a concentration of coal-burning power plants. ▪ Another question was: can the precursors of acid deposition arising in the Eastern United States cross the Atlantic Ocean to reach Western Europe? Yes, but whether amounts

³⁶ Khoo, H. C. Civic groups call for name and shame on Asia's haze. *Reuters News Service, Singapore*, October 20, 2006, <http://www.reliefweb.int/rw/RWB.NSF/db900SID/YAOI-6UR5BZ?OpenDocument>.

transported significantly increase acid deposition in Europe is less clear. ■ Or, what is the origin of the springtime haze seen in the Arctic? This haze of metals and other particulates covers an area equivalent to 9% of the Earth's surface. It was tentatively attributed to industrial emissions in Europe, Asia, and North America. However, a recent tracking down of the haze's origin indicates that much is from forest and agricultural fires in Siberia and Kazakhstan.³⁷ ■ Struggling to understand the journeys of wind-borne pollutants, researchers ask increasingly complex questions. International teams work from aircraft, ships, ground-based stations, and satellites. Using sophisticated instruments, scientists follow pollution over Asia, Africa, Europe, North and South America, Australia, and Antarctica. The data gathered allows them to piece together pictures of how pollutants move with the wind. The final destination of a traveling pollutant varies with seasonal storm conditions, and with the winds prevailing at different times of the year.

Mammoth quantities of PM

Giant dust storms

Billions of tons of dust move through the atmosphere every year. ■ One example of momentous dust storms are the great yellow clouds – observable from space – created by giant dust storms (sand storms) in Mongolia's and China's expanding Gobi Desert. Tracing this dust over thousands of miles, it was seen being borne across the Pacific Ocean into the United States. There, after crossing San Francisco on the western coast, it moves east to Colorado. After one large Gobi storm in 2001, the dust reaching Boulder Colorado reduced sunlight over the city by about 25% before moving onward further east. This dramatic effect occurred although the dust, by the time it reached Boulder had been traveling over a week spreading out and being diluted as it went. See Box 5.8. ■ Transboundary dust pollution can become routine. The US EPA reports that, on some days a quarter of the PM above Los Angeles can be traced to China, a figure that it is believed could increase to a third.³⁸

Transporting disease Think about dust originating in the Sahara and Sahel regions of North African deserts. This dust can be blown across the Atlantic to the Caribbean Islands and to Florida. On some Miami summer days, the dust contributes upwards of $100 \mu\text{g}/\text{m}^3$ of PM. Now, consider that the US EPA standard for PM_{10} is $50 \mu\text{g}/\text{m}^3$ over a 24-hour period (or 150 maximum for any single hour). Policy makers have noticed this pollution from afar, and are gathering data that may be useful in the future when setting air standards. ■ These traveling dust storms carry bacteria and fungi, some infectious. It is possible to culture, pathogenic bacteria, viruses, and fungi collected in the Caribbean that originate in Africa. Much larger numbers of infectious agents are found on days when much dust blows in from Africa than on days bringing little dust. Coral researchers were able to link a fungus blown in from Africa to a major disease of the Caribbean Sea Fan. ■ Fungal spores, transported from

³⁷ Perkins, S. Plumes of Arctic haze traced to Russia, Kazakhstan. *Science News* **175**(96), March 14, 2009, http://www.sciencenews.org/view/generic/id/40872/title/Plumes_of_arctic_haze_traced_to_Russia_Kazakhstan.

³⁸ Yardley, J. China's next big boom could be the foul air. *New York Times*, October 30, 2005, http://www.nytimes.com/2005/10/30/weekinreview/30yardley.html?_r=1&oref=slogin

Box 5.8

Pollution up close

Disastrous fires and great dust storms seen from space are described as “gigantic yellow blobs.” However, living in the midst of a storm is different than observing it from afar. Figure 5.7 shows the view on a Chinese street one morning in April 2002. Photographer Zev Levin said this dust, which arose from a Mongolian Gobi Desert storm restricted visibility to half a block.³⁹

The storms from China have major impacts in Seoul, Korea, 750 miles (1207 km) from the origin of the sand/dust storms.⁴⁰ Author Howard French commented, “It hid Seoul from view throughout the morning, obscuring the sunrise just as surely as the heaviest of fogs. Clinics overflowed with patients complaining of breathing problems, drugstores experienced a run on cough medicines and face masks that supposedly filter the air. Parks and outdoor malls were nearly empty of pedestrians.” Major economic impacts also result – flight cancellations and worker absenteeism. Manufacturing activities can be interrupted – the semiconductor industry greatly depends on clean conditions. The “season of yellow dust” has come regularly to Korea in recent years. Author French notes that they are “a disturbing reminder for Asians of global interconnectedness and the perils of environmental degradation.” In Seoul the usual level of particulate matter is $70 \mu\text{g}/\text{m}^3$. Korean health officials consider that a level of $1000 \mu\text{g}/\text{m}^3$ poses serious health threats. However, a recent dust storm from China raised it to $2070 \mu\text{g}/\text{m}^3$. The dust also carries arsenic, cadmium, and lead. Even further-away Japan is increasingly affected. China has acknowledged the problem and is meeting with Japanese and South Korean officials to discuss prevention.

In China itself the problems are greater.⁴¹ The storms originate in the country’s rapidly expanding Gobi desert. From there, the dust blows across the West Sea and reaches South Korea and Japan. Prolonged drought is responsible for part of the Gobi desertification. But the Chinese Forestry Administration blames about two-thirds of the 1 million miles² (2.6 million km²) desertification on poor agricultural practices and deforestation. According to China’s estimates, more than a quarter of its land area has become desert. The desert, which continues to expand, is now only about 150 miles (240 km) from the capitol Beijing. China’s State Environmental Protection Administration says 90% of China’s usable natural grasslands suffer from varying degrees of degradation. Quite aside from affecting human health and quality of life, desertification affects food production. With its population of 1.3 billion, many believe that China will soon need to import increasing quantities of grain.

Desertification⁴² The Xinhua News Agency says that China has completed the first 5 years of a process to build another Great Wall – a green wall of trees and grasses skirting 2800 miles (4500 km) around the 350 000 km² (135 000 mi²) Taklimakan desert, an area of almost 500 000 km² (193 000 mi²). A Forestry official said this “gigantic project will alleviate damage

³⁹ For a number of dust-storm views, see Ostapuk, P. Asian (and other) dust storms. *Paul Ostapuk*, 2001, <http://www.lakepowell.net/asiandust.htm>.

⁴⁰ Brown, L. R. *The Earth Policy Reader (Part I Deserts invading China)*. New York: W. W. Norton & Co., 2002, http://www.earth-policy.org/Books/Epr/Epr1_ss1.htm.

⁴¹ Lyn, T. E. In Inner Mongolia, steppes are turning to sand. *Reuters News Service, China*. July 9, 2007 <http://uk.reuters.com/article/lifestyleMolt/idUKT3183820071008>.

⁴² Ellis, L. Desertification and environmental health trends in china. Woodrow Wilson International Center, China Environmental Forum. April 2, 2007, http://www.wilsoncenter.org/index.cfm?fuseaction=topics.item&news_id=231756&topic_id=1421.



Figure 5.7 Chinese street during a dust storm (view from a hotel room). Credit: Dr. Zev Levin, Tel Aviv University

from sandstorms to China, slow down the pace of global desertification, reduce the amount of floating dust and accumulate experience for desert control in China and worldwide.” They project that the buffer zone will reduce wind speeds as much as 50% and cut sand and dust as much as 99%. The desert encirclement will take 10 years. Longer-range plans may take 70 years. A side effect will be the necessity of moving 180 000 people now living in the area near Beijing. The government also will impose strict logging bans in the Yellow and Yangtze River watersheds. Local governments not complying with the new rules will lose government funding.

Cameroon in West Africa into the Caribbean’s Dominican Republic “almost certainly” caused rust disease in sugarcane, devastating that industry for a time. Two European researchers note, “plant quarantine has restricted the movement of many pathogens, but it has not halted those that cause such destructive diseases.”⁴³

Dust storms are intensifying

Dust and sand storms have existed since time immemorial, as has their transport by winds over thousands of miles. But human actions have aggravated the growth of dry lands and deserts, and thus the number and intensity of storms. Those in northeast Asia originate in northern China and Mongolia and blow across China, the Korean Peninsula and Japan. An early record of a Chinese dust storm is from the year 1550: “The tiles on the house roof, grass on the fields and leaves on the trees were entirely covered by yellow and white dusts; when the dust was swept, it wiped away like dirt.” Currently, they may be blowing through China, South Korea, and Japan five times more frequently than 50 years ago, and their intensity has

⁴³ Brown, J. K. M. and Hovmöller, M. S. Review: aerial dispersal of pathogens on the global and continental scales and its impact on plant disease. *Science*, **297**(5581), July 26, 2002, 537–541.

also increased.⁴⁴ Japan is concerned about these dust storms from China and has started to aid China in monitoring to monitor this “yellow sand.”⁴⁵

Expanding deserts⁴⁶

The world’s expanding deserts (desertification) represent a major and urgent environmental issue. To varying extents, desertification already impacts nearly over 40% of the Earth’s land area and 1 billion people. There is concern that the number of affected people may double, leading to increasing poverty and food insecurity.

Causes of desertification

Desertification can be natural as when it results from a long-lasting drought. However, growing human populations increasingly stress the world’s dry lands by land misuse including poor irrigation practices, livestock overgrazing, over-cultivation of soils, and deforestation. Desertification is most pronounced in Africa where 65% of the agricultural land may be degraded. It is an increasing problem in Latin America and Asia. In Mexico, 85% of the land is threatened by desertification, a situation that may contribute to the immigration of nearly 1 million Mexicans a year to the United States as people move off land that is becoming unusable. There is major concern that desertification will become an increasing security threat.⁴⁷

Dried up water bodies

One obvious cause of increasing dry and desert lands is loss of water bodies. ▪ North Africa’s Lake Chad was once as large as Lake Erie in North America, but 50 years of drought combined with over-pumping of lake water for irrigation has reduced the lake’s size to 5% of its 1960 size. The lake’s now dry bed is “pumping dust everywhere, all year long, almost every day.” It is blown, depending on the season, to Europe, the United States and elsewhere. ▪ The Aral Sea was the world’s fourth largest water body until the Soviets diverted its waters for farm irrigation. Now a huge portion of the lakebed is exposed to the

⁴⁴ Kim, J. Asian sandstorms intensifying, response far off. *Reuters News Service*. April 1, 2004, <http://www.planetark.com/avantgo/dailynewsstory.cfm?newsid=24531>.

⁴⁵ Japan gave China 5.12 million euros to set up this monitoring system, which also monitors acid rain at 50 locations around China. Japan also promotes the Acid Deposition Monitoring Network in East Asia, which collects data to use in combating air pollution and acid rain.

⁴⁶ Desertification is a process that occurs when land has been over-cropped, over-grazed, improperly irrigated, or deforested. As the land degrades, the soil becomes increasingly unproductive, and vegetation thins or disappears. The rate of desertification in the world is speeding up. Africa is the worst affected continent; two thirds of its land is either desert or dry lands. The US is also affected – almost a third of its land is affected by desertification. In Latin America and the Caribbean the proportion is one quarter and, in Spain, one fifth.

⁴⁷ See Doyle, A. Desertification threat to global stability: UN study. *Reuters News Service*. June 28, 2007, <http://www.planetark.org/dailynewsstory.cfm/newsid/42845/story.htm>.

wind. ■ In the State of California, Owens Lake, a hundred years ago, was the size of the Sea of Galilee. Then, its waters were diverted to Los Angeles for use there. Owens Lake dried up exposing thousands of hectares of salty silt, now “the biggest single dust source in the United States.”

Reducing desertification

Halting desertification is not impossible. It does require major effort and money to set up and maintain anti-desertification programs. Such efforts integrate the best of traditional agricultural practices including terracing and water harvesting. They also include very modern techniques, such as satellite imagery to follow how effectively programs are working. Genetic engineering of animals and crops better able to live in these arid areas may also play an important role. When desertification has been caused naturally, by a long drought, it may be reversed by normal rainfall over a period of time.

SECTION V

Air pollution in less-developed countries

The World Bank reports⁴⁸ that urban air pollution is a leading cause of premature deaths in South Asian cities. The World Health Organization (WHO) attributes 3 million deaths a year to outdoor air pollution. This figure is expected to worsen unless major efforts are taken to reduce emissions. ■ Cities with worsening pollution are largely found in poor countries. Twelve of the world’s most polluted cities are in Asia. Breathing the air in New Delhi is estimated to be equivalent to smoking two packs of cigarettes a day. Coal burning is the major source of air pollution in some less-developed countries, but more and more motor vehicles increasingly aggravate the problem.

What are the impacts on children?

Many millions of children in less-developed countries suffer exposure to gross air pollution. In a 1999 publication, Drs. Devra Davis and Paulo Saldiva reported⁴⁹ that children in 200 cities are exposed to PM, nitrogen dioxide, and sulfur dioxide at levels 2–8 times greater than the *maximum* that the WHO considers acceptable. This gross pollution impairs the respiratory system and lowers resistance to infection. About 80% of all infections induced

⁴⁸ Kogima, M. and Lovei, M. Coordinating Transport, Environment, and Energy Policies for Urban Air Quality Management. *World Bank Perspectives*, 2001, <http://www.giteweb.org/csd/masami.pdf>.

⁴⁹ Davis, D. L. and Saldiva, P. *Urban Air Pollution Risks to Children: A Global Environmental Health Indicator*. Washington, DC: World Resources Institute, 1999.

by pollution in these countries occur in children under 5 years old. Reasons for young children's susceptibility were discussed in Chapter 3. Air pollution is also responsible for at least 50 million cases of chronic cough in children under age 14 in less-developed countries. Children at highest risk live in the megacities of Mexico, India, China, Brazil, and Iran,⁵⁰ but smaller cities can be highly polluted too. ■ Children in more-developed countries also sometimes suffer exposure to high pollutant levels. Indeed, some of the highest nitrogen dioxide levels in the world are found in New York, Paris, Tokyo, and Los Angeles. Moreover, the WHO determined that PM_{2.5} pollution causes 7–10% of respiratory infections in European children, and as many as 21% in the most-polluted European cities.

Brown Asian hazes^{51,52}

During January to March each year, an Asian atmospheric brown cloud (ABC) overlies much of the Indian Ocean and the land areas of South Asia, an area equivalent to the size of the continental United States. About 75% of the aerosols in the haze are of human origin: burning biofuels (wood, dung, and agricultural wastes) and forest fires. Burning fossil fuels in motor vehicles and other petroleum-based combustion sources also contribute. ■ The haze is darker than usually seen in Western countries because incomplete combustion of biofuels yields more black carbon (soot). The haze also contains fly ash, sulfates, nitrates, mineral dust, and gases such as carbon monoxide. The aerosol hazes most common in western countries are whitish due to a predominance of sulfate and nitrate aerosols; these reflect sunlight and cool the atmosphere. Conversely, a sooty aerosol absorbs sunlight and warms the atmosphere, and may contribute significantly to global warming. At the same time it results in surface cooling.⁵³ ■ Also, because the haze absorbs sunlight it reduces sunlight reaching the ocean and agricultural fields, and alters rainfall. This would reduce photosynthesis by ocean plankton and by plants such as rice on land. Some other scientists don't believe the relationship is straightforward, and the brown haze continues as an active area of investigation.

Air pollution in Calcutta

A six year study by a respected Indian cancer institute concluded that 70% of the inhabitants in Calcutta, a city of 18 million suffer from respiratory disorders such as asthma caused by air pollution.⁵⁴ They reported a strong correlation between high air pollution and lung cancer incidence: Calcutta has the highest lung-cancer rate of any Indian city (18.4 cases per 100 000 people). Its choking air pollution is largely attributed to

⁵⁰ A city with a population of 10 million or more is designated a megacity.

⁵¹ Atmospheric brown cloud (quick facts; brown haze composition; cause; effects) *Asia Development Bank*, 2009, <http://www.adb.org/vehicle-emissions/General/Environment-cloud.asp>.

⁵² Casey, M. Pollution Haze over the Indian Ocean Contributes to the Melting of Glaciers. Associated Press, August 2, 2007, http://www.irrawaddy.org/article.php?art_id=8085.

⁵³ Gustafsson, O. *et al.* Brown Clouds over South Asia: biomass or fossil fuel combustion? *Science* **323**(5913) January 23, 2009, 495–498.

⁵⁴ Bhaumik, S. Air pollution suffocates Calcutta. *BBC News*, http://news.bbc.co.uk/2/hi/south_asia/6614561.stm.

motor vehicle emissions of which the worst offenders are the 50 000 auto rickshaws that use a fuel made out of kerosene and gasoline. ▪ The government seems incapable of reducing emissions. A previous deadline ordered all vehicles manufactured before 1990 to be taken off the roads or else converted to burn propane, a clean fuel. However, removing polluting vehicles would have eliminated most of the city's transportation, buses and trucks, and also taxis and auto-rickshaws. Indeed, only about 20% of the city's registered vehicles have reported for emission tests. Calcutta is far from alone in suffering from grossly polluted air. The WHO reports that air pollution in major Southeast Asian and Chinese cities contributes to 500 000 deaths a year.

Air pollution in Shenzhen, China – what is the true cost of products imported from China?

Researchers from several universities studied what proportion of major air pollutants in the PRD region on China's south coast were attributable to the goods manufactured there for export to North America, Europe, and other parts of Asia.⁵⁵ Their careful study examined the manufacturing facilities themselves, and also power plants generating electricity for them, trucks transporting raw materials to and finished goods away from facilities, and ports and ships. In one city of 11 million, Shenzhen, they found that 89% of the sulfur dioxide, 91% of the nitrogen oxides, 71% of PM and 75% of VOCs emitted by the industrial sector were due to manufacturing goods for export. Other areas had smaller, but still significant percentages. ▪ The products produced are inexpensive and one reason is that factories use few environmental controls. As one study author stated, "we get the benefits of the cheap goods, and they absorb the air pollution." Researchers examined pollution-control technologies that could limit emissions, and found air quality could be improved 5–30% depending on the controls used at a cost of only 0.3–3.0% of the value of the goods produced. A spokesperson for Environmental Defense, an advocacy group noted that this study illustrates "how the global economy links all of us in terms of environmental impacts."

How can air pollution be lessened?

Reducing gross pollution in less-developed countries is a daunting task. However, small steps taken incrementally and consistently can make a difference.

- Mexico City⁵⁶, like Calcutta, has at least 18 million residents. But by 2006, an activist was able to note "We are still among the 10 most-polluted cities in the world, but . . . better than New Delhi or Bangkok. We used to be in first place." In the past two decades, the city has very slowly improved its air. It ridded the city of older inefficiently operating

⁵⁵ Christen, K. Linking China's air pollution to exports. *Environmental Science & Technology*. **40**(7), April 1, 2006, 2073–2074.

⁵⁶ Bradley, T. Once world's smoggiest, Mexico City cuts pollution. *Forecast Earth*, December 30, 2008, <http://climate.weather.com/articles/mexicocity122901.html>.

cars, made only unleaded gas available, and required motor vehicles to have catalytic converters. Now, the city is setting up lanes dedicated to buses only. And Mexico passed a law to half the level of sulfur dioxide and PM that cars could emit. Also helping Mexico City was a World Bank investment of \$1.1 billion to promote clean energy and transportation. Public outrage is also given credit: beyond just public health personnel speaking about unhealthy air, “The interesting thing was the public alarm.” And, Mexico’s gradual democratization made public outrage something that was allowed which, albeit sluggishly, gets a response.

- Beijing⁵⁷: temporary or permanent improvement? Beijing, the 2008 host of the Summer Olympics made major efforts to improve its air quality, which was among the worst in the world. It moved polluting factories away from the city or closed them. Coal-burning facilities converted to natural gas. Laws regulating car emissions became the tightest in China. New clean taxis replaced older vehicles. Subway lines were expanded to lessen the need for autos. Millions of trees were planted. However, the question is: how well will these improvements hold as the city moves further from the Olympics, especially as the city uses more and more cars and construction continues unabated?
- Cities with two-stroke vehicles. The World Bank points out that two-stroke engines are commonly used in less-developed countries. These emit large quantities of PM_{2.5}. Because totally banning two-stroke vehicles is not practical, the Bank suggests strategies to get drivers to maintain vehicles better to reduce emissions, which also saves drivers money. The Bank urges governments to adopt policies pushing a switch to less-polluting four-stroke engines
- Citizen activists. Many believe that the problem of severe air pollution is too great to leave to the government. An active citizenry needs to promote environmental stewardship.
 - India is reported to have a quarter-million citizens’ organization and grassroots movements working on environmental and other issues.
 - Likewise, citizens in other countries increasingly involve themselves in environmental action—note Mexico City above.
 - However, in countries with corrupt governments, citizens’ actions place them in danger of retaliation.

Reducing pollution in Eastern Europe

Outside motivation sometimes stimulates environmental cleanup. Many Eastern European countries wanted to join the European Union (EU). To do so, they needed environmental laws equivalent to existing EU countries. The “Black Triangle” is a region overlapping the borders of Poland, the Czech Republic, and Germany, which gained its name from notorious air pollution. These countries began reducing emissions in various ways including shutting down many old factories and power plants. Between 1989 and 1999 sulfur dioxide emissions decreased 92%, nitrogen oxide emissions 80%, and total particulates 96%. This happened at the same time that road traffic greatly increased. The region now has air quality comparable to the rest of the EU.

⁵⁷ Stone, R. China’s environmental challenges: Beijing’s marathon run to clean foul air nears finish line. *Science*, 321(5889) August 1, 2008, 636–637.

Transboundary pollution: “air pollution knows no borders”

Asian pollutants don’t stop at the American West coast. As first seen in 2004, they can proceed much further. Dark, sooty clouds, containing ozone and fine particles, were discovered far above Portsmouth, New Hampshire, and other cities on the East coast by teams of scientists, working aboard a dozen aircraft.⁵⁸ Working as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) the scientists collected air samples through probes inserted through airplane windows. The pollutants studied were traveling too high to impact ground-level air quality although air mixing could happen under some circumstances or pollutants could impact climate if their levels continue to increase. Scientists further tracked the pollutants across the Atlantic Ocean to Europe. This study was examining Asian pollution. However, future results may find that North American-produced pollution may reach and impact European countries. One environmentalist noted that, “I think the most profound thing that you draw from this [study] is that the globe is one air shed.”

Reducing transboundary pollution: past and current efforts

Transboundary pollution travels by air and water beyond borders drawn by humans. International treaties and agreements *partially* control such transboundary air pollution.

- Canada and the United States have agreements on a number of shared pollutants. One limits the movement of acid rain pollutants between the two countries.
- Many other treaties have been developed under the aegis of the United Nations Environmental Program (UNEP). As part of the Convention on Long-Range Transboundary Air Pollution, European countries adopted a Protocol in 1999 leading to major emission cuts for sulfur dioxide, nitrogen oxides, VOCs, and ammonia.
- Countries in the European Union have strict emission standards.

Additional countries joining the EU must meet the same standards – this increases the area within which pollutants are well controlled.

- Many other nations are also party to environmental treaties. In recent years, the POPs treaty banned or severely limited 12 persistent, bioaccumulative and toxic organic pollutants. Others well-known international agreements include the Montreal Protocol on substances responsible for depleting the ozone layer, and the Kyoto Protocol to reduce greenhouse gases. Some treaties provide technical assistance and money to poor countries to enable them to live up to the agreements.
- As time passes, the international community deals with increasingly complex issues. Think about the implications of the major dust and sand storms or of the particulates resulting from the mammoth Indonesian forest fires, which affect many countries.

⁵⁸ Ebbert, S. Asian grit aloft in New England, Pollutants found to travel globally. *Boston Globe*. 9 August, 2004, http://www.boston.com/news/local/new_hampshire/articles/2004/08/09/asian_grit_aloft_in_new_england/.

Future efforts

The ICARTT scientists, noted above, commented that pollution moving inter-continentially may lead to a need for more international agreements to control pollutants at their source.⁵⁹ At some future point, say if American air quality is threatened by pollution from Asia, it may be cheaper to help the less-developed countries producing it to control their emissions than it would be accentuate efforts being made in the United States.

Questions 5.4

- 1 Future policy makers in one country may need to confront problems that go beyond their own borders. One possible instance: they may need to set ambient air standards specific to different locales in their country – depending on how much pollution from other countries those locales receive – rather than using one nationwide standard. (a) How can countries respond if pollution at distant sites continues to worsen? (b) What responsibility does an impoverished nation have to control pollution originating within its borders? (c) What responsibility do wealthy nations have to assist them?

Delving deeper

1. The world's response to desertification "must be equal to that demanded by global warming, the destruction of the ozone layer, and the loss of biodiversity." So said Klaus Toepfer, former Director of UNEP. Do you believe that China's efforts to set up a tree wall to combat desertification are likely to be successful? Why? Explore web resources as to what else is being done around the world to halt or slow desertification.
2. Consider products manufactured for export in China in facilities with poor pollution controls. What can we, as individuals, do about this? What should our government be doing? What should the local and national governments in China be doing?
3. Do you believe that we could lower our consumption while still maintaining what you personally would consider good living standards? How would you go about doing this?

Further reading

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⁵⁹ Swart, L. and Perry, E. *Global Environmental Governance: Perspectives on the Current Debate*. New York: Center for UN Reform Education, 2007, <http://www.centerforunreform.org/node/251>.

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“A thing is right when it tends to preserve the integrity, stability, and beauty of the biotic community. It is wrong when it tends otherwise.”

Aldo Leopold

Chemical fate and transport is a concept now familiar to you, how chemicals move in the environment and change into other chemicals. You have seen pollutants that travel hundreds or thousands of miles and those that end up in unexpected places. Now, follow the story of acid deposition (acid rain). The precursors of acid rain are gases, sulfur dioxide and nitrogen oxides. But these gases are converted into particles and aerosols and particles, and it is these that actually deposit onto, and acidify, soil and water. And that is not the end of their journey.

In this chapter, Section I identifies the major acid precursors that lead to acid deposition, and overviews a major study carried out in the United States, and still ongoing to better understand acid deposition. Section II examines the adverse effects of acid deposition on aquatic life, and on forests and their soils. Section III looks at the emission sources of acid-forming pollutants, and reducing those emissions. It points out that emissions, although lowered are not eliminated; thus, consequences linger. Section IV examines the partial recovery of systems as emissions are reduced. Section V moves on to acid deposition in the international scene.

SECTION I

Acid pollutants¹

Sulfur dioxide (SO₂) and nitrogen oxides (NO_x) are the major precursors of acid deposition. After emission, these gases react with oxygen² in the atmosphere to form acid chemicals – review Figures 5.3 and 5.4.³ If moisture is present, SO₂ and NO_x convert to sulfuric and nitric acids, aerosols, which deposit with rain, snow, and fog. Sometimes acidic fog directly contacts – and damages – trees growing at high elevations or in coastal

¹ Acid rain and the facts. *Environment Canada*, March 29, 2005, <http://www.ec.gc.ca/acidrain/acidfact.html>.

² The reaction also includes “oxidants” such as the very reactive hydroxyl radicals, so more than oxygen is involved.

³ These are simplifications. Nitrogen and sulfur oxides are undergoing many reactions in the atmosphere.

Box 6.1

Atmospheric deposition

Atmospheric deposition goes beyond the deposition of acid pollutants. It is a phenomenon in which airborne chemicals or particles – be they acids, metals, organic chemicals, microbes, or pollens – deposit from air onto land and water. Acids are among many pollutants deposited. Rain can wash them out of the atmosphere. Dry particulates can settle out on their own. Consider an example not involving acid: there is no record that DDT or PCBs were used in the forests of New Hampshire, but both are found in soils there, presumably airborne from other locations. Supporting this interpretation is the fact that their concentrations are higher at higher elevations than lower, especially on slopes facing prevailing winds. The levels of DDT and PCBs found do not appear to threaten forest health. Unfortunately, in other cases, as is often true with acid deposition, damaging quantities of air pollutants can be deposited.

regions. ▪ In dry conditions, SO_2 and NO_x are converted to tiny solid particles of sulfate salts and nitrate salts, which slowly settle out by gravity. About half of acid deposition is dry. Dry deposition is more likely near emission sources. ▪ Other chemicals contribute to acid deposition too although in much lower amounts. In particular, carbon dioxide in a moist atmosphere is converted to carbonic acid (H_2CO_3). Small amounts of organic acids such as formic and acetic acids are often present in the atmosphere too, emitted by natural processes and industrial activity. But sulfur and nitrogen aerosols present the major problem.

Background⁴

Acid deposition was first described in 1852. In the first half of the twentieth century, severe damage to trees and vegetation was seen near smelters,⁵ which often emit large quantities of SO_2 . SO_2 emissions from electric power plants also sometimes damaged local vegetation and water. It was not until the late 1950s that the existence of acidic lakes in North America and Europe was established. And it took nearly another two decades to recognize acid's impact on fish. ▪To protect local communities, the 1970 US Clean Air Act required power plants and smelters to build emission stacks 1000 feet (305 m) above ground level. The expectation was that pollutants released at this height would become so diluted in the atmosphere that they could cause no harm. After high stacks were built, local damage did abate. However, a different problem began to emerge: stack emissions of SO_2 and NO_x are carried long distances by the wind. As they travel, these gases are converted to acid aerosols in the atmosphere; the wet aerosols rain out, and the dry aerosols settle out by gravity onto

⁴ Acid rain, atmospheric deposition and precipitation chemistry. *USGS*, National Atmospheric Deposition Program (no date), <http://bqs.usgs.gov/acidrain/>.

⁵ A smelter is a facility that melts or fuses ores that contain metals in order to separate out the metals contained in the ores. Metal ores are often rich in sulfur.

Box 6.2

Basic chemicals in atmosphere and soil

Atmosphere

In addition to acid chemicals in the atmosphere, there are also alkaline ones, *base cations*. The base cation present in the largest amount is *ammonium*, NH_4^+ ⁶. Major sources of ammonia, NH_3 are agricultural. Ammonia has a sharp pungent smell that you would probably recognize. Over the years as livestock operations have increased in size and concentration, there have been increasing emissions of NH_3 from both solid and liquid waste. Ammonia reacts with moisture to form NH_4^+ . The nitrogen from fertilizer is a significant, but smaller source of NH_4^+ . Motor vehicles are a source too. NH_4^+ is a base, which reacts with acid chemicals (acid anions) in the atmosphere: it neutralizes a portion of the acid with the result that the deposition is less acid. Another characteristic of NH_4^+ is that it is bioavailable to plant life and is a nutrient to plants and trees. *However*, remember that the dose makes the poison: if too much NH_4 falls, there will be too much bioavailable nitrogen, which can lead to decidedly harmful effects. The deposition of nitric acid/nitrate is also a source of bioavailable nitrogen. Problems associated with too much bioavailable nitrogen will be discussed in Chapter 9.

Soil

Base cations are naturally present in soil too. The most important are calcium (Ca) and magnesium (Mg), which are also important plant and tree nutrients. Depending on the concentration of Ca^{++} and Mg^{++} cations in the soil, part or all of the falling acid can be neutralized. This, to varying extents, prevents soil acidification. But remember that if acid deposition continues, more and more of these important base cations are neutralized. A weakly alkaline soil may have all its base cations neutralized. Equally problematic is the fact that Ca and Mg were mostly bound in soil before the acid reacted with them. The acid can solubilize them, allowing them to be washed away in rainfall into local water bodies. And because Ca and Mg are nutrients, the soil becomes less hospitable to the trees growing within it. Another problem is that acid solubilizes aluminum (Al) from soil; as the levels of Al increase, they can exert toxic effects on the trees; washed off into water bodies, Al can be toxic to aquatic life.

land, water, and onto human-made structures. Earth and water serve as sinks for these acid pollutants. Compared to concentrations at points of emission, these pollutants *are* greatly diluted. Moreover, some soils are alkaline enough to continue to neutralize acid deposition over long periods. (See Box 6.2.) However, an acidic soil cannot buffer acid, and a weakly alkaline soil buffers does so only to a limited extent. Thus, with continued acid deposition soils acidify. Once on land, acidic chemicals are also carried off by rainfall into nearby streams and lakes. Acid pollutants are stored in winter snow; in spring as the snow melts, the acids soak into soil or run off into water bodies. Acid also falls directly into water bodies.

⁶ NH_4 is actually NH_4^{+2} , which forms from the reaction of NH_3 with water. The NH_4^{+2} cation can associate with the anions, SO_4^{-2} and NO_3^{-2} .

Table 6.1 Effect of low pH on life in water: read in association with Figure 6.1

pH	Effect on life in water
6	Snails and crayfish begin to die
5	Fish eggs do not hatch. Some fish die
7	Seven is a neutral pH
4.5–5	Fish species such as bass and trout begin to die
4	May flies and frogs begin to die

Box 6.3**pH**

The term “pH” refers to how acid or how alkaline (basic) a solution is. Water with a pH of 7 is neutral. As pH increases above 7, a solution is increasingly alkaline. As pH decreases below 7, it is increasingly acid. The pH scale is logarithmic, so each pH unit represents a 10-fold difference in concentration: A pH of 5 is 10 times more acid than a pH of 6. A pH of 4 is 100 times more acid than pH 6. The only water that has a neutral pH is distilled water, or water that has undergone reverse osmosis; in these cases other chemicals have been removed leaving pure water.⁷

▪ Because of naturally occurring acids in the atmosphere, especially carbonic acid, the pH of rain is below 7. However, a pH of 5.6 or less often indicates the influence of human activities. Since 1965, much rain and snow in the northeastern United States has had a pH of 4.05–4.4, well below 5.6. Most of the United States east of the Mississippi River, including the southeast, experiences acid rain to varying degrees. In a few cases, rain has been measured with a pH as low as that of vinegar, about 3, and the even more acidic lemon juice. See Figure 6.1 and Table 6.1.

Runoff and direct deposition can lead to water acidic enough to harm or kill fish and other aquatic organisms. And, as first seen in Norway and Germany in the 1960s, forest growth may begin to decline and trees to die.

The US government spent a half-billion dollars in the 1980s on the National Acid Precipitation Assessment Program (NAPAP), a study carried out by teams of scientists throughout the country. NAPAP’s goal was to understand acid deposition and its effects. Many factors complicated their studies: ▪Rain does not have a normal pH because acidic and alkaline substances are naturally present in air and affect the pH of rain to varying degrees. Rain, in the eastern United States is often naturally acidic. ▪The pH of lakes and streams varies. Some are naturally acidic; so it is important to know the historical pH. ▪ Only a limited impact of acid deposition on forests was seen in the 1980s, but evidence of damage became clearer as the years passed (see below). ▪ In 1990, the US Congress, in its Clean Air Act Amendments mandated reductions in SO₂ and NO_x emissions, but only from fossil-fuel burning power plants. NAPAP periodically reports to Congress on how cuts in emissions from power plant are progressing, how well ecological systems are

⁷ Water properties: pH. USGS, November 7, 2008, <http://ga.water.usgs.gov/edu/phdiagram.html>.

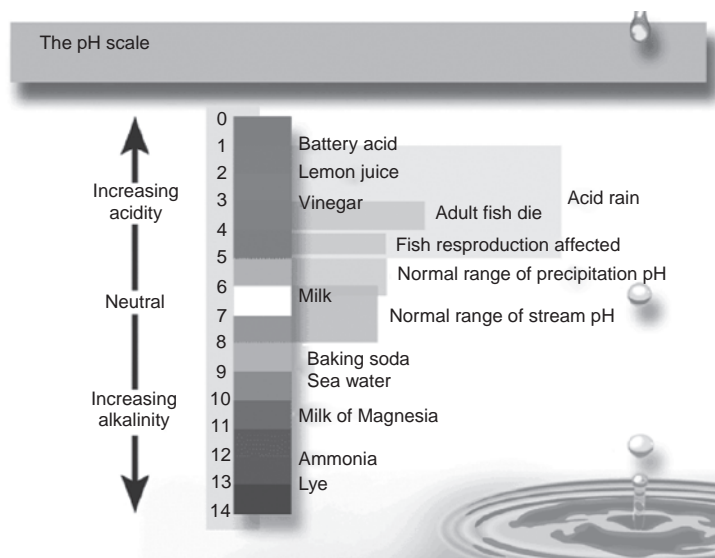


Figure 6.1

The pH of common substances and the pH of rain. Credit: USGS and Environment Canada

recovering, and projections on how further reductions would be useful. Its most recent report was in 2005.

SECTION II

What are the adverse impacts of acid deposition?

On water and aquatic life

In 1990 NAPAP reported that acid deposition had caused some US surface waters to acidify. Fish and other aquatic life including snails and crustaceans, had been adversely affected in 15% of New England's lakes. New York's Adirondack lakes suffered even more. More than 40% of its lakes were chronically or episodically acid; many had few or no fish. As a water body becomes progressively more acid individual fish may die, fish numbers decrease, and the number of fish species fall also (Figure 6.2). Surviving fish may be smaller and less able to cope. Fish are especially stressed if excess aluminum is also present. Too much Al results when acid solubilizes it from soil, freeing it to run off into water bodies. ■ In post-1990 studies, investigators looked at the number of fish species living in each of 1469 Adirondack lakes. No fish at all lived in 346 of the most acidic lakes; these lakes also had higher Al levels. In the other 1114 lakes, the lower the pH of the lake, the lower the number of species found. In Figure 6.2, the number of lakes at each pH range is shown by the "N" at the top of the column of fish.

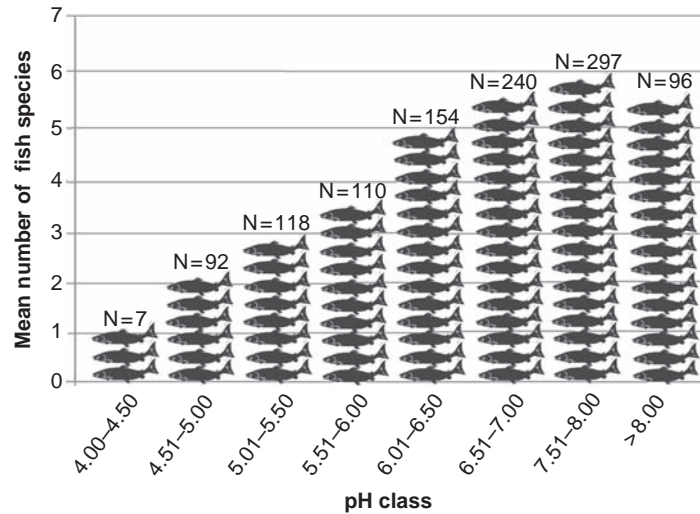


Figure 6.2

Number of fish species in each pH range. Credit: Reprinted courtesy of the Hubbard Brook Research Foundation

On forests and forest soil

Does acid deposition impact forests and their soils?

Forests suffer dieback and decline every 50–200 years, brought about by a combination of stresses and old age. During its 1980–1990 studies, NAPAP had difficulty assessing to what extent acid deposition was adversely affecting forests. This was because of other stresses on forests that included drought, temperature extremes in winter and summer, insufficient nutrients in soil, insect attacks, and fungal infections. In addition to such natural stresses, pollutants other than acid can have major impacts on forest health; ground-level ozone is a major example. In the 1980s, NAPAP researchers saw that red spruce trees growing at high elevations in the northeastern United States were in direct contact with acidic clouds or fog; these showed a reduced tolerance to winter cold. Researchers concluded this was the only clearly adverse effect of acid on forests. However, even at the time, some scientists objected saying that even if disease, not acid deposition was the apparent cause of death in some forests, acid deposition may have left trees vulnerable to disease. Moreover, analogous to the development of chronic diseases in humans, adverse impacts on trees of acid deposition may not show up for many years. And, meanwhile, the release of acid precursors although lessened, has continued and acid deposition continues.

Acid deposition does damage forests and soil

A 1996 *Science* article described serious damage due to acid deposition in the Hubbard Brook Experimental Forest in New Hampshire. Data had been collected on this forest for

more than 30 years, but was not examined until the mid 1990s. Analysis showed that the level of organically bound calcium – a nutrient – in forest soil was only half its 1960s level. Meanwhile, by 1987, this forest had stopped growing. Suspicion as to the cause centered on the lost Ca. Acid deposition can also deplete Mg from soil, another tree nutrient. Acid depletes Ca and Mg by solubilizing them from soil allowing them to wash away in rain or melting snow. As acid deposition continues, more Ca and Mg are lost. ▪ Worsening the problem, Ca and Mg are not just nutrients. As base cations (alkaline chemicals) they help neutralize the acid, so their loss means an even more acidic soil. Weathering of rock can replace Ca and Mg, but that takes many years. ▪ Recall that acid also solubilizes aluminum from soil and, at high levels Al interferes with uptake of Ca, Mg, and water by tree roots. Moreover, as Al runs off into and accumulates in water bodies, it can poison aquatic life. Soils in the northeastern United States are often acidic or poorly buffered (i.e., only weakly alkaline). Thus it was not surprising that it was in the northeast, specifically in the state of New Hampshire that the first ill effects of acid deposition were demonstrated. ▪ But more basic soils – those capable of neutralizing acid – can also acidify over time. Only recently have well-buffered soils such as some in the southeastern United States also become acid saturated, so that acid began to run off into lakes and streams there. Concurrently, fish began to decline there also.

Examine what can happen to trees as acid deposition continues to fall over time (Figure 6.3). Notice the loss of needles from the spruce and the loss of foliage from the sugar maple. These trees are also more readily damaged by cold weather. The H^+ shown in the “raindrop” is the acid hydrogen ion. As the soil becomes acid, Ca and Mg dissolve from

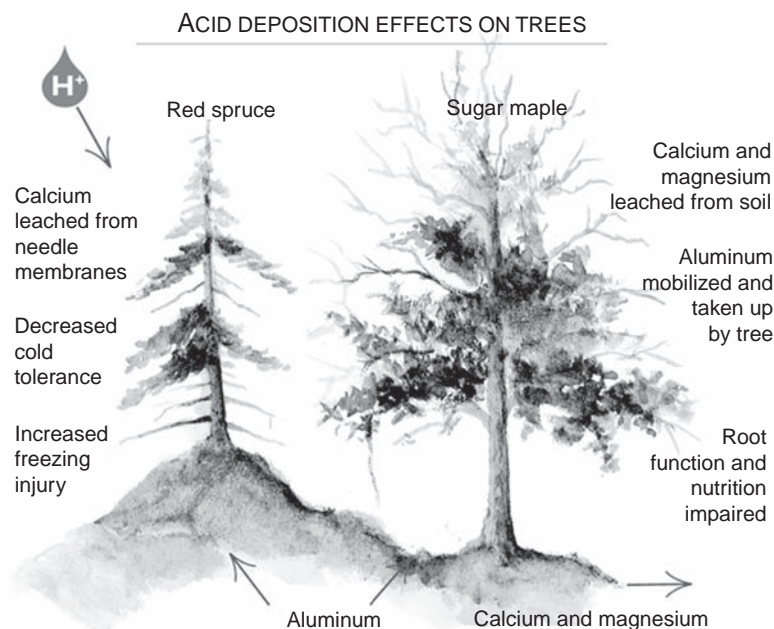


Figure 6.3

Effects of acid deposition on trees. Credit: Reprinted courtesy of Hubbard Brook Research Foundation

soil, and are lost to rain runoff (as indicated by the lower-right arrow). Also, not all the Al dissolved from soil runs off. That remaining, if its level is high enough, can inhibit the uptake of essential nutrients and water into the trees.

Other impacts of acid deposition

Acid deposition can strikingly increase the erosion rate of stone and metal structures. Some European monuments have been badly damaged, as have some stained glass windows and other cultural resources. ▪ Acid aerosols produce hazes that reduce visibility. ▪ Chapter 5 noted the health impacts on humans of acid aerosols.

SECTION III

What are the sources of acid precursors?⁸

Sources of SO₂ and NO_x are seen in Figure 6.4. Coal-burning electric power plants generate the majority of SO₂, about two-thirds, but only about a fifth of NO_x. The 1990 Clean Air Act Amendments mandated emissions reductions only from fossil fuel-burning power plants. For SO₂, that may be reasonable, but less so for NO_x. It is transportation, motor vehicles, that emit more than 50% of NO_x.

How can emissions of acid-precursors be reduced?

Sulfur dioxide

Sulfur dioxide emissions peaked in the United States at about 31 million tons (28.1 tonnes) in 1970. With increasingly strict controls mandated by the first Clean Air Act (1970), emissions fell and continued to do so. In 2005, SO₂ emissions from all sources in the United States, not just power plants, were 50% lower than in 1970. Expectations from the 1990 Clean Air Act Amendments were that emissions should fall to 15 million tons (13.6 million tonnes) in 2010; they met that goal by 2005. ▪ Power plants can cut SO₂ emissions in several ways. One is to burn coal with low sulfur content, a P² method. Another is to use effective technologies to capture the SO₂ formed. ▪ A different type of legislative tool, *emissions trading* (also called *cap and trade*), started after 1990, uses market incentives: an individual utility has a SO₂ emission allowance. If it emits less than its allowance, it can sell the unused portion to a utility emitting more than its allowance. Thus, a facility unable or unwilling to reduce its emissions for whatever reason buys emission rights from a

⁸ (1) Air emission sources, sulfur dioxide. *US EPA*, October 21, 2008, <http://www.epa.gov/air/emissions/so2.htm>

(2) Air emission sources, nitrogen oxides. *US EPA*, October 21, 2008, <http://www.epa.gov/air/emissions/nox.htm>.

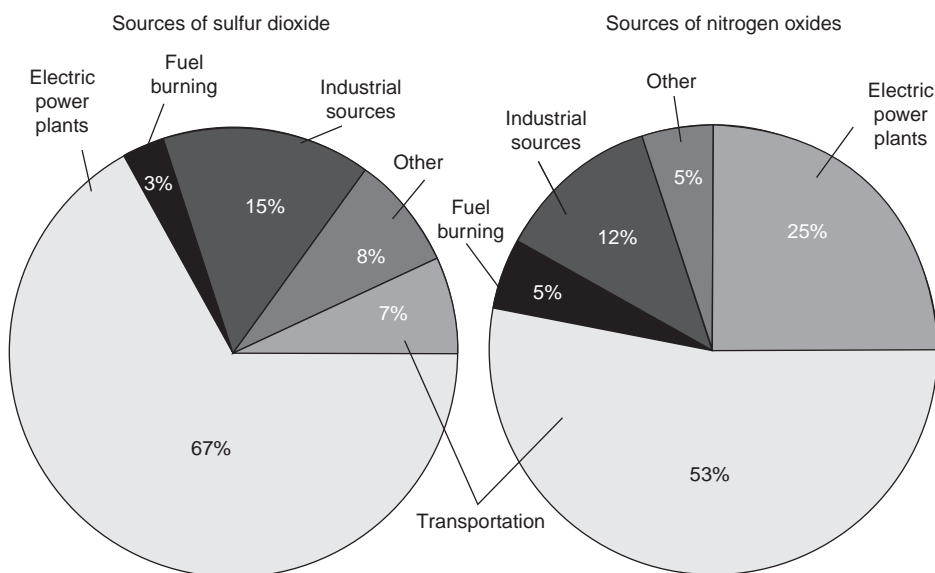


Figure 6.4

Sources of pollutants that form acid deposition

low-emissions facility. Facilities selling make money, those buying also believe it is to their financial advantage, and pollution is cut overall.

Nitrogen oxides⁹

Emissions of NO_x are harder to control than those of SO_2 . This is because most NO_x emissions result from a reaction between atmospheric oxygen and nitrogen at high temperatures.¹⁰ This is frustrating because high temperatures are otherwise desirable to increase the efficiency of combustion. Meanwhile, it is the US motor vehicle fleet that emits the highest percentage of NO_x , not power plants. Unfortunately, the US Congress has done little to increase the fuel efficiency of the nation's car fleet although it began to slowly do so late in the years of the first decade of the twenty-first century. Still NO_x has been lowered: in 2005, NO_x emissions in the United States were 30% lower than in 1970.¹¹

⁹ NO_x : what is it? where does it come from? US EPA, April 8, 2008, <http://www.epa.gov/air/nitrogenoxides/>.

¹⁰ Atmospheric nitrogen is N_2 , two nitrogen atoms bound together in a very stable form. Nitrogen must be "fixed" into a nitrogen oxide compound, into ammonia or into an organic chemical in order for plants to be able to use it. In this text forms of nitrogen that plants can use are called *reactive* or *fixed* nitrogen. These forms are *bioavailable* to plants.

¹¹ Recall that NO_x not only contributes to acid rain, but is an ozone precursor. It also contributes to the unhealthy levels of bioavailable nitrogen in waterways (Chapter 9). Meanwhile, the number of motor vehicles has been growing too, along with an increasing number of miles that each is driven making it difficult to further lower NO_x emissions.

SECTION IV

Recovering from acidic deposition

The first step needed was to lower emissions of SO₂ and NO_x which, as just noted, has been accomplished to a degree. Lowered emissions lead to less acid deposition, which – over time – leads to less acidic water and soil. Recovery would mean a return to the conditions that existed perhaps 100 years ago.

US lakes and streams

Acid deposition can impair lakes and streams in three ways: acidify their waters, i.e., lower their pH; decrease their ability to neutralize incoming acid; and increase Al concentrations. As levels of Al continue to increase, they, in combination with increased acidity, have a toxic impact on aquatic life. ■ After the Clean Air Act Amendments were passed in 1990, some reductions in acidity were noticed as early as 1993. The US Geological Survey reported that, at 9 of 33 sites monitored precipitation was less acidic than in 1980, and sulfate was down at 26 sites. But the pH of rain in US northeastern states remained acid, with a pH of 4.4 in 1997 (more than 10 times more acid than background pH). A positive finding in the year 2000 was that the number of acidic lakes in the Adirondack Mountains of New York had decreased by one third, compared to 1990. ■ However, despite lowered SO₂ and NO_x emissions, and thus, lowered levels of acid deposition, a 2005 NAPAP report states that many lakes and streams remain acidified,¹² and their fish and other aquatic life continue to suffer. Effects in some locations may not be reversible at all.

Also, keep in mind that although acid emissions are reduced, emissions still continue albeit at a lower level, and so acid deposition continues too. The acids are inorganic and continue to accumulate in soils and waters. Moreover, once soil and water chemistry are perturbed, they are slow to revert to former conditions. NAPAP concluded that further cuts in SO₂ and NO_x from power plants *and* from motor vehicles were needed in order to further reduce the number of acidic lakes and streams in the United States.¹³

¹² *National Acid Precipitation Assessment Program Report to Congress: An Integrated Assessment*, 2005 stinet. dtic.mil/cgi-bin/GetTRDoc?AD=ADA465644&Location=U2&doc=GetTRDoc.pdf

¹³ An excellent summary of acid deposition is found at *Acid Rain Revisited, Update II: Advances in Scientific Understanding Since the Passage of the 1970 and 1990 Clean Air Act Amendments*. Hubbard Brook Research Foundation, <http://www.hubbardbrookfoundation.org/article/view/12940/1/2076/>.

Questions 6.1

When answering these questions, recall the toxicology concepts in Chapter 3. Think about how interacting factors – chemical and otherwise – can cause adverse effects.

1. Explain how bioavailable nitrogen – essential to plant life – can adversely impact growing trees.
2. What does the following statement made by Professor William Smith of Yale's School of Forestry and Environmental Studies mean to you? "The integrity, productivity, and value of forest and other wild systems are intimately linked to air quality. We must elevate considerations of environmental health to the same level as concerns for human health."
3. Look at Table 2.1 again. See that in 1990 the US EPA's Science Advisory Panel rated acid deposition as a medium environmental risk (as opposed to a high or low risk). Consider the additional information now available. How would you now rate acid deposition? Explain.

SECTION V**Transboundary issues¹⁴**

Within the continental United States, SO₂ and NO_x emissions from large coal-burning power plants in Midwestern states are blown, with prevailing northeasterly winds to New York, New England, and Canada. To a lesser extent, acid pollution moves from Canada into the United States. ▪ Some members of the European Union (EU) such as Norway and Sweden had been harmed by transport of acid pollutants blown into them from Central and Eastern Europe, countries including Poland and Bulgaria. However, these latter two countries before joining the EU had to improve their environmental performance to meet the same standards as other EU countries, including greater limitations on SO₂ and NO_x emissions. As each new country joins the EU, its borders are enlarged, thus controlling pollution over an increasingly large area. Because of international agreements to limit emissions of SO₂ and NO_x, acid deposition in European countries is expected to continue to decrease in the coming years. ▪ See Box 6.4 for movement of China's emissions of acid precursors into Korea and Japan.

¹⁴ International transport of air pollution. *US EPA*, 2008, <http://www.epa.gov/airtrends/2008/report/InternationalTransport.pdf>.

The international picture

Europe¹⁵

Damage from acid deposition was more severe in Central and Eastern Europe than in the United States. Waters and soils suffered three times greater acidification. Forest death was more obvious. Norway and Sweden were especially hard hit with transboundary acid suffered widespread acidification of lakes and streams. Fish such as trout disappeared from thousands of lakes and salmon from many rivers. ▪ And in one locale of Germany, a study indicated that the bioavailable nitrogen resulting from the nitrogen in acid deposition was a greater problem than the acid sulfur. Bioavailable nitrogen is often the limiting factor in tree growth with trees absorbing and using all they receive. However, as acid deposition continued over the years, the trees could not use all the nutrient nitrogen deposited. Many believe that excess bioavailable nitrogen in forest soil was responsible for the forest deaths seen in Germany. ▪ Their explanation follows: trees responded to increased bioavailable nitrogen by growing faster than usual. Rapid growth further weakened trees already weakened by ozone and other pollutants. Trees eventually became unable to handle natural stresses such as weather extremes or insect attacks. A situation similar to that at Hubbard Brook occurred: excess acid leached Ca and Mg from the soil, which were then carried off by rainwater. A vicious circle ensued: with loss of the alkaline calcium and magnesium, soils become progressively less able to neutralize acid deposition, and tree roots are damaged. ▪ This study is relevant to the United States too where until recently, sulfur in acid deposition was the major concern. As SO₂ emissions are controlled albeit imperfectly, the less well controlled nitrogen oxides pose increasing concerns.

Working on recovery

Because acid pollutants disrespect borders, an international solution was needed for acid deposition. In 1979, more than 30 European countries agreed to the Convention on Long-Range Trans-boundary Air Pollutants; this obligated countries to reduce SO₂ emissions 30% below 1980 levels by 1993. Countries used a number of approaches to accomplish this such as burning natural gas (a fuel containing smaller amounts of sulfur than coal). Their efforts led to SO₂ emissions being lowered by about 50% and NO_x emissions by 20%. Some signs of recovery were seen with, for instance, some waters becoming less acidic, but more was needed. ▪ Another agreement, signed in 1999 called for an 80% reduction in sulfur emissions and 50% reduction in nitrogen emissions by 2010 (relative to 1980). As of 2005, acid deposition had declined by 60% and more signs of recovery in lakes and streams have been seen.¹⁶ However, complete recovery may take many years although one model simulation

¹⁵ Exposure of ecosystems to acidification: assessment. *European Environmental Agency*, February, 2008, <http://www.eea.europa.eu/themes>.

¹⁶ Wright, R. F. *et al.* Recovery of acidified European surface waters. *Environmental Science & Technology*. **39**(3), February 1, 2005, 49A–72A.

predicted that by 2016 most waters, except those in southernmost Norway, will have recovered. Nevertheless, one group of investigators noted that this does not mean that the waters will have returned to their pre-acidification “natural” state. Moreover, forest soils still have reduced capacity to neutralize acid deposition because of decades of acid deposition.¹⁷

Asia

During January to March each year, a brown haze overlies much of the Indian Ocean and the land areas of South, Southeast and East Asia (Chapter 5). Then during the summer rains, the acidic pollutants contained within the haze fall, damaging food crops. Thirteen Asian countries are now working together and with the UN to assess the impacts of acid deposition, how to lower acid emissions, and lower the movement of a country’s emissions into other nations.¹⁸ One early step taken was to set up an acid deposition monitoring network in India, Thailand, and Nepal. Local people are trained to measure acidity and operate monitoring stations.

Box 6.4

Acid deposition in China¹⁹

Most of China’s many coal-burning power and industrial plants do a poor job of controlling SO₂ and NO_x emissions. And, concurrent with very rapid ongoing industrial growth, China is building about one new power plant each week, almost all of which burn coal, which is relatively cheap and plentiful. In 2004, coal accounted for 69% of China’s energy with coal consumption increasing a phenomenal 20% a year.²⁰ Emissions of SO₂ continue to increase.²¹ Coal-burning power plants emit less NO_x than SO₂, but as more and more are built, NO_x emissions also continue to increase. Moreover, NO_x emissions are increasing in tandem with a rapidly increasing car fleet – up from 6.2 million vehicles in 1990 to 36 million in 2003, and still rapidly growing. Ammonia emissions from intensive agriculture are also high, three times greater than NO_x emissions.

Xinhua, China’s news agency, citing a parliamentary report, reported that a third of China receives rainfall with pH values lower than 5.6, i.e., rain more acidic than natural rain.²² More than half of 696 cities and counties monitored received acid deposition. Xinhua further noted

¹⁷ Wright, R. F. *et al.* Recovery of acidified European surface waters. *Environmental Science & Technology*. **39**(3), February 1, 2005, 49A–72A.

¹⁸ *Overview of EANET (Acid Deposition Monitoring Network in East Asia)*, January, 2008, <http://www.iiasa.ac.at/rains/meetings/10thMICS-Asia/Ueda.pdf>. Countries participating in EANET are Cambodia, Laos, Myanmar, China, Indonesia, Japan, Malaysia, Mongolia, Philippines, Republic of Korea, Russia, Thailand and Vietnam. EANET is now one of a number of regional monitoring networks in the world.

¹⁹ Larssen, T. Acid Rain in China. *Environmental Science & Technology*, **40**(2) January 15, 2006, 418–425.

²⁰ China’s coal contains, on average, 1.1% sulfur, but in some areas it is as high as 4%.

²¹ Third of China “hit by acid rain”. *BBC News*, August 27, 2006, <http://news.bbc.co.uk/2/hi/asia-pacific/5290236.stm>.

²² Acid rain affects large swathes of China. *Reuters* (Xinhua news agency), August 28, 2006, <http://www.planetark.org/dailynewsstory.cfm/newsid/37849/story.htm>.

that SO₂ emissions rose 27 percent between 2000 and 2005 to 27.5 million tons (25 million tonnes). This makes China the world's top SO₂ emitter. The deposition of acidic sulfur compounds is at least as high as seen in central Europe's "Black Triangle" in the early 1980s, an area that was particularly hard hit by acid deposition. Higher levels of acid deposition have been seen in China's industrial cities as compared to its forests.²³

In the most polluted areas of China's forests, pines have suffered severe needle loss. However, these forests are also impacted by other stresses. Thus, the role of acid deposition is not clear, but it is known from other countries' experience that soil acidification will negatively impact forests. And large amounts of aluminum have been released from forest soil, high enough to damage tree roots. However, deposition of large amounts of calcium (from dust storms)²⁴ may counter the aluminum impact. •Surface water acidification is not now seen as a large problem. However, too few investigations have been carried out to really know.

Despite realizing that significant potential damage to both forests and water bodies may be occurring, little is known about specific impacts. More studies are needed on forests and whole ecosystems before an effective strategy can be developed. China, cooperating with a Norwegian group, set up five sites around the country, the Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems. This program is carefully monitoring and studying air pollution, precipitation, and effects on soil, water, and vegetation in areas considered to be vulnerable to acid deposition.

The Chinese government now considers acid deposition and, more generally, air pollution as among high-priority issues that must be addressed.²⁵ At the same time, the need for electricity continues to grow. China has begun requiring electric power plants and large industrial facilities to capture part of their SO₂ emissions. The government is also asking households to switch to gas or electricity when possible or use lime-containing coal briquettes that capture SO₂. Analysts believe that acid deposition will cause increasingly serious effects unless China and other Asian countries reduce SO₂ and NO_x emissions.

Further reading

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²³ There is uncertainty in this statement as Chinese monitoring programs focus on urban areas and on the pH of precipitation.

²⁴ This alkaline dust neutralizes part of acid deposition, as does ammonium. However, as noted earlier in the chapter, the ammonium, once deposited can be chemically converted to acidic compounds. Moreover, these nitrogen compounds contribute to problems of too much bioavailable nitrogen in some locales.

²⁵ Fu, B., Zhuang, X., Jiang, G., Shi, J. and Lu, Y. Environmental problems and challenges in China. *Environmental Science and Technology*, **41**(22), 15 November 2007, 7597–7602.

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Anyone who has kids must be ... concerned about the climate future we're leaving behind for them. The choices that we make today on the "what to do" about climate change will have long lifetimes ... Our actions are changing the climate on a global scale. It's happening now. We can't pretend it's not there.

Ben Santer, climate modeler at the US Department of Energy's Lawrence Livermore National Laboratory

Climate change is nothing new. About 18 000 years ago, Earth was experiencing the last of many ice ages, from which it only emerged about 10 000 years ago.¹ More recently, between the years 1430–1850 portions of the Earth passed through a little ice age. The role of greenhouse gases, especially water vapor and carbon dioxide (CO₂), in warming the Earth is also ancient, and indeed has long served life on Earth well. Figure 7.1 shows a representation of this phenomenon. Radiation from the sun reaches and warms the Earth's surface. In turn, Earth emits radiant heat (infrared radiation) back toward space, part of which is captured by heat-trapping water vapor and greenhouse gases. Without the "greenhouse effect" to trap this warmth, the Earth could be colder by 95°F (35°C), and not support life as we know it. However, the last century has brought greater warming beyond that which can be accounted for by natural causes, and warming is occurring at a faster rate.² It is this, which we examine in this chapter.

In an 1896 publication, Swedish chemist Svante Arrhenius noted that, "We are evaporating our coal mines into the air." He stated a novel thought: Earth's climate would warm as we continued to burn coal, which would increase the level of atmospheric CO₂. An American, P. C. Chamberlain came to similar conclusions also in the 1890s. They believed this because they knew that CO₂ absorbs and traps the infrared radiation emitted from the Earth. So, increasing levels of atmospheric CO₂ would lead to increasing temperatures. Living in a very cold climate Arrhenius relished the possibility, and believed it might prevent the onset of another ice age.

In this chapter, Section I asks, what pollutants are involved in global warming? Section II explores why increasing levels of greenhouse gases concern us. Section III goes into sources of greenhouse gases and their environmental fate. Section IV briefly examines international agreements to reduce greenhouse gas emissions, especially the Kyoto Protocol. Section V

¹ Glacial cycles, each about 100 000 years long, are controlled by "shakes, wobbles, and tilts" in the Earth's orbit which, in turn, determine the amount of sunlight falling on and warming the planet as it moves around the sun. In each of eight cycles of atmospheric change over 800 000 years, when CO₂ and methane reached peak levels, the world experienced warm, inter-glacial periods. (1) Brook, E.J. Tiny bubbles tell all. *Science* **310**(5752), November 25, 2005, 1285–1287. (2) British Antarctic Survey, Natural Environment Research Council, 2007, <http://www.antarctica.ac.uk/indepth/icecore/page1.php>.

² For a brief overview of warming trend, see: Gribbin, J. and Gribbin, M. Genesis of Eden. *New Scientist*, July 13, 1996, <http://www.dhushara.com/book/diversit/co2.htm>.

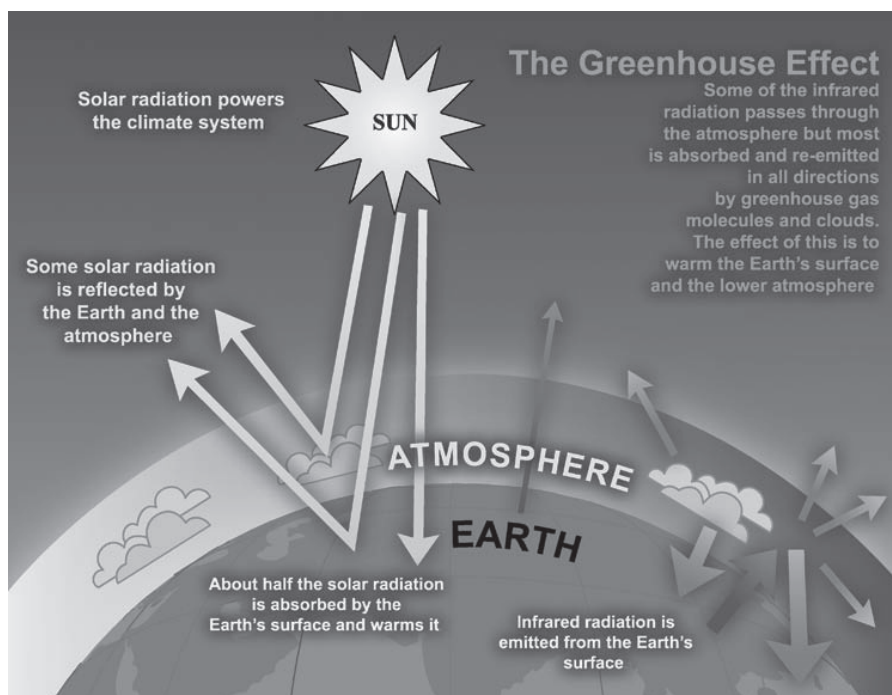


Figure 7.1

The greenhouse effect. Credit: IPCC, 2007

goes on to using conservation and efficiency to reduce CO₂ emissions; cuts in GHG emissions other than CO₂; and reducing population growth. It explores what corporations, states, cities, and nations are doing, including less-developed countries, especially China. Section VI asks how biological, physical and chemical sequestration of CO₂ can mitigate the impacts of increased temperatures. Section VII examines what a greenhouse future may look like.

SECTION I

Greenhouse pollutants of concern^{3,4}

Levels of major greenhouse gases are seen in Table 7.1 along with their *greenhouse warming potentials* (GWP) as compared to CO₂. Historic atmospheric levels are compared

³ Atmospheric concentrations of greenhouse gases. *US EPA*, March 14, 2009. <http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewInd&ch=46%20&subtop=342&lv=list.listByChapter&r=188193>.

⁴ *Fundamentals of Physical Geography* (2nd edn.), <http://www.physicalgeography.net/fundamentals/contents.html>, is an excellent place on the Web to obtain an overview of physical geography (including maps, GIS, and remote sensing). It covers matter, energy, and the universe; our atmosphere, its components and functions; the hydrosphere (the water on the Earth including bodies of water, water vapor, ice; the lithosphere (the solid part of the Earth's crust), and the biosphere. Its glossary of terms is at <http://www.physicalgeography.net/glossary.html>.

Box 7.1

IPCC – an important organization

Interspersed within Chapter 7 is information from the IPCC (Intergovernmental Panel on Climate Change), a scientific body, which evaluates climate change. Established in 1988 by the UN organizations, the World Meteorological Organization and the UN Environment Program, IPCC does not itself do research. Rather it analyzes the work of thousands of established climate scientists whose work has been peer reviewed and published in scientific journals. The IPCC has provided four major assessment reports (1990, 1995, 2001, 2007). Its reports are widely cited and respected, establishing “what is considered the gold standard of consensus on climate change science.” The IPCC’s 2007 report represents six years of work using input from 1,00 authors and 2500 scientific expert reviewers from more than 130 countries. As part of its considerations the IPCC also tracks 20 climate models from all over the world.

There is a growing awareness: in its 1990 report, the IPCC was careful in how it stated whether the Earth was warming and whether, if it was warming, humanity was primarily responsible, “The observed increase could be largely due to natural variability” In 1995, the IPCC’s statement was stronger, “The balance of evidence suggests a discernible human influence on global climate.” By 2001, it stated, “There is new and stronger evidence that most of the warming over the last 50 years is attributable to human activities.” Then, most recently, in its 2007 report, it reports with 90% certainty that human activities, especially the burning of fossil fuels, have caused global warming this past 50 years.⁵

to current levels. The warming potential of CO₂ is low compared to the other gases shown: nonetheless it is the major greenhouse gas because major quantities are emitted. Second in importance is methane, present in much smaller amounts, but with a high GWP. Molecule for molecule, methane has about 25 times the warming potential of CO₂. Water vapor is also an important greenhouse gas, but is almost all natural and not a result of industrialization. Soot from incomplete combustion is also considered a greenhouse “gas,” which we’ll come back to later.

In Figure 7.2, notice that most of CO₂ in the world is emitted by natural systems and absorbed by natural systems (atmosphere, water, vegetation, and soils). More than 6.6 billion tons (6 billion tonnes) of CO₂ are emitted by human actions each year, a small quantity compared to natural amounts. However, natural systems are absorbing less than half of anthropomorphic emissions meaning that human actions are adding more than 3.3 billion tons (3 billion tonnes) each year to the atmosphere. The result is that atmospheric CO₂ has built up from 280 ppm in the pre-industrial world to 387 ppm in May, 2008. A striking record of increasing CO₂ concentration is seen in Figure 7.3. The see-saw effect in the figure shows Earth’s respiration. In the cold season, plants in the northern hemisphere

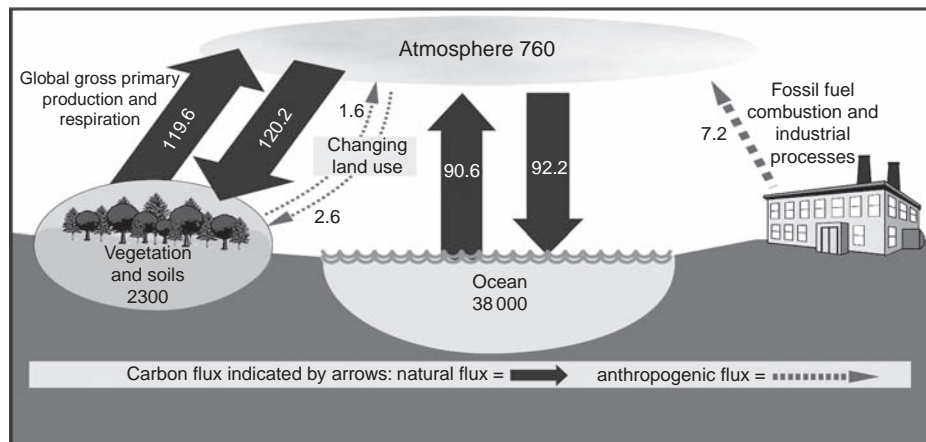
⁵ Coauthors of the 2007 report are Rajendra K. Pachauri, IPCC Chairman, and Susan Solomon, NOAA atmospheric scientist who says, “The work is several steps beyond what was possible with the third report.” See: Ekwurzel, B. Findings of the IPCC Fourth Assessment Report: Climate Change Science, a summary. Union of Concerned Scientists summary, July, 2007, http://www.ucsusa.org/global_warming/science/ipcc-highlights1.html.

Table 7.1 Historic as compared to current levels of atmospheric greenhouse gases

	Pre-industrial revolution	Current level	Warming potential CO ₂ = 1	Lifetime in atmosphere
Carbon dioxide (CO ₂)	280 ppm	387 ppm	1	~100 years
Methane (CH ₄)	700 ppb	1791 ppb	25	12 years
Nitrous oxide (N ₂ O)	270 ppb	321 ppb	300	114 years
Ozone (O ₃) ³	25 ppb	31 ppb	–	hours/days
The gases below are examples of greenhouse gases found in the atmosphere in trace amounts				
CFC-12	Zero	539 ppt	10 900	100 years
Halon 1211	Zero	4.39 ppt	1890	16 years
Sulfur hexafluoride (SF ₆) ⁴	Zero	6.2 ppt	22 800	3200 years

Note: Parts per billion (ppb) is a thousand-fold lower concentration than parts per million (ppm). Parts per trillion (ppt) is a million-fold lower than ppm.

Information from: Blasing, T. J. Recent greenhouse gas concentrations. *CDIAC*, December, 2008, http://cdiac.ornl.gov/pns/current_ghg.html.

**Figure 7.2**

Global carbon cycle (in billion metric tons carbon). Credit: IPCC, 2007

don't grow, or grow less, so less CO₂ is taken up from the atmosphere. In the warm season the opposite is true.

Ice core studies of greenhouse gases

The information in Table 7.1 indicates that levels of greenhouse gases in the atmosphere have increased in recent centuries. But how can we know the atmospheric levels

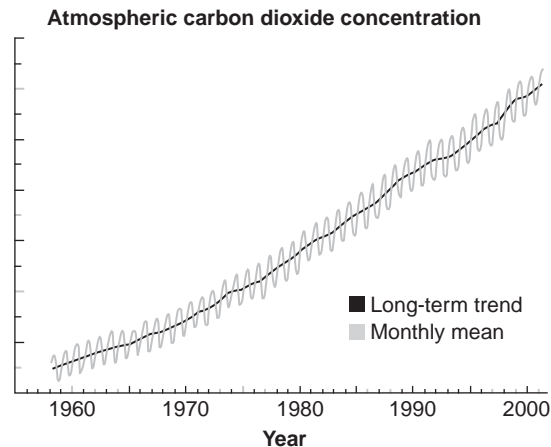


Figure 7.3 Increasing levels of carbon dioxide in the atmosphere since 1958. Credit: NASA Earth Observatory

of these gases hundreds or thousands of years ago? The answer lies in air bubbles trapped in ancient layers of Arctic and Antarctic ice (Box 7.2 and Figure 7.4). Analyzing these bubbles provides concentrations of carbon dioxide, methane, nitrous oxide, and other gases that existed as long ago as 740 000 years ago.⁶ The bubble “is a direct link to the atmosphere,” says ice-core scientist Mark Twickler. Ice bubble records show that at no time in the past 650 000 years have atmospheric carbon dioxide and methane levels been higher than those given in Table 7.1 for CO₂ and methane for the years *before* the Industrial Revolution.⁷ In other words, atmospheric levels of CO₂ and methane “exceed by far the natural range over the last 650 000 years.” ■ Because the bubbles also provide information with which to calculate temperature for the time they were trapped (Box 7.2), it’s possible to show that glacial (cold) periods correlate with low levels of atmospheric CO₂ and that the interglacial (warm) periods have higher CO₂ levels.

⁶ This ice core record of over 740 000 years is a highly regarded achievement. It comes from the European Project for Ice Coring in Antarctica, an international collaboration of scientists, engineers, and drillers. The 740 000 year record includes eight full glacial cycles. Dr. Robert Mulvaney of the British Antarctic Survey commented that “The most significant thing ice cores have told us is that greenhouse gases are so well-related to climate, and that at no point in the last three-quarters of a million years have carbon dioxide and methane reached anywhere near the levels they are at today.” For further emphasis of this point, BAS scientist Eric Wolff says, “existing levels of carbon dioxide and methane are far higher than anything seen during these earlier warm periods.” See *The Ice Man Cometh*. British Antarctic Survey, 2007, <http://www.antarctica.ac.uk/indepth/icecore/page1.php>.

⁷ The industrial revolution refers to a time starting in the late 1700s when, in parts of Europe and the United States, machines increasingly replaced work previously done by hand.

Box 7.2

Information in ice

Ice sheets started out as snow laid down one layer at a time, year after year. Similar to tree growth rings, individual years can be discerned over many thousands of years. Over hundreds of thousands of years, lower layers become more distorted due to the weight upon them of more and more snowfalls. Scientists painstakingly collect ice borings to great depths from Greenland and Antarctica, and analyze them in a variety of ways. The data gleaned tell us what greenhouse gases were trapped at identifiable times in the past, and in what amounts. We also learn what other gases, metals, and dust were present and when. For example the dates, thousands of years ago when Greeks and Romans most heavily mined lead and copper are laid down in specific layers. So too are the years in which large dust storms occurred. More recently, the years that nuclear bombs were tested in the atradioisotopes laid down in the ice. Similar studies can be done with ocean sediment borings, but ice borings provide finer detail.

Just as remarkable, researchers can determine the temperature corresponding to the years that a layer was laid down. Two stable isotopes of the element, oxygen make this possible, ^{16}O (the common form of oxygen), and a heavier isotope, ^{18}O . In warm years, more of the heavier isotope ^{18}O occurs in the atmosphere than in cooler years, and the correlation between temperature and the ratio of these two isotopes of oxygen is strong. Thus, the results allow us to see how climate cycles waxed and waned over hundreds of thousands of years.⁸



Figure 7.4 Air bubbles trapped in an ancient core of ice. Credit: Edward Brook, Oregon State University

⁸ For more information on how temperature can be determined in this manner, see Jouzel, J. A 740 000-year deuterium record in an ice core from Dome C, Antarctica. Carbon Dioxide Information Analysis Center. December, 2004, <http://cdiac.ornl.gov/trends/temp/domec/domec.html>.

Box 7.3

Questions and answers on global climate change⁹

- 33 frequently asked Global Change Questions. *CDIAC, Oakridge National Laboratory*. <http://cdiac.ornl.gov/faq.html#Q22>.
- 11 frequently asked Global Warming Questions. *National Oceanic and Atmospheric Administration, National Climatic Data Center*. <http://www.ncdc.noaa.gov/oa/climate/globalwarming.html>, May, 2008.
- Global Warming, Questions & Answers. *NASA Earth Observatory*. <http://earthobservatory.nasa.gov/Study/GlobalWarmingQandA/>.
- Greenhouse gases, frequently asked questions. *National Oceanic and Atmospheric Administration, National Climatic Data Center*. <http://www.ncdc.noaa.gov/oa/climate/gases.html#wv>.

SECTION II

Why increasing levels of greenhouse gases are of concern

Earth is warming

Temperature measurements over more than 100 years between the early twentieth century and now indicate that Earth's average surface temperature has risen about 0.8°C (about 1.44°F); moreover, it has risen 0.6°C (1.08°F) in the past three decades.¹⁰ The increase has not been smooth (Figure 7.5), but the steady upward trend is clear. The year 2005 was the warmest in more than 100 years, and very similar to 1998, the warmest previous year. NASA's John Hansen states that it is no longer correct to say that "most global warming occurred before 1940." Rather, global warming was slow, with large fluctuations, in the century leading up to 1975; subsequently it has warmed almost 0.2°C (0.36°F) per decade.

▪ An increase of 1.4°F seems modest. But consider that the average temperature at Earth's surface is only 15°C (59°F). During the last major ice age, ending about 10 000 years ago, temperatures were only about 5°C colder than today. Temperature has varied only about 2°C since then. As will be noted below, profound effects have occurred with this "small" increased temperature.

One major complication in determining the reality of warming has been the *heat island* effect. Many early recording stations were located where cities subsequently grew up. A city, with its paving and buildings, absorbs more heat than a rural area, sometimes dramatically more. Thus, rising temperatures were to be expected in urban locales.

⁹ You may also like to examine the website <http://gristmill.grist.org/skeptics>, *How to Talk to a Climate Skeptic*, a series by Coby Beck containing responses to the most common skeptical arguments on global warming.

¹⁰ Hansen, J., Ruedy, R., Sato, M. and Lo, K. GISS Surface Temperature Analysis. NASA Goddard Institute for Space Studies and Columbia University Earth Institute, December 15, 2008, <http://data.giss.nasa.gov/gistemp/2005/>.

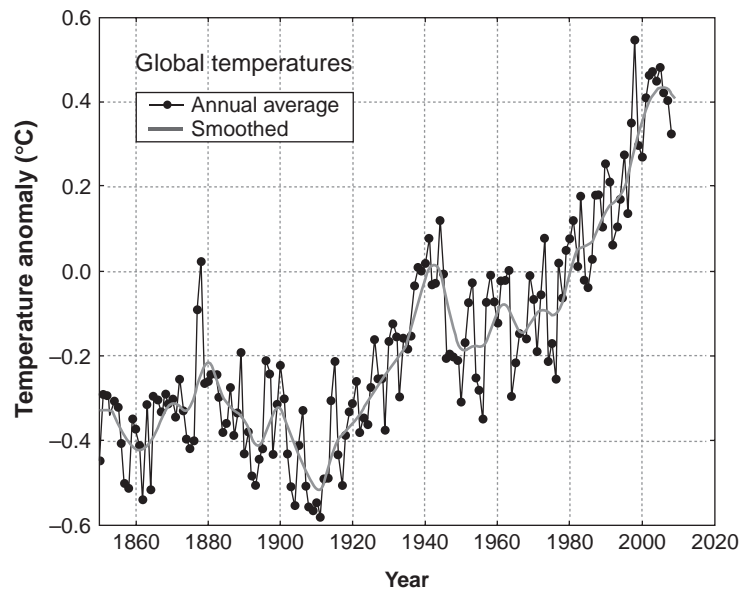


Figure 7.5 Global average temperatures over the years. Credit: Climatic Research Unit of the University of East Anglia and the Hadley Centre of the UK Meteorological Office

However, different methods of calculating temperatures, using ice cores, tree rings, and other historical data all consistently point to a temperature increase over the past century.

▪ A perplexing issue emerged. For the years 1979 to 1994, satellite records of temperature made in the atmosphere above the Earth showed – as compared to surface temperatures – that no warming had occurred. Then, in 2005, not one, but three research papers published in the journal *Science*, noted a number of problems with the satellite record. Upon making corrections for these problems, it was apparent that the satellite data too showed warming of the atmosphere commensurate with the warming observed at Earth's surface.¹¹

Warming is consistent around the world

Temperatures have risen on six continents. What has happened in the seventh continent, Antarctica, is not yet clear although melting is occurring. There is no way that natural variability could account for this widespread, near universal warming over the past few

¹¹ “The papers found that uncertainties in the satellite observations are far larger than [had] been portrayed. Satellites drift in their orbits. These drifts affect the section of the atmosphere that can be observed from space and the time of day at which a satellite “sees” a particular location on Earth’s surface. Another problem is that satellite instruments don’t perform identically when you put them in the harsh environment of space.” Thacker, P. D. The many travails of Ben Santer, an interview with Ben Santer. *Environmental Science & Technology*, 40(19), October 1 2006, 5834–5837. These problems led to biases between the instruments on different satellites. Moreover, temperature sensors on weather balloons made it difficult to compare old and new temperature measurements made from weather balloons. After corrections were made, researchers all agreed that the Earth’s atmosphere, the troposphere, has been warming.

decades. Among the warming regions, the greatest warming has been seen at high latitudes in the northern hemisphere.

How is global warming showing itself and why does it matter?

Increasing ocean temperature

Climate models (described below) indicate that the Earth's oceans will warm before Earth's atmosphere does. Previously, there were too few temperature measurements in the ocean to check out this projection, but oceanographers kept looking, and were eventually recovered literally millions of old measurements that had been made by dropping temperature sensors into the sea. Some dated back to the mid-1950s. The information had not been systematically recorded, and had been stored in many different places and ways. However, when these data were analyzed they indeed showed the predicted ocean warming. Between 1955 and 1995, both the north and south Pacific Ocean, the Atlantic Ocean, and the Indian Ocean showed an average warming of 0.11°F (0.06°C) between the surface of the ocean and a depth of 1.86 miles (3000 m). This difference seems very small, but think: if you calculate the volume of the ocean down to a depth of 1.86 miles (3000 m), the result is an enormous amount of stored heat. Indeed, researchers at the US National Oceanic and Atmospheric Administration (NOAA) calculated that the oceans were holding ten times more heat than the amount, which has gone into warming the global atmosphere and into melting sea ice and glaciers. They noted that *the oceans are playing a major heat-trapping role*, indeed absorbing 80% of the heat added to the climate.

Just as Earth's surface temperature did not increase smoothly over time, neither did ocean warming. As projected by climate models, an increased amount of heat was stored in the oceans for years before that temperature rise was detected over land. ■ NOAA has set up a temperature monitoring system, *Argo* (Figure 7.6). Argo spans the oceans worldwide with 3000 free-floating packages of instruments to continuously monitor temperature, salinity, and velocity of the upper oceans and relay the data to satellites. Data collected will create a weather map of the ocean down to 6560 feet (2000 m), helping to improve seasonal climate forecasts. Argo also is improving accuracy of estimates of sea level rise.¹²

Snow and ice are melting

Alaska

In the US state of Alaska the temperature has risen by 3°C (5.4°F) in the past 30 years, four times greater than the average global increase. This has led to the melting of Alaskan

¹² International Argo Effort Launches 3 000th Float, November 2, 2007, http://www.noaanews.noaa.gov/stories2007/20071102_argo.html.

**Figure 7.6**

Preparing to deploy Argo float. Credit: Pien Huang & Scripps Institution of Oceanography

glaciers at what a University of Alaska research team calls an “incredible rate,” much faster than was previously thought would happen. A few exceptions have gained mass. Using aircraft-carried laser devices, researchers measured the volume of 67 Alaskan glaciers. They compared this information to aerial photographs taken between the 1950s and the early 1970s, and to contours of US and Canadian topographic maps. Their resulting calculations gave a surprising result – the melting Alaskan glaciers have contributed at least 9% of the sea-level rise seen in the twentieth century. Researchers asserted that the glacial melting is faster than anything that has happened in at least 10 centuries. The rapid increase in Arctic temperatures has also affected the lives of people and animals: ▪ So much ice has melted that polar bear habitat has been impacted. In May 2008, the United States made the decision to protect polar bears under its Endangered Species Act. ▪ Another example: Alaska’s permafrost (permanently frozen subsoil) is beginning to thaw. This is resulting in sagging roads, sinking pipelines and rapid multiplication of insects that feed on the State’s spruce forest. Some trees are showing their roots as the permafrost melts.

Melting, flowing and sliding ice

In the Arctic, more generally, ice has been rapidly melting. Since satellite measurements began 30 years ago, the Arctic has lost more than 20% of its ice. The rate of loss began

accelerating in 2002 to the extent that, in summer 2007 the Northwest passage across the top of Canada became fully navigable. If the current rate of melting continues, the summertime Arctic could be totally free of ice by 2030.¹³ ■ In Greenland, glacial ice is being lost to the sea through melting. But there is also an increased rate of flow of the ice itself into the sea, at least in the summer. This happens because as meltwater accumulates in surface lakes on the ice, its weight opens cracks, through which water drains to the base of the ice. There, in contact with bedrock, the water lubricates the rock surface, allowing a “speed-up” of the ice’s sliding into the ocean. However, it appears that the speed of flow of the outlet glacier (the tongues of ice sheets penetrating into the ocean) is more important; this also could be affected by warming.¹⁴

Around the world

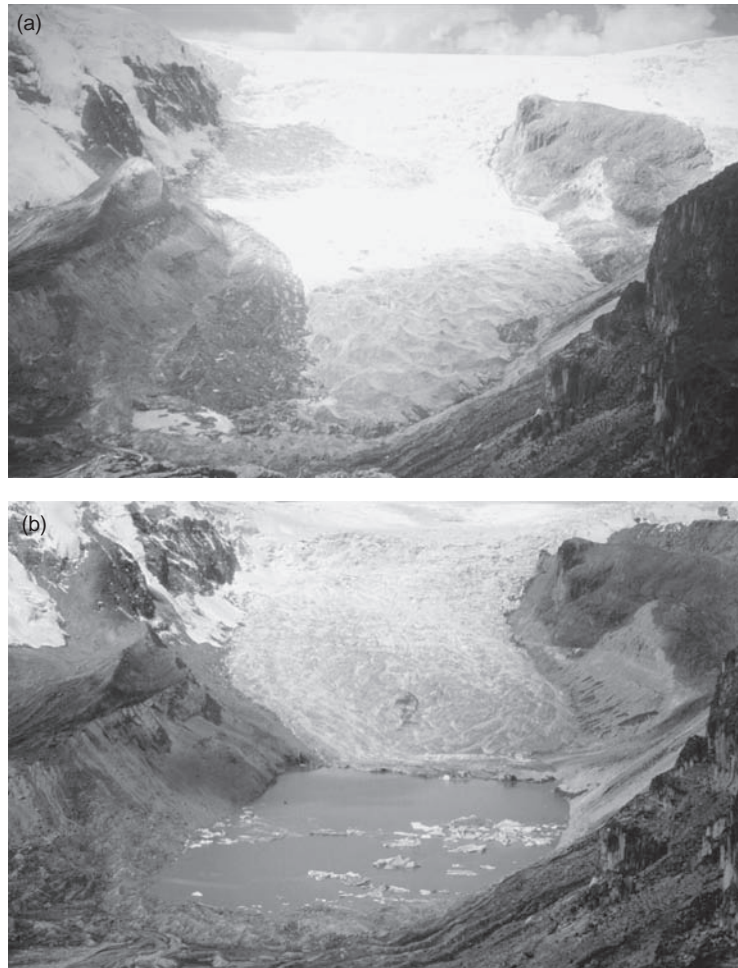
Glaciers and permafrost have decreased in both hemispheres. Mountain glaciers and snow cover have declined worldwide. ■ The phenomenon of glaciers sliding into the ocean is also happening in the Antarctic. ■ Mountain glaciers in places as far apart as Peru and Tibet are melting – in the Alps, Himalayas, and Andes. Moreover, runoff from melting begins earlier in the year. Figure 7.7 shows Peru’s Qori Kalis. This glacier shrank 33 times faster between the years 1998 and 2000 than it did between 1963 and 1978. The bottom photograph in the figure shows how much of the glacier melted and the 10-acre lake formed from the melt.¹⁵ ■ In Nepal and Bhutan, many lakes around melting glaciers are dangerously full. If they overflow, their contents may flood the narrow valleys below where the country’s population lives. ■ At the location of the world’s highest peak in the Himalayas, people climbing the mountain must now walk for 2 hours from base camp to reach ice whereas in 1953 Sir Edmund Hillary stepped directly onto ice from the base camp. ■ Many other glaciers around the world are melting too, more rapidly than before.

Communities below mountain glaciers use water from normal glacial melting for drinking and farming, and the meltwater also keeps water levels high in rivers that support hydroelectric dams. When the glaciers begin to melt more rapidly, communities and rivers below would initially have plenty of water. But, as melting continues, critical water shortages would arise. Moreover, if rivers no longer support hydroelectric dams, people may use more oil or coal to generate electricity leading to even more greenhouse gas emissions. ■ In Kashmir (India and Pakistan) where many small glaciers have disappeared from the western Himalayas, water levels in most streams and rivers have fallen by about two-thirds in

¹³ Adam, D. Loss of Arctic ice leaves experts stunned. *Guardian Unlimited*. September 4, 2007, <http://www.guardian.co.uk/environment/2007/sep/04/climatechange>.

¹⁴ (1) Kerr, R. A. A Worrying trend of less ice, higher seas. *Science*, **311**(5768), March 24, 2006, 1698–1701. (2) Kerr, R. A. Greenland ice slipping away but not all that quickly. *Science*, **320**(5874), April 18, 2008, 301. (3) King, M. Meltwater speeds up ice sheet slippage. *NewsLink Newcastle University*, April 23, 2008, <http://www.ncl.ac.uk/press.office/newslink/index.html?ref=1208936591>.

¹⁵ Loss of the glacier is not as simple as ice melting due to warmer temperatures. It has to do with any given year’s balance of ice and snow. If there is more snow in a particular year, the glacier is whiter and brighter and thus reflects sunlight, and has reduced melting, even if it’s warmer. Other factors are also at play, but increased warming over the years does lead to more melting. Engelhaupt, E. Peru’s glacier meltdown threatens drinking water supplies. *Environmental Science & Technology*, **41**(20), 6880, October 15, 2007.

**Figure 7.7**

- a Peru's Qori Kalis glacier in 1978. Credit: Dr. Lonnie Thompson, Ohio State University
b Peru's Qori Kalis glacier in 2000. Credit: Dr. Lonnie Thompson, Ohio State University

40 years. As glaciers disappear from the Himalayas, hundreds of millions of people could have their water supplies threatened.¹⁶ India depends on rivers fed by Himalayan glaciers. The west coast of North America also strongly depends on water from mountain glaciers in mountains such as the Rockies. A few of the world's glaciers have added mass or are losing ice due to natural causes.¹⁷ The interior of Antarctica has cooled in recent decades, but the

¹⁶ Kashmir's climate crisis. *Environmental Science & Technology*, **41**(24), December 15, 2007, 8209.

¹⁷ Kenya's Mount Kilimanjaro is losing ice due to natural causes. It began melting in the late 1800s with most of the ice's retreat occurring before 1953. For unknown reasons, atmospheric circulation over the Indian Ocean strengthened in a way that led to less rain and snow fall on East Africa. (Kilimanjaro's shrinking snow not sign of warming. *Reuters News Service*, June 12, 2007, <http://www.reuters.com/article/scienceNews/idUSN1225401620070612>).

Antarctic Peninsula warmed so much, 2.5°C (4.5 F) this past 50 years that it lost a Rhode-Island sized chunk of its ice shelf in 2002.

Sea levels are rising

Sea-level has risen about 400 ft (130 m) since the peak of the last ice age about 18 000 years ago. Most of that occurred prior to 6000 years ago. From 3000 years ago to the start of the nineteenth century sea level hardly rose at all. Then, the rate sped up, especially in the last 100 years. Globally, sea levels rose 4 to 8 inches (10 to 20 cm) in the twentieth century. You can see the eating away of some shorelines that resulted if you compare pictures of lighthouses taken a hundred years ago or more to present pictures, showing them now much closer to the water. Space-based technology is now used to study changes. A United States–French satellite began calculating changes in sea levels in 1992. Now a newer satellite, Jason, with better instrumentation continues to assess rising sea levels, especially along low-lying coastlines such as found in certain island nations, in Bangladesh, and parts of coastlines in other countries. One billion people could become homeless if the sea rose 1 m (3.28 feet). In Bangladesh alone, 15–20 million people would be displaced by a 1 m rise.

Why are sea levels rising?

Since 1961, the world's oceans have been absorbing more than 80% of the heat added to the climate. ■ As they warm, the water expands and sea level rises. ■ Meltwater from melting mountain glaciers runs off into the ocean, as does meltwater from, and breaking off of, ice from Greenland and Antarctic ice sheets. As land ice melts into the oceans, sea level rises due to an increased quantity of water within them. ■ Some scientists believe that part of the increased sea level is natural, due perhaps to changes in land movement.

Assessing global climate change

General circulation models

Each issue discussed above was investigated using scientific instrumentation collecting data from space, air, earth, and sea. To be useful, this massive amount of information must be integrated into a usable picture that makes it possible to see climate holistically, and to project future climate. To accomplish this, scientists use computer models: *general circulation models* (GCMS). What are model expected to do? Dr. Benjamin Santer of Lawrence Livermore National Lab, says, “We ask how well they simulate the present-day climate, the daily temperature cycle, the march of the seasons. We see how well they capture modes of climate variability that we care about, such as El Niño. We test their ability to reproduce changes in climate over the twentieth century. In some cases, we even ask how faithfully

Box 7.4

Can natural changes account for observed warming?

Could natural forces (*external forcings*) account for Earth's warming as opposed to human forcings? To answer, we look for what Ben Santer of the Lawrence Livermore National Lab calls "unique signatures." As of now, we keep finding a human signature, a human forcing. However, in some cases, natural impacts can partially explain some global-warming phenomena.

Atmospheric warming

Could variation in the sun's radiation affect climate? The little ice age that lasted about 300 years, until 1850 occurred when solar activity was very low. Some researchers are examining a possible correlation between an 11-year sunspot cycle and Earth's temperature. Between 1958 and 1995 Earth's temperature cycle did match the sunspot cycle. But the high point of the sun's output raises surface temperature by 0.2°F at most. ▪ Moreover, if a warmer sun was responsible, the whole atmospheric column would warm, which has not happened. Instead, the troposphere – the lowest layer of the atmosphere – has warmed; the higher stratosphere has cooled. This pattern indicates human causation. The IPCC in its 2007 report concludes that humankind's industrial emissions have had five times more effect on climate than any fluctuation in solar radiation.¹⁸

Ocean warming

Could the warming of the oceans be due to heat coming from Earth's hot core? This would warm the lower levels of the ocean first. But, in fact the greatest warming is at the surface and the warmth tapers off as one goes deeper. ▪ Also, note that *all* ocean surface waters are warming. Thus, although variations in El Niño activity have been suggested as a natural cause for ocean warming, in El Niño phenomena, one part of the ocean heats up while another cools.¹⁹ ▪ To account for the surface warming of all oceans, we need to have a net heat source, in this case a warming atmosphere.²⁰

they can reproduce climates of the distant past – like the last ice age.”²¹ Models over the years have become increasingly complex as more and more variables are considered.

Each GCM incorporates somewhat different information on greenhouse gas characteristics and their sources and environmental sinks; atmospheric and ocean circulation; clouds and aerosols; reflectivity of snow, land, and water; and many other variables. Each takes a given set of conditions and makes future projections from them. It projects temperatures,

¹⁸ Researchers at Duke University estimate that 10–30% of the rise in global surface temperature is due to increased solar irradiance. They suggest that global climate models need to include solar activity accounting: Scafetta, N. and West, B. Solar cycles impact warming. *Environmental Science & Technology*, 40(1), January 1, 2006, 5.

¹⁹ El Niño can, for limited periods of time, increase global average warming. However, the observed warming is regionally variable and some areas are cooler.

²⁰ (1) Begley, S. and Murr, A. Which of these is not causing global warming today? *Newsweek*, July 2, 2007, 48–52. (2) Begley, S. The truth about (global warming) denial. *Newsweek*, August 13, 2007, 20–29.

²¹ Thacker, P. D. The many travails of Ben Santer, an interview. *Environmental Science & Technology*, 40(19), October 1, 2006, 5834–5837.

rainfall, and snowfall patterns, storm severity, sea level, and more. Some successful projections have been made. GCMs successfully projected the climate cooling effect of the eruption of the Philippine's Mt. Pinatubo in 1990, which injected huge quantities of sulfur dioxide and particulates into the atmosphere. They also had success in reproducing the global warming of the past century. ▪ One variable that scientists continue to struggle with is the effect of atmospheric particulates on climate. Sulfate aerosols increase the reflection of radiation from the sun back into space, which cools the troposphere. They also absorb infrared radiation from the Earth, but overall are agreed to have a cooling effect. However, as noted in Chapter 5, soot aerosols may have a net warming effect. ▪ Clouds are another uncertainty. High clouds appear to enhance the greenhouse effect, but low clouds reflect incoming sunlight back into space and have a cooling effect. The current net effect of clouds is cooling.

Modelers usually interpret data conservatively, not wanting to provide unnecessarily dire projections, especially when a process is not well understood. Sometimes that results in the real world being more alarming than the models. This happened when the National Snow and Ice Data Center analyzed nearly 60 years of sea ice records from satellites, ships, and airplanes using models. The simulation indicated that Arctic ice had been disappearing at an average rate of 2.5% a decade since 1953. However, when, as is possible, actual measurements were made the reality indicated that it was disappearing at 7.8% per decade.²² ▪ Models are powerful, but cannot give absolute answers. A major limitation of GCMs is that they cannot predict what will happen in any particular small region, such as a state or province. Certain areas may cool not warm, which does not necessarily contradict climate models. GCMs are only as accurate as the information incorporated into them and must be continuously modified as additional data are gathered. But information remains incomplete. ▪ Among projections that are common to all GCMs is that, once warming begins, it will continue for hundreds of years. This is another reason to take global warming seriously, even though uncertainties remain.

Intergovernmental Panel on Climate Change (IPCC)

The IPCC performs ongoing analyses of climate change and issues a report every 5 or 6 years. Many conclusions from the most recent IPCC report (2007)²³ are interspersed throughout this chapter. Consider also the following conclusions on a warming world. That Earth's climate is now warming is "unequivocal as is evident from increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global mean sea level." Also 11 of 12 years before 2007 rank among the hottest years on record. Records started in 1850, when sufficient worldwide temperature measurements began. Moreover, in the past half-century "cold days, cold nights, and frost have become less frequent, while hot days, hot nights, and heat waves have become more frequent." What is

²² Engelhaupt, E. Models underestimate global warming impacts. *Environmental Science & Technology*, **41**(13), July 1, 2007, 4488.

²³ Ekwurzel, B. Findings of the IPCC fourth assessment report: climate change science, a summary. Union of Concerned Scientists, July, 2007, http://www.ucsusa.org/global_warming/science/ipcc-highlights1.html.

the cause? The authors of the 2007 IPCC report say “It is very likely that [human-caused] greenhouse gas increases caused most of the average temperature increases since the mid-twentieth century.”

SECTION III

What are sources of greenhouse gases and what is their environmental fate?

Note, in Figure 7.8 the term *carbon dioxide equivalent*. To understand this term, see Table 7.1. Notice that CO₂ has a warming potential of 1 whereas methane is 25. The carbon dioxide equivalent takes into account both the concentration of a greenhouse gas such as methane and its warming potential.

Greenhouse gases and their sources are considered individually in the text below. However, it is useful to consider a summary of the gases as a group and their sources by industrial sector such as industry or forestry. This is done in the IPCC figure, Figure 7.9.

Overview of greenhouse gases

Carbon dioxide does not strongly absorb infrared radiation (heat). However, because CO₂ is emitted in much greater quantities than any other greenhouse gas, it is the major greenhouse gas. Others of importance are methane, ground-level ozone, and nitrous oxide. CFCs and a number of other trace gases also absorb infrared radiation. ▪ Some scientists now call for *soot* (not a gas!) to be included in the list. ▪ Greenhouse gases are minor components of

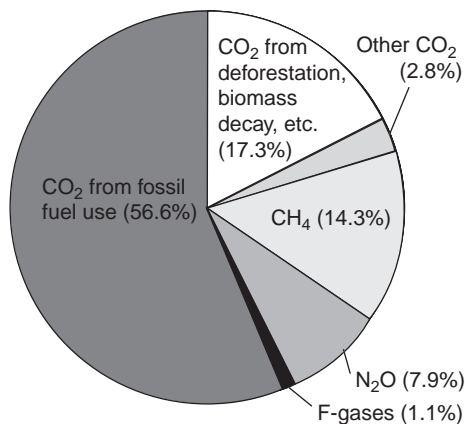


Figure 7.8

Share of global emissions, in carbon dioxide equivalent, 2004. Credit: IPCC

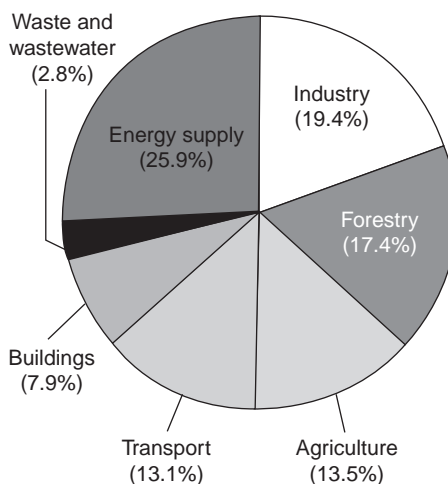


Figure 7.9

Percentage of global emissions by various sectors, 2004. Credit: IPCC

atmospheric gases, but this does not detract from their seriousness. The concentration of even the most abundant greenhouse gas, CO₂ is only about 387 ppm (0.0387%) – compare this to nitrogen’s 78.1% and oxygen’s 21%. However, neither nitrogen nor oxygen absorbs infrared radiation. Water vapor is the most plentiful greenhouse “gas” with a concentration of almost 1%, and global warming skeptics sometimes give this as a reason to discount the influence of other greenhouse gases. However, we know that CO₂, methane, nitrous oxide, and other greenhouse gases absorb infrared radiation coming from the Earth, and that their atmospheric levels have increased and continue to increase. We also know that ice-core records of 800 000 years shows that CO₂ levels were higher during warm periods and lower during cold periods (albeit one must be careful about attributing causality). Moreover, over 800 000 years CO₂ levels did not increase beyond 280 ppm whereas now they are nearly 40% greater.

Water vapor

As warming occurs, the atmosphere is able to hold more moisture. It has, in fact, been shown that atmospheric content of vapor has increased since 1988, something that natural variability cannot account for. Commenting on this phenomenon, climate modeler, Benjamin Santer said, “This is the first identification of a human fingerprint on the amount of water vapor in the atmosphere.” Because it acts as a greenhouse gas, an increased level of water vapor in the atmosphere absorbs more infrared radiation from the Earth which, in turn, further warms the atmosphere. This is a so-called *positive feedback loop*. Research on increased water vapor is still in its early stages.²⁴

²⁴ Humans increase moisture content of atmosphere. *Chemical & Engineering News*, **85**(39), September 24, 2007, 72.

Carbon dioxide

CO₂ accounts for about 75% of the current warming. ▪ Worldwide, the major human source of CO₂ is fossil fuel combustion (coal, petroleum, and natural gas). Fossil fuels are responsible for ~80% of anthropogenic CO₂ emissions. Coal has the greatest carbon content, and thus emits more CO₂ when burned than petroleum does. Natural gas, with the lowest carbon content among the three, emits the least. Worldwide, electric power plants are the major source of CO₂ emissions including the United States and China. Globally, transportation is second. In the United States, petroleum-fueled motor vehicles contribute about 25% of CO₂ emissions. ▪ Deforestation (especially tropical deforestation) is second to fossil-fuel burning as a CO₂ source. This happens because when felled trees are burned, their stored carbon is released as CO₂ to the atmosphere. Worsening this situation, deforestation leaves fewer growing trees to take up atmospheric CO₂. ▪ Trees grown on a sustainable basis make no net contribution to CO₂ levels. *Sustainable growth* occurs when – on a long-term basis – no more tree biomass is harvested than what grows. ▪ Natural CO₂ emissions sources are large (Figure 7.2), releases from oceans and land; these include plant respiration; microbe respiration as they decompose dead plant and animal matter; and animal expiration, including human expiration. Volcanoes are, periodically, a large natural source.

Only in recent decades have we considered CO₂ in outside air as a pollutant. CO₂ is, after all, vital to life. ▪ Trees, plants, phytoplankton, and photosynthetic bacteria, capture CO₂ from air and through photosynthesis make carbohydrates, proteins, lipids, and other biochemicals. Almost all biochemicals found within living creatures derive directly or indirectly from atmospheric CO₂. Likewise, the hydrocarbons in coal, petroleum, and natural gas, were first formed as biochemicals in living creatures. ▪ Moreover, CO₂ is a waste gas respired by animals, plants and many bacteria.²⁵

CO₂ sinks

CO₂ is a fairly inert chemical and thus about 45% of the CO₂ emitted by human activities survive 100 years, some considerably longer. Strikingly, the 2007 IPCC report indicates that 20% of the 2007 fossil fuel emissions of carbon dioxide are expected to remain in the atmosphere for thousands of years. ▪ The remaining CO₂ enters two major sinks. One is *oceans*, which contain about 50 times more carbon than does the atmosphere. The second is *terrestrial biomass* including trees and grasses, which store about three times more CO₂ than the atmosphere (see Figure 7.2). ▪ Together, terrestrial ecosystems and oceans absorb up to half the CO₂ generated by human activities. These sinks have slowed the rate of increase in atmospheric CO₂, but they do not assimilate all the human-generated CO₂. ▪ Because of the long atmospheric lifetime of CO₂ levels continue to increase as more and more is emitted. Moreover, oceans may become less dependable sinks: CO₂ is less soluble in warmer water, so oceans will be less able to absorb it. This may already be happening in the Southern

²⁵ Students sometimes think that atmospheric CO₂ level is increasing due to an increasing human population expiring CO₂. This is not true. See *Frequently Asked Global Change Questions*. CDIAC, <http://cdiac.ornl.gov/faq.html#Q22>.

(Antarctic) Ocean.²⁶ Also, as water becomes more acidic, it is less able to absorb CO₂. ▪ The fate of CO₂ Absorbed into a terrestrial sink, much CO₂ is incorporated into biochemicals in plants and trees; the same is true of CO₂ taken up by photosynthetic bacteria in oceans. ▪ However, when CO₂ enters ocean waters, its fate can be different (Box 7.5).

Box 7.5

“The other CO₂ problem”: affecting the pH of the oceans²⁷**Calcium carbonate shells**

To examine “the other CO₂ problem,” look first at life in the oceans and the chemical, calcium carbonate, which is critical to building the shells of myriads of tiny creatures at the base of the oceans’ food chains, coral, plankton, some protozoa, and algae. Their calcium carbonate (CaCO₃) shells have been stable in ocean water because the oceans’ higher layers are super-saturated with CaCO₃ – there is always enough to build and maintain the shells. Supersaturated waters are what one researcher called “shell friendly.”

Fate of CO₂ in the oceans

When CO₂ reacts with water, *carbonic acid*, a weak acid is formed. Carbonic acid contributes little to acid deposition on land. But Earth’s oceans are a major sink for CO₂ and they have absorbed ~550 billion tons (500 billion tonnes) over the past 200 years, and continue to absorb about 2.2 billion tons (2 billion tonnes) a year, about 30% of the CO₂ emitted to the atmosphere from the combustion of fossil fuel. So – although carbonic acid is weak and oceans hold massive quantities of water – carbonic acid has initiated the process of *ocean acidification*.²⁸ The ocean’s pH has decreased by about 0.1 pH unit, about a 30% rise in acidity.

Why does acidification matter?

More CO₂ in the ocean means waters of a lower pH, less able to hold carbonate. This means less carbonate with which to build shells. Many studies have begun examining what happens under these circumstances. One active investigator is Ulf Riebesell, who examined coccolithophores (a class of phytoplankton). In experimental tanks he found a clear relation between rising CO₂ levels and the ability of these organisms to make normal shells. In another study actually done in the ocean, Riebesell used large sacks of ocean water in a fjord near Bergen, Norway; these bags held many types of shell-building creatures. Again, he saw that increased levels of CO₂ led to less calcification.²⁸

²⁶ LeQuere, C. Saturation of the Southern Ocean CO₂ sink due to recent climate change. *Science*, **316**(5832), June 22, 2007, 1735–1738.

²⁷ (1) Zeebel, R. E., Zachos, J. C., Caldeira, K. and Tyrrell, T. Oceans: carbon emissions and acidification. *Science* **321**(5885), July 4 2008, 51–52. (2) Petkewich, R. Off-balance ocean: acidification from absorbing atmospheric CO₂ is changing the ocean’s chemistry. *Chemical & Engineering News*, **87**(8) February 23, 2009. Web Exclusive <http://pubs.acs.org/cen/science/87/8708sci2.html>. (3) Hansson, L. Coral reefs may start dissolving when atmospheric CO₂ doubles. European Project on Ocean Acidification, March 13, 2009. <http://oceanacidification.wordpress.com/>.

²⁸ Ruttimann, J. Sick seas (the rising level of carbon dioxide in the ocean). *Nature*, **442**(31), August, 2006, 978–980. <http://perso.crans.org/pruvost/442978a.pdf>.

Methane

Methane (CH₄), a simple hydrocarbon gas, accounts for about 20% of the greenhouse effect, second in importance only to CO₂. Its atmospheric concentration is only 1720 ppb, a level more than 200 times lower than that of CO₂, *but* molecule for molecule, methane has ~25 times greater global warming potential (GWP, ability to absorb Earth's infrared radiation) than does CO₂. Fortunately, its atmospheric lifetime, 12 years or less is much shorter. As is the case for CO₂, the atmospheric CH₄ level "exceeds by far the natural range over the last 650 000 years." Also like CO₂, levels of methane have increased at a rate "very likely ... unprecedented in more than 10 000 years." Surprisingly, starting in 1980, methane's atmospheric levels almost stabilized. However, in 2007 they sharply increased, possibly because of increasing emissions from Arctic wetlands and rapid industrialization in Asia.²⁹

Methane sources³⁰

- Anthropogenic sources About half of methane emissions result from human activity.³¹ In the United States, three major methane sources are the production, distribution, and use of energy; waste management; and agriculture.
 - Energy: methane escapes during coal mining; natural gas (mostly methane) production and use; and from the flaring of natural gas from oil wells.
 - Waste management: decomposition of organic solid waste in landfills (food, paper, wood, and plant debris) is a large source of US emissions. US landfills by themselves emit about 7% of the world's methane.
 - Agriculture: a dairy cow belches up to 53 gallons (200 l) a day; methane is also produced during manure management. Rice paddies are a major agricultural source, especially considered worldwide.
 - Hydroelectric dams can be large sources too as vegetation rots beneath their reservoirs.
- Natural sources: When microbial action occurs with little or no oxygen, there is likely to be methane generation.
 - Worldwide, natural wetlands release about three-quarters of naturally emitted methane.
 - Tropical termites release another 11% as a result of their symbiotic relationship with microorganisms. Tropical insects or those living indoors, for instance, cockroaches, produce especially large amounts.
 - Oceans emit perhaps 8% of global methane.
 - Of much interest is the recent confirmation that methane is emitted by at least some living plants, which may change some of the percentages just given.³²
- An unusual natural source: Methane hydrates are solid "cages" of water molecules containing methane, which currently emit only a little methane. These clathrates are

²⁹ Carbon dioxide, methane rise sharply in 2007, April 24, 2008, <http://yubanet.com/usa/Carbon-Dioxide-Methane-Rise-Sharply-in-2007.php>.

³⁰ Methane, sources and emissions. *US EPA*, 2006, <http://www.epa.gov/methane/sources.html>.

³¹ First note that *aerobic* bacteria, those using oxygen, metabolize organic material to CO₂ and water. However, the end product of *anaerobic* bacteria (bacteria not using oxygen) is methane. Methane is generated under conditions with little or no oxygen as when vegetation rots underground or underwater as in swamps, bogs, or rice paddies, landfills and open dumps, and in the stomachs of ruminant livestock and termites.

³² Chatterfee, R. Methane-making plants in Inner Mongolian steppe. *Environmental Science & Technology*, **42**(1), January 1, 2007, 4–8.

found deep underground in polar regions and in ocean sediments of the world's outer continental margin. When recovered in icy chunks and lit, they will ignite. There is great interest in exploiting methane clathrates for fuel. Geologist Arthur Johnson states "the question now is not whether industry will exploit hydrates but how soon." Others are concerned about methane being released by clathrates.³³

- A worrisome methane source: Permafrost in Siberia and Alaska contain immense quantities of organic material, much stored since the last ice age. Average temperatures in Alaska, western Canada, and eastern Russia are 4–7°F (3–4°C) warmer than 50 years ago. Some permafrost has begun thawing, and its organic material is being metabolized by anaerobic microbes. In some Siberian lakes formed by melting permafrost, methane is bubbling to the surface. These are circumstances posing great concern.³⁴

Fate of methane

Through reactions that begin with the hydroxyl radical, methane is oxidized to CO₂ and water. This reaction provides a major source of water vapor to the upper stratosphere. ▪ Soils that are well aerated do absorb some methane too as the soils contain "methanotrophs," bacteria using methane as food and oxidizing it to CO₂.

Ozone³⁵ and ozone sources

Ground-level ozone (O₃) is a GHG whose levels have increased about 25% as compared to the pre-industrial era. The IPCC now considers ozone to be the third most important greenhouse gas after carbon dioxide and methane, accounting for about a seventh of global warming. However, ozone is more difficult to study because its lifetime is so short in hot sunny weather that there is not time for it to mix well in the atmosphere or be transported long distances. Thus, ozone-induced warming takes place where the ozone is generated in western North America, Eastern Europe, and Central Asia. ▪ The story changes in the winter and spring: cool conditions allow ozone to last long enough to be transported to the Arctic from its sources. There its heat-absorbing properties become especially important: a NASA study concluded that tropospheric ozone accounts for one-third to a half of the observed

³³ Bohannon, J. Weighing the climate risks of an untapped fossil fuel. *Science*, **319**(5871), March 28, 2008, 1753.

³⁴ (1) Markey, S. Thawing permafrost could supercharge warming, study says. *National Geographic News*, June 15, 2006, <http://news.nationalgeographic.com/news/2006/06/060615-global-warming.html>. (2) Walter, K. M., Zimov, S. A., Chanton, J. P., Verbyla, D. and Chapin, III, F. S., Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. *Nature*, **443**, September 7, 2006, 71–75. (3) Zimov, S. A., Schuur, E. A. G., and Chapin, F. S. Permafrost and the global carbon budget. *Science*, **312**(5780), June 16, 2006, 1612–1613.

³⁵ In the stratosphere, ozone absorbs ultraviolet light from the sun, preventing harmful radiation from reaching the Earth. When stratospheric ozone is destroyed by free radicals (produced from CFCs), a cooling effect is exerted. This partially offsets the warming effect of ground-level ozone. However, as CFCs are eliminated from the stratosphere, less ozone will be destroyed and there will be less offsetting of ground-level ozone's warming effect.

warming in the Arctic winter and spring.³⁶ This remarkable finding needs further study. If confirmed, it provides yet another reason to reduce ground-level ozone.

Ozone's fate

Ozone (O_3) is a very reactive chemical, much more so than ordinary oxygen, O_2 . Ozone “prefers” to become the more stable O_2 . So, as you might expect, O_3 is easy to destroy. ▪ Two ozone molecules can react with one another to yield three molecules of O_2 . ▪ High energy radiation from the sun can photolyze O_3 (cause it to decompose). ▪ More likely than these reactions is O_3 coming in contact with many other substances – your lungs, your eyes, your sweater, or any material that allows it to react in such a way that one of its oxygen atoms can be stripped away leaving the more stable O_2 .

Nitrous oxide

Nitrous oxide (N_2O) accounts for about 5% of the greenhouse effect. Although its atmospheric concentration is only 320 ppb, it has 300 times greater ability to absorb infrared radiation than CO_2 does. Its atmospheric lifespan, over 100 years, is similar to that of CO_2 . ▪ The major natural sources of N_2O emissions are microbes that breakdown nitrogen chemicals in soil – especially wet tropical forest soils – and in the oceans. Such bacterial action is nothing new. ▪ However, when humans add nitrogen-containing fertilizers or till the soil, it stimulates growth, and the microbes convert the fertilizer to other chemicals including N_2O . ▪ Fossil-fuel burning in motor vehicles and in electric power plants also produces some N_2O . ▪ In Box 7.6, below, see that the livestock sector may have replaced transportation as the largest source on N_2O .

▪ Nylon and nitric-acid production produce a small amount.³⁷

Fate of N_2O

As you may surmise from its long lifetime, N_2O is fairly inert in the atmosphere. However, it can move from the troposphere to the stratosphere, where it is converted to the nitric oxide radical ($NO\cdot$), capable of destroying stratospheric ozone. Thus nitrous oxide is a naturally occurring regulator of stratospheric ozone.

³⁶ Cole, S. NASA study links “smog” to Arctic warming. *Goddard Space Flight Center*, March 14, 2006, http://www.nasa.gov/centers/goddard/news/topstory/2006/troposphere_ozone.html

³⁷ Recall from Chapters 5 and 6 that nitrate and nitric acid are deposited to earth and water including oceans. Moreover, as seen in Chapter 9, nitrogen fertilizer running off with rainwater also reaches the oceans. Together these represent a significant portion of the bioavailable (fixed) nitrogen reaching the ocean. There they fertilize marine plant life, which, as it grows, is able to take up more atmospheric CO_2 , removing as much as 10% of anthropomorphic CO_2 . However, some of the nitrogen compounds are then converted into N_2O , which is released to the atmosphere. And, because N_2O is such a powerful greenhouse gas, this cancels out about two-thirds of the plants removal of CO_2 . This study indicates that human-produced nitrogen compounds that reach the sea lead to a significant increase of the greenhouse gas, nitrous oxide, to the atmosphere. Atmosphere threatened by nitrogen pollutants entering ocean. *ScienceDaily*, May 16, 2008, <http://www.sciencedaily.com/releases/2008/05/080515145350.htm>.

Box 7.6

Livestock and greenhouse gas emissions

The UN's FAO (Food and Agriculture Organization) has reported on the massive environmental impact of the livestock industry.³⁸ It examined the worldwide impacts both of raising and feeding livestock, and demonstrated its major environmental impact. The livestock sector contributes to major water pollution problems, and to pollution resulting from land degradation. *It also contributes an estimated 18% of all anthropogenic greenhouse gas emissions worldwide* calculated as CO₂ equivalents: this is as much as the transportation sector. For individual gases, this breaks down to 9% of CO₂ emissions, 37% of methane, and 65% of nitrous oxide. Raising livestock is also responsible for about two-thirds of anthropogenic ammonia emissions which contribute to acid deposition. In addition to pollution, the livestock sector is also a major source of land and water degradation. Although the report is somber, the authors make recommendations as to how to reduce the environmental impact of livestock production including how to better grow feed for livestock. Senior author, FAO's Henning Steinfeld noted, "Urgent action is required to remedy the situation."

Other greenhouse gases

Looking at Table 7.1 you see that the last three gases are examples of very potent greenhouse gases, CFC-12, halon-1211 and SF₆ (sulfur hexafluoride). Together along with other members of their respective families they represented about two percent of US greenhouse gas emissions in 2006. None have natural sources. ▪ Sulfur hexafluoride (SF₆) is used in magnesium smelting and as an insulator in electrical equipment. ▪ The synthetic chemicals, CFCs and halons, are potent greenhouse gases, but the Montreal protocol has banned them, and it's possible these two categories of chemicals may disappear as greenhouse gases. We will return to CFCs in Chapter 8.

Soot as a greenhouse "gas"

Prior to 2001, Western scientists had been familiar only with North American and European sulfate hazes. These cool the atmosphere by reflecting sunlight back into space, and also (when present in clouds) make clouds more reflective. ▪ But the brown Asian hazes (Chapter 5) contain more soot than most Western hazes. Soot appears to absorb sunlight and heat the atmospheric layers in which it is found. A recent study indicated that the IPCC has underestimated the impact of black carbon on global warming.³⁹

³⁸ Steinfeld, H., Gerber, P., Wassenaar, T. *et al.* C. Livestock's long shadow, environmental issues and options. *UN Food and Agriculture Organization*, 2006, <ftp://ftp.fao.org/docrep/fao/010/a0701e/a0701e00.pdf>.

³⁹ Service, R. F. Study fingers soot as a major player in global warming. *Science*, **319**(5871), March 28, 2008, 1745.

Questions 7.1

- 1 How does the eruption of a volcano such as Mt. Pinatubo lead to a temporary cooling of the climate?
- 2 Trees that are grown on a sustainable basis have no net emission of CO₂. What does this mean?
- 3 Some still are not sure if the climate warming that we see is (a) due to natural cycles or (b) is human induced. What actions should humans take if scenario (a) is correct? If scenario (b) is correct?
- 4 Consider the following: energy usage generates the greatest amount of greenhouse gases; energy generation and usage, quite aside from greenhouse gases, produces major environmental damage; energy availability is a national security issue for many nations. Given such facts, do you still see a major difference in how we should respond to scenario (a) and scenario (b) in question 3?
- 5 What does the following statement mean: Sustainably-grown trees and other biomass make no net contribution to carbon dioxide?
- 6 The expiration of CO₂ by more than 6 billion people on Earth doesn't make a net contribution to atmospheric CO₂. Nonetheless, there is an association between growing population and greenhouse gas emissions. (a) How does a growing human population lead to increased CO₂ emissions? (b) To increased methane emissions? (c) To increased nitrous oxide emissions?
- 7 Why does increasing industrialization in poor nations increase CO₂ emissions more than if that increasing industrialization was occurring in well-to-do countries?
- 8 Other than reducing greenhouse gas emissions, what are three additional environmental reasons to reduce fossil fuel use?
- 9 Trees, especially young rapidly growing trees, serve as an important terrestrial sink for CO₂ by taking it up from the atmosphere. What are three *other* environmental reasons to avoid deforestation?
- 10 Review the uncertainties related to global climate change. Which among them do you consider most legitimate? Explain.
- 11 Climate warming is expected to increase ground-level air pollution. Why?
- 12 Think about a college campus. What steps could be taken, without cost, to reduce greenhouse gas emissions? What steps would cost only a little money? Which would have longer pay back times?
- 13 What is the meaning of the word (verb), *project* as used by the IPCC?
- 14 The IPCC believes that 75% of the warming expected in the twenty-first century will be due to CO₂. What does this tell you about the predominating fuel that the world's people will be burning?
- 15 Go to the Climate change calculator at *American Forests*, <http://www.americanforests.org/resources/ccc/>. Use the calculator to determine how much your household contributes to atmospheric CO₂. Based on your finding at this site: (a) What steps could you take to reduce your personal greenhouse gas emissions? (b) Which are you most likely to take?

SECTION IV

Using international agreements to reduce greenhouse gas emissions

The Rio agreement

In 1992 at the UN Earth Summit in Rio de Janeiro, many countries signed an agreement under the UN Framework Convention on Climate Change. Its objective was to stabilize “greenhouse gas concentrations . . . at a level that would prevent dangerous anthropogenic interference with the climate system.” About 150 countries ratified the Convention, agreeing to return their greenhouse gas emissions to 1990 levels by 2000. However, emissions in the United States and many other countries continued to climb. Obviously, stronger measures were needed: a plan that clearly specified exactly what reductions in greenhouse gas emissions would occur and by when.

Kyoto Protocol

In the Kyoto Protocol adopted in late 1997, industrialized countries agreed to reduce GHG emissions at least 5.2% below 1990 levels between the years 2008 and 2012. The European Union is committed to an 8% reduction. The treaty was in effect once it had been ratified by at least 55 nations producing more than 55% of the developed world’s greenhouse gases. It is legally binding to those that ratify it. If a country fails to make the cuts, it will need to make both the initial promised cuts and 30% more. The US Administration of President George Bush in 2001 refused to ratify this “fatally flawed” document.⁴⁰ The Obama Administration, on the contrary, is becoming active in reducing GHG emissions. A major Bush Administration objection to Kyoto was that it does not require less-developed countries to reduce GHG emissions, even those that ratify the treaty. They were exempted because industrialized countries were largely responsible for current levels of atmospheric greenhouse gases and are better able, financially and technically, to lead the way to reductions. Nonetheless, rapidly increasing emissions from less-developed countries could overwhelm reductions made in industrial countries. China and India plan to build hundreds of new coal-powered electric power plants. This presents a serious problem relative to future world emissions.

⁴⁰ A full six years later the Bush administration called on the world’s major emitters of greenhouse gases, fifteen nations to reach a consensus on an emissions goal, but left it up to each nation to decide how to meet that target. Most other nations did not react kindly to this belated proposal. The US plans to cut *carbon intensity*, that is, GHG emissions per dollar of economic output. Some less-developed countries may choose to do this as it may be less strict than caps on emissions.

Making Kyoto work—emissions trading or tax

- Recall from Chapter 6 emissions trading as applied to power plants emitting sulfur dioxide. Analogously, in *Greenhouse Gas Trading*, a company reducing GHG emissions more than required by a *cap and trade* (emissions trading) law could sell that amount to a company emitting too much CO₂. The buyer receives credit just as if it had made the reduction. ■ The European Union sees this as the most cost-effective way to meet the 8% reduction in GHG emissions required by Kyoto. It has set up a market under which 12 000 power plants and energy-intensive industries (e.g., steel making) are given carbon dioxide quotas. If they overshoot their quota, they buy allowances in the market or pay a financial penalty. If they emit less, they can sell the quotas.
- Another approach is a *carbon tax*, a fee levied on the carbon content of a fuel, or on the amount of CO₂ that a facility releases; thus there is no limit on emissions so long as the tax is paid. However, regulators could raise the tax over time, providing an incentive to cut emissions more.
- A different type of carbon “tax” is in effect in the province of British Columbia (Canada). Both businesses and residents pay a carbon tax on their gasoline, diesel, natural gas, coal, propane, and home heating fuel. The tax starts at \$10 per metric tonne of carbon emitted and rises by \$5 each year until it reaches \$30 a tonne. The tax is actually revenue neutral as its income will be returned via tax cuts and other means. The tax is expected to cut CO₂ emissions 5–10% over the first decade, but if the tax keeps increasing, the expected reductions will be greater. The measure has received considerable support in British Columbia and there is hope other locales will follow suit.⁴¹

Making Kyoto work: flexibility mechanisms

Flexibility mechanisms are one means a nation can use to get credit for reducing emissions. These were set up to provide flexibility in how countries can pursue GHG reductions. ■ In the *Clean Development Mechanism*, a rich nation finances projects in less-developed countries and receives credit (carbon offsets) as if it had made the cuts itself. It may plant a forest to take up atmospheric CO₂, pay for renewable energy projects such as solar roofs or wind farms (to provide electricity without producing CO₂), help countries build energy-efficient factories, or to capture and use methane from landfills. Hundreds of such projects are already in operation around the world. ■ These mechanisms are intended to *supplement not replace* direct actions by a country or company such as reducing fossil fuel use.

Kyoto Protocol reductions but a small beginning

If industrialized countries ratifying the treaty fulfill their commitments, they will need to have reduced GHG emissions (primarily CO₂ and methane) about 5.2% below 1990

⁴¹ (1) Pelley, J. Carbon cap or tax? *Environmental Science & Technology*, **42**(8), April 15, 2008, 2214. (2) Pelley, J. First sweeping carbon tax in North America. *Environmental Science & Technology*. **42**(8), March 17, 2008, 2215.

emission by the year 2012. This is indeed a modest reduction considering that cuts of 60% or more are deemed necessary to stabilize climate, so Kyoto can be but one small step toward much more ambitious cuts. However, Kyoto is stimulating the research and development necessary to more ambitious reductions in emissions while also bringing alternative and sustainable energy sources to fruition. This happened in the United States too as, even under the Bush administration many states, cities and corporations chose to move forward on their own. Before 2012 the world will presumably be better able to move to more ambitious reductions.

SECTION V

What measures are being used to reduce GHG emissions?

International agreements set up what final results need to be, but how do individuals, businesses, cities, states, and nations actually make reductions in GHG emissions?

Conservation and efficiency to reduce CO₂ emissions⁴²

Remember the concept of pollution prevention from earlier chapters, conservation. Use less fossil fuel and use it more efficiently – produce more energy per amount used. ▪ As of now, buildings account for 72% of US electricity consumption and also emit 38% of human-generated CO₂.⁴³ So we need to make all new construction energy efficient and retrofit older buildings for energy efficiency. ▪ Have utilities use “co-generation,” which allows more of the energy produced to be captured and used. ▪ Use more energy-efficient industrial motors and household appliances. ▪ Greatly improve the efficiency of motor vehicles. ▪ Work on widespread adoption of energy sources that don’t emit greenhouse gases including wind, solar, and, more controversially, nuclear power. ▪ Emphasize individual and business conservation including simple measures such as replacing all incandescent lights with much more efficient compact fluorescent lights (CFLs). Improve appliance circuits so they don’t draw current after being turned “off.” ▪ To promote conservation by industry,

⁴² To provide a sense of how much efficiency improvements could accomplish, see the report: Reducing US greenhouse gas emissions: how much at what cost? McKinsey & Company and The Conference Board, December, 2007, www.mckinsey.com/greenhousegas. The authors did a detailed analysis of opportunities to reduce CO₂ and other GHG emissions. They concluded that the US could reduce emissions 40% by 2030 at “manageable costs. Almost 40% of the reductions are options that would pay for themselves over their lifetimes. Examples are improving energy efficiency in buildings, appliances, and industry. The costs would be about one trillion dollars, that is about 1.5% of the \$77 trillion in investments the US economy expects to make over this period. Also: Gardner, T. US lifestyle won’t have to change in CO₂ cut. *Reuters News Service*, December 3, 2007.

⁴³ Green building research. US Green Building Council, 2008, <http://www.usgbc.org/DisplayPage.aspx?CMSPageID=1718>.

tax carbon emissions as the Scandinavian countries started doing nearly 20 years ago.

- Conserving forests, especially tropical forests, is critical as these sequester large amounts of carbon. Deforestation now accounts for 20% or more of current anthropogenic CO₂ emissions. Moreover, there is the concurrent need to conserve forest habitat.

Reducing population growth

A US National Academy of Sciences report stated that population growth is the major single driver of atmospheric pollution.

- A growing population leads to growing use of fossil fuels and greater pressures to cut forests, which both enhance CO₂ emissions.
- As population increases, so does agricultural activity, both more cattle and more rice paddies leading to enhanced methane emissions.
- The United States lacks a population policy and population is growing ~1% a year. Not surprisingly, CO₂ emissions have increased almost in lock step.

Industry action to reduce GHG emissions

Just before the Bali climate change conference (December 2007), 150 major transnational corporations endorsed mandatory cuts in GHG emissions. Among them were Coca-Cola, General Electric, Shell, Nestlé, Nike, DuPont, Johnson & Johnson, British Airways, and Shanghai Electric.⁴⁴ They stated that the scientific evidence for climate change is “now overwhelming,” and believe a legally binding agreement will “give business the confidence to make those long-term investments in lower-carbon technologies.” What are there other reasons that businesses could choose to support reductions in GHG emissions?

- Some have financial stakes, e.g., those making energy-efficient products and environmental controls.
- Many insurance companies work to combat global warming. They insure against climatic events such as severe storms and fear the increased incidence of extreme events that warming can bring. These could lead to major financial losses.
- Some US companies feared the economy would be harmed if the United States is *not* part of the Kyoto protocol because European companies will get a head start in developing “climate-friendly technologies.” That may be occurring. Others believe that emission controls will be mandated, and want to get a head start.
- Many recognize that projects to reduce CO₂ emissions also result in energy conservation meaning less is spent on energy.

A number of global corporations have pledged to reduce greenhouse gas emissions at all their facilities. Some also provide technical advice to other businesses. Those voluntarily reducing GHG emissions provide examples for others. But most observers believe that voluntary cooperation is not enough. After the Kyoto protocol entered into force, businesses in countries that ratified it need to adhere to specific reductions.

- Many energy conservation

⁴⁴ Eilperin, J. 150 global firms seek mandatory cuts in greenhouse gas emissions. *Washington Post*, November 30, 2007, A03.

and efficiency measures are appropriate to almost all companies. General Electric in its *Ecoimagination* program, started in 2004, committed to reducing its GHG emissions 1% by 2012 and to improve energy efficiency 30% by the end of 2012 (compared to 2004). One percent is modest, but without this action, GHG emissions would likely have grown by about 30% by 2012 based on GE's projected growth. As of 2007, GE's GHG emissions from operations were reduced 8% compared to 2004, and its energy intensity reduced by 33%. However, many industries oppose mandatory cuts in GHG emissions: these include many of the oil and coal industries, as well as those manufacturing motor vehicles.

Reductions in specific greenhouse gases

Most of the GHG reductions noted under Industry action relate to carbon dioxide. Other greenhouse gases must also be reduced.

Reducing greenhouse gases with high GWP

- Some of DuPont's facilities release the high GWP N_2O and the very high GWP fluorochemicals. See Table 7.1. By 2010, DuPont plans to reduce emissions of these by 65% compared to 1990. Also, DuPont pledges not to increase energy use as compared to 1990, but to increase its use of renewable energy, enough to provide 10% of its energy needs by 2010.
- Motorola uses the strong infrared absorbers, perfluorocarbons (PFC) to etch and clean semiconductors. It aims to half their use by 2010 by finding other means of cleaning. The World Semiconductor Council urged its members to reduce PFC emissions 10% by 2010 as compared to 1995.
- Twelve magnesium-producing companies formed a partnership to find means to reduce emissions of the potent GHG sulfur hexafluoride (SF_6) which has a GWP 23 000 times that of CO_2 . SF_6 is used to produce magnesium and magnesium parts and, as societal use of magnesium increases so will SF_6 use unless steps are taken.

Reducing CFCs

CFCs have a very high GWP. Adoption of the Montreal Protocol (Chapter 8) has already resulted in major reductions in these human-made gases. It is calculated that the Montreal Protocol had more impact in reducing greenhouse gas emissions than the first phase targets of the Kyoto Protocol, which specifically addressed heat-trapping gases.⁴⁵

Reducing methane emissions

The US EPA has a number of voluntary programs directed toward reducing methane emissions. Each differs depending on the source of the methane. ▀ Landfills Between

⁴⁵ Chatterjee, R. Sharing sustainable solutions. *Environmental Science & Technology*, **41**(10), May 10, 2007, 3398–3399.

40–60% of the gases emitted from landfills is methane. The EPA encourages capturing the methane and burning it for energy. ▪ Livestock Large facilities maintain lagoons and holding tanks filled with liquid manure. These generate methane.⁴⁶ The EPA encourages technologies to recover and burn the methane for on-farm energy. ▪ Animal belching Work is ongoing to change animal diets so that they generate less methane. ▪ Coal mining An emphasis is put on recovering and using the methane trapped in coal deposits instead of venting it to the atmosphere. ▪ Natural gas and oil industry The EPA has programs to reduce methane emissions during production, transmission, and distribution of natural gas (methane). ▪ Growing rice The level of methane emission varies with soil conditions, production practices, and climate. Methane emissions are reduced by drying out rice paddies when not in use.⁴⁷ Agricultural techniques are being developed, which may have lower methane emissions. ▪ Municipal and industrial wastewater treatment plants Wastewater can be treated to remove organic material that would otherwise be available to the anaerobic bacteria.

Reducing nitrous oxide emissions

The major human-generated emissions of N₂O come from agriculture, mostly from fertilizing soils with nitrogen fertilizers. American farmers often use too much fertilizer on farm crops. So, to reduce N₂O emissions, it is important to reduce applications of nitrogen fertilizer. For several reasons farmers often don't want to do this.

Reducing soot

Soot has a much shorter atmospheric life than any of the greenhouse gases: it can be rained out of the atmosphere within a week or two. Thus, if soot production was significantly reduced, an impact would be quickly seen. However, reducing soot means that burning fossil fuels – and burning wood, dung, and other natural materials – need to be more efficient. As addressed in earlier chapters, efficient combustion can greatly reduce, even eliminate, soot. However, in less-developed countries that burn biofuels, it is difficult to make burning efficient – picture a woman cooking over an open fire. Nonetheless, there is ongoing effort to provide efficient wood-burning stoves to people who must cook this way. There is also pressure on governments of less-developed countries to ban inefficient two-stroke engines from vehicles.

City, state, and national efforts to reduce greenhouse gases

In the absence of federal action in the first 8 years of this century, many US states and cities began to take steps voluntarily. Many committed themselves to deep cuts in GHG emissions.

⁴⁶ Manure deposited directly onto pastures, or handled when it is dry, generates very little methane.

⁴⁷ Flooded rice paddies produce methane as conditions are ideal for anaerobic bacteria that produce methane: wet soil, organic compounds, and little oxygen.

State GHG reductions

- A group of Midwestern US states from Ohio west to Kansas – together representing the world's fifth largest producer of GHG (behind the whole of the United States, Russia, China, and India) developed a climate change accord. Governors of the 19 US states in the Western Governors' Association likewise formed a consortium to reduce GHG emissions; so did the northeastern States.
- None went so far as California,⁴⁸ which, by itself, is the world's sixth largest economy with the highest population of any US state. It is particularly concerned by studies showing the risk of climate change to California including coastal flooding, beach erosion, and loss of wetlands. California already had a head start in reducing GHG emissions because of energy policies passed many years ago: *California already uses only 7000 kilowatt-hours of electricity per capita a year, whereas the average in other US states is 12 000*. This happened because of policies taking such actions as mandating energy-efficient appliance standards, codes reducing energy use in new-home construction, and tax credits that assist alternative energy sources such as solar and wind. In 2006 California went much further: Governor Arnold Schwarzenegger issued an executive order committing California to lowering GHG emissions 11% by 2010 (as compared to 2000 levels), 25% by 2020, and 80% by 2050. The 2050 target is particularly notable because climate scientists say that reductions as much as 80% below 1990 levels are needed to avert dangerous global warming. ■ As just noted, California already had a framework to assist in its ambitious new program. Other examples of ongoing state programs are a voluntary program to encourage solar roofs for new homes; a mandate that utilities derive 20% of their power from renewable sources by 2010; and a law requiring cars to lower their CO₂ emissions – something strongly opposed by car manufacturers. Meanwhile, a 2006 University of California study found that capping carbon emissions, far from dragging the state's economy down, is expected to boost business while also creating 17 000 jobs. ■ Indeed, Senator Timothy Wirth (Colorado) believes that if the United States ratified Kyoto (or more likely now, its follow up treaty) this would encourage intensive research and development in technologies that would “create jobs and launch an era of economic growth akin to the start-up phase of the Internet.”

Cities⁴⁹

Cities have also become active. Greg Nickels, the mayor of Seattle, a city of 575 000 launched the US Mayors Climate Protection Agreement. Within a year he recruited 275 mayors representing 48 million Americans. Their goal is to match the targets of the Kyoto Protocol and reduce GHG emissions 7% by 2012. In Seattle, Nickels took novel initiatives

⁴⁸ (1) Pelley, J. California's Schwarzenegger does heavy lifting on global warming. *Environmental Science & Technology*. 39(5) August 1, 2005, 318A. (2) California confronts climate change. *Environmental Science & Technology*. 40(20), October 15, 2006, 6189–6191.

⁴⁹ (1) Milliken, M. and Wakabayashi, D. Seattle's green mayor brings Kyoto to the backyard. *Reuters*, August 4, 2006, http://www.enn.com/top_stories/article/4807. (2) Gardner, T. World mayors to meet in NY to fight global warming. *Reuters*, May 14, 2007.

such as urging residents to build rental units in their yards to help prevent sprawl, while giving new residents the opportunity to walk to work. Seattle provided its meter readers with Segways with which to get around the city, not automobiles. Its public electric plant, Seattle City Light, became the first major US utility to achieve zero net emissions of greenhouse gases. Mayor Nickels pledged that, “We will come up with a menu of things that other cities and states and ultimately the country can use as a menu for how we achieve this goal.” Many other mayors, in the United States and internationally are also taking, sometimes bold, steps to reduce emissions. ■ Another organization of cities around the United States and internationally was Cities for Climate Protection. Each city calculates its GHG emissions, sets a target for reducing them, and develops plans to meet its target. Boston, Massachusetts, committed itself to reducing municipal energy use 10%. Boston is taking efforts such as reducing energy use by streetlights, buildings, and transportation. Boston and other cities see reducing GHG emissions as also saving money through increased energy efficiency, while reducing local air pollution, and developing new jobs that involve creating, installing, and maintaining new technologies.

Nations

New Zealand pledged to become a zero-waste nation (Chapter 18). This included becoming carbon-neutral.⁵⁰ Germany, despite planning more coal-burning power plants is on track to meet its obligations to reduce GHG emissions under the Kyoto accord. Moreover, Germany – despite the fact that coal currently provides more than 60% of its energy – has legislation to cut GHG emissions by 36%.⁵¹ To do so, it is increasing use of renewable power sources, wind and geothermal, from less than 6% to at least 25%, and requiring that new buildings, including homes, be 30% more energy efficient. It wants to raise taxes on cars with poor gas mileage and require that emissions from new cars be reduced by half, which the auto industry strongly protests.

Less-developed countries

It was difficult for those negotiating Kyoto to get nations to agree to reduce GHG emissions 5% below 1990 levels. Even 5% is difficult because energy production increases each year in much of the world: it is difficult to produce more energy from burning more fossil fuels while also working to reduce GHG emissions although Germany is taking that route. A major reason the United States gave when refusing to ratify Kyoto is that less-developed countries were not required to reduce GHG emissions. However, the United States has ~17 times greater emissions per capita than does India. And the tiny emissions of impoverished nations such as those in sub-Saharan Africa are much lower still. These countries are and will be impacted by climate change, but did not contribute to the GHG burden. This situation

⁵⁰ It will commit to practices that don’t add more CO₂ to the atmosphere: some CO₂ will be emitted by motor vehicles and power plants. However, it will ensure that it has enough trees, and take other measures, to offset those emissions.

⁵¹ Germany takes dramatic step on climate change in Bali. *Christian Science Monitor*, December 5, 2007. <http://www.csmonitor.com/2007/1205/p10s01-woeu.html>.

Box 7.7

China's CO₂ emissions

China has recently become the world's largest emitter of CO₂. However, on a per capita basis US emissions remain way above China. China, even more than the United States, is a major user of coal: in 2005 China burned 2.23 billion tons (2 tonnes) up from 1.3 billion tons (1.18 tonnes) in 2000. Eighty percent of its electricity generation is from coal. In 2006, it built, on average, about two large coal power plants a week. Even as China plans to double its efficiency of energy use, you can see the immense problem that CO₂ emissions pose. ▪ The United States in 2005 used 1.13 billion tons (1.03 billion tonnes) in 2005 and generated half of its electricity from coal.

Meanwhile, India another large and growing user of coal consumes considerably smaller amounts than does China: 360 million tons (327 million tonnes) in 2000 up to 460 million tons (417 million tonnes) in 2005. About 68% of India's CO₂ emissions are from coal.

China's GHG emissions: ▪ Per capita emissions still remain low in comparison to the United States. ▪ China is a major manufacturer of consumer goods – which lead to large quantities of GHG emissions—because it exports so many goods to the United States and Western Europe, so the West is, in a very real sense, responsible for significant amounts of China's emissions. In fact, 5.3 million tons (4.81 million tonnes) of its carbon emissions go into international trade – almost 20% of the total global emissions accounted for by international trade.⁵² ▪ It has *avoided* emissions: recall that growing trees serve as a sink for atmospheric CO₂. China has massive reforestation projects. One is intended to stop desertification: forest cover in 1980 was 12%, in 2005 it was 18%, and is still growing. Its strict population-control policy could also be considered avoided emissions; its population is about 300 million fewer (and thus has lower emissions) than without population control. ▪ China's Gross Domestic Product grew, on average, 9.5% a year over 27 years, but CO₂ emissions grew only 5.4% a year. So, during this intensive industrial growth, carbon intensity (carbon emissions per unit of GDP) decreased (probably because the government is emphasizing energy efficiency).⁵³ ▪ An encouraging point is that China is developing renewable energy projects even more rapidly than it is building coal-fired plants – hydroelectric, nuclear, biomass, wind, and solar. China is a top manufacturer of solar equipment and wind turbines. ▪ Still, there remains cause for major concern.

led most developed countries to conclude that they must lead: find means to lower their own GHG emissions, develop new technologies, and transfer those technologies to poor nations. Thus, only industrialized nations are formal parties to the Kyoto Protocol. Some less-developed countries did decide to sign the treaty. Although they have no target to reduce emissions, they become eligible to receive assistance from developed nations. For instance, some coal-burning utility companies fund reforestation or energy-efficiency projects in poorer nations. They have found that they can accomplish GHG reductions more cheaply by doing these projects than by making major modifications to their own facilities, and they

⁵² Chatterjee, R. Carbon embodied in international trade. *Environmental Science & Technology*, **42**(5), March 1, 2008, 1391–1392.

⁵³ (1) Zeng, N., Climate change: the Chinese challenge. *Science*, **319**(5864), February 8, 2008, 730–731. (2) Salt surge puts crops in peril. *The National*, March 11, 2009, http://www.enn.com/top_stories/article/39441.

receive credit for emissions reduction. For its part, the less-developed country receives a worthwhile project.

SECTION VI

Can we mitigate the impacts of increased temperatures and of continuing GHG emissions?

Reductions in GHG emissions resulting from Kyoto won't halt warming, but rather will slow the increase in atmospheric CO₂ concentration and then, if we continue the reductions, eventually level them off. Meanwhile, because the CO₂ already added to the atmosphere will remain there for many years, our first choice, pollution prevention is not possible. So, what can we do to control the impact of this CO₂, i.e., to mitigate the impacts of climate change already "within the system"?

Adapting to climate change

What are feasible ways to halt the intrusion of salt water moving into groundwater and into drinking-water systems in New York and other coastal cities? In Bangladesh, salt water intrusion from a rising sea is already making soil more saline and reducing agricultural yields.⁵⁴ Many farmers switch to growing shrimp, but that has its own problems including unemployment for former farm workers. Are there actual mitigation actions can they take? ▪ *Mitigation* is alleviating the impacts of climate change. One is to erect seawalls to prevent coastal flooding as seas levels rise. New Bedford, Massachusetts has long had a rocky hurricane barrier. Or a seawall may help to stop salt water intrusion into groundwater and into drinking water. ▪ In Italy, the city of Venice introduced adjustable barriers to prevent tidal flooding. The Netherlands – which could see all its land eventually be below sea level – has constructed barricades to regulate the inward flow of the sea, and is working on measures such as houses that bob up and down as the seas come and go. ▪ But what about poor countries such as low-lying Bangladesh mentioned above? Research is ongoing to develop crops adapted to saline soil and to warmer climates. Currently, rice yields drop ~15% for each 1°C (1.8°F) rise in temperature, and salty soils reduce agricultural yields.⁵⁵ For those raising animals, finding breeds able to tolerate warmer temperatures would be a welcome mitigation measure.

⁵⁴ Bangladesh Rising sea levels threaten agriculture. *IRIN*, March 14, 2009, <http://www.irinnews.org/Report.aspx?ReportId=75094>.

⁵⁵ Aglay, D. Scientists breed rice to defy climate change. *Reuters*, April 12, 2006, <http://www.planetark.com/dailynewsstory.cfm/newsid/35978/story.htm>.

Adapting to continuing releases of CO₂ by sequestration

One measure to prevent some of the consequences of climate change is to prevent a portion of CO₂ emissions from entering the atmosphere, by biological, physical or chemical means.

- Biological sequestration A growing forest, especially a tropical one very effectively takes up CO₂ from the atmosphere. Protect existing forests and practice reforestation.⁵⁶ Another approach is introducing *biochar* into soil to enhance its ability to store CO₂ while also benefiting soil quality.⁵⁷
- Carbon capture and storage (CCS) Physical methods can be used to capture CO₂ emissions at their source – most often coal-burning power plants – and store them in a way that prevents their return to the atmosphere. The captured CO₂ can be injected into deep geological formations or into aquifers under sea or land.^{58,59} If pumped to a great depth CO₂ would be subjected to enough pressure that it becomes viscous, as viscous as honey. Several industrial-scale sequestration projects are under way. Norway The best known of these is in Norway where CSS has been used since 1998. Trapping and sequestering CO₂ emissions is expensive. Norway has had a *carbon tax* since 1991, about \$50 per ton of CO₂ emitted. This tax stimulated oil and gas companies to consider how to minimize CO₂ emissions. Statoil, Norway's state-owned oil company recovers natural gas, which is contaminated with 9.5% CO₂. They must reduce this to 2.5%, the limit for commercial natural gas. Thus Statoil had to trap CO₂ anyway, so it cost the company relatively little to do the following: since 1998, it has pumped about 10 million tons (9.1 million tonnes) of CO₂ into an immense offshore aquifer 2625 feet (800 m) below the floor of the North Sea. This process adds about 1% to the cost of natural gas production, small compared to the carbon tax. The storage aquifer is a porous sandstone formation filled with salt water; Norway's Petroleum Research group believes the storage is permanent and safe, even in an earthquake. Statoil says that calculations show that "enough capacity exists in North Sea aquifers to sequester CO₂ emissions from all EU power plants for hundreds of years. Modeled results indicate it would take over 10 000 years before even small amounts of the CO₂ would escape up to

⁵⁶ Careful planning is needed for reforestation projects because planting large numbers of trees can reduce the water available for other purposes, drinking, irrigation, etc. Jackson, R. B. Trading water for carbon with biological carbon sequestration. *Science*, **310**(5756), 1944–1947, December 23, 2005.

⁵⁷ Laird, D. The charcoal vision: a win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agronomy Journal*, **100**(1), 2008, <http://terrapreta.bioenergylists.org/lairdcharcoalvision0408>.

⁵⁸ (1) Doyle, A. Petrify, liquefy: new ways to bury greenhouse gas. *Reuters*, May 8, 2008, <http://www.enn.com/pollution/article/35968>. (2) Australia begins burying carbon dioxide underground. *Toronto Globe and Mail*, April 2, 2008. (3) Hileman, B. and Johnson, J. Driving CO₂ underground. *Chemical & Engineering News*, **85**(39), September 24, 2007, 74–81, <http://pubs.acs.org/cen/government/85/8539gov1box.html>. (4) Engelhaupt, E. What to do with greenhouse gases? *Environmental Science & Technology*. **41**(17), September 1, 2007, 5925–5926.

⁵⁹ McCoy, M. and Johnson, J. Climate change, dealing with CO₂, technologies to capture greenhouse gas advance. *Chemical & Engineering News*, **87**(14), April 6, 2009, 5.

the floor of the ocean. Norway sees carbon-sequestration as a major project – their “moon landing.” Prime Minister Jens Stoltenberg stated, “It is our vision that within 7 years we will have put in place capture and storage technology.” Indeed, done with careful safety and environmental precautions, and if affordable, the project could be as significant as a moon landing.⁶⁰ ■ Although Norway believes that CO₂ from any source including coal-burning power plants could be so stored, currently, no commercial-scale power plants sequester CO₂. United States Within the United States legal and safety worries are major hindrances. Half of US electricity and a third of its anthropogenic CO₂ come from 1500 coal-fired plants, many approaching 40 years of age. To retrofit these for CO₂ capture would be exceedingly expensive. IPCC estimates a carbon emissions tax would need to be \$25–30 a tonne (1.2 ton) to be economically viable; this would significantly increase the cost of electricity. And, for many plants, it would be physically impossible as equipment for a 500-MW (megawatt) plant can take 6 acres (2.4 hectares) of space. CCS worries A big worry is possible leakage from underground sites.⁶¹ what if a CO₂ storage site was disturbed by an earthquake? A leak could kill nearby life while also increasing atmospheric levels of CO₂. ■ So, sequestering is of great interest and is being intensively researched, but is still far from being practical.

- Chemical sequestration Ideally CO₂ would be used as a feedstock to make useful chemicals,⁶² but there are major difficulties. CO₂ has such a long life in the atmosphere because it is not a reactive chemical. Its lack of reactivity hinders its easy conversion to other chemicals. But most intimidating is that human activities, especially fossil-fuel burning produces 26.5 *billion* tons (24 billion tonnes) a year of CO₂ – of this amount currently about 127 *million* tons (115 million tonnes) are put to use. So it is staggering to ponder capturing all that CO₂ let alone putting it all to use once captured. One product remains a possibility and a subject of research: capture CO₂ and convert it, via the molecule CO (carbon monoxide), into hydrocarbons. Burn the hydrocarbons for energy, as one does gasoline.⁶³ This would close the cycle–fuel to CO₂ and back to fuel. Unfortunately, as currently carried out the process requires a great deal of energy. A potentially better variation on this scheme is to develop a system of artificial photosynthesis – use solar energy and CO₂ to produce (through a series of reactions) immense quantities of burnable hydrocarbons. Research on this possibility is in very early stages. It is very far from reality. For the foreseeable future capturing CO₂ and physically sequestering a portion of it will be a more likely way to manage CO₂.

⁶⁰ Leonard, A. Norway’s moon shot, *Salon*, March 5, 2008, http://www.salon.com/tech/htww/2008/03/05/norways_moon_shot/.

⁶¹ The worst known example was a natural eruption of CO₂ from Lake Nyos (Cameroon) in 1986, which killed more than 1 700 people and many animals. CO₂ is not a chemical toxicant, but when concentration is high enough it displaces oxygen so that suffocation occurs.

⁶² Ritter, S. K. What can we do with carbon dioxide? (finding ways to convert CO₂ into fuels and other value-added products). *Chemical & Engineering News*, **85**(18), April 30, 2007, 11–17.

⁶³ Chang, K. Scientists would turn greenhouse gas into gasoline. *New York Times*, February 19, 2008, http://www.nytimes.com/2008/02/19/science/19carb.html?_r=1&oref=slogin.

Questions 7.2

- 1 Eastern European countries decreased their greenhouse emissions since 1990 whereas Western European countries did not. Check the internet to find the reason for this difference.
- 2 (a) What is your reaction to the Statoil project? (b) More generally, what is your reaction to physically sequestering CO₂?

Delving deeper

1. Yale's School of Forestry and Environmental Studies has a new website. In an easily-understood way, it synthesizes the results of thousands of policy simulations from 25 models being used to predict the economic impacts of reducing US carbon emissions. See <http://www.climate.yale.edu/seeforyourself>. The site identifies the seven key assumptions accounting for most of the differences in the projections of the 25 models. It shows the US economy growing strongly even as carbon emissions are reduced. Under more favorable assumptions, the economy would even grow more rapidly as GHG reductions occur than if they continue to increase as is now happening. Access this site, think through the issues involved, prepare for and do a brief presentation, or write a short essay.
2. Notice important missing points in the discussion of clean-coal technology. They seldom include the damaging ways that we mine coal, especially extreme methods such as mountain-top removal. Nor do discussions often include better management of the immense amounts of several different types of waste ash produced when coal is burned. Do a brief research paper on clean coal technology that *includes* a life-cycle assessment of the subject (not just CCS). Present your conclusion on what clean coal actually means and how, if at all we can attain it.
3. CO₂ is "nontoxic, nonflammable, and essentially free for the taking." Why then is it so difficult to make use of this gas? See Ritter, S. K. What Can We Do With Carbon Dioxide? *Chemical & Engineering News*, 85(18). April 30, 2007, 11–17. Come to a conclusion that you are willing to defend on the likely future for the use of CO₂.

SECTION VII

What does a greenhouse future hold?^{64,65}

To get a sense of the scope of the 2007 IPCC report, see <http://www.ipcc.ch/>.⁶⁶ Or, see a summary of IPCC's report prepared by the Union of Concerned

⁶⁴ Kintisch, E. Global warming: projections of climate change go from bad to worse, scientists report. *Science*, 323 (5921), March 2009, 1546–1547.

⁶⁵ Kolbert, E. *Field Notes from a Catastrophe: Man, Nature, and Climate Change*. London: Bloomsbury Publishing, 2006.

⁶⁶ IPCC's four 2007 reports are at <http://www.ipcc.ch/>. (1) The physical science basis (2) Impacts, adaptation, and vulnerability (3) Mitigation of climate change (4) AR4 synthesis report. Start with the Synthesis Report.

Scientists.⁶⁷ It is difficult to briefly summarize what greenhouse future we can expect as that depends upon, among other things future levels of heat-trapping gas emissions will be. In turn, particular levels give rise to different future scenarios. The IPCC based its projection of climate change scenarios in the second half of the twenty-first century on six possible GHG emission scenarios. ▪ Its best estimate is that global average temperatures will rise 3.1 to 7.2°F (1.8 to 4.0°C) by 2100 (relative to 2000).⁶⁸ ▪ Because of a lag in response to levels of greenhouse gases in the atmosphere, it is projected that even if humanity could hold atmospheric levels of greenhouse gases at current levels, Earth would still warm about 0.1°C (0.18°F) per decade for the next few decades.

What are the implications of temperature increases? The exact degree to which we can expect the following will, of course depend on temperature increases.⁶⁹

Not all implications are listed here. There are many others such as loss of biodiversity as temperatures rise, and the impacts of earlier springs.

- Loss of sea ice in both the Arctic and Antarctic will continue.
- By the end of this century, the global average sea-level will rise between 7 and 23 inches (17.8 cm and 58.4 cm) above the 1980–1999 average. The Atlantic Ocean meridional overturning circulation may be 25% slower.⁷⁰ Despite this, Atlantic regional temperatures are projected to rise overall due to increases in heat-trapping emissions. ▪ Coastal flooding will increasingly occur with rising sea level. People, already poor and overcrowded, may be forced from homes in low-lying countries such as Bangladesh. Even prosperous nations such as the Netherlands, long accustomed to fighting back the sea, may lose land. Even in less critically affected regions a rising sea-level can do great damage. Beaches will erode harming beach-front property. Storm surges along coastlines may increase. A higher sea level means salty water can infiltrate fresh ground water in coastal areas, making it undrinkable. Infiltration of ocean water can also destroy coastal ecosystems, and the species they support. Inland wetlands and ecosystems are also at risk.
- Storms of increased severity are expected because trapped heat energy drives atmospheric air and oceanic water circulation. Such circulation *has been* a positive force because it distributes heat energy more evenly around the world making Earth, on average, a more moderate place to live. Hurricanes and typhoons also feed on this warmth so, as the energy in air and water increases, storms may grow in intensity.
- There will be more extreme heat, heat waves, and heavy precipitation. Rainfall patterns would be altered with some areas getting more rainfall, and others suffering more

⁶⁷ Ekwurzel, B. Findings of the IPCC Fourth Assessment Report: Climate Change Science. Union of Concerned Scientists Summary, July, 2007, http://www.ucsusa.org/global_warming/science/ipcc-highlights1.html.

⁶⁸ The full range of possible temperature increases range between 1.4 and 5.8 °C (34.5 and 42.4°F). The reason for this wide spread of temperatures depends on which GCM is used, and the information entered into it. In other words, there are still many unanswered questions as to how much temperature will rise.

⁶⁹ Only some implications are listed here. There are many others such as loss of biodiversity as temperatures rise, and the impacts of earlier springs.

⁷⁰ The term *meridional overturning circulation* (MOC) is also called thermohaline circulation. It refers to the ocean circulation driven by differences in water density due to heat content (thermo) and salt content (haline). The MOC is an important means of bringing heat to polar regions. If it slows down this heat transfer would slow down.

droughts. How this works: on warmer days more water evaporates into the air leading to more clouds and rainfall. But moisture can also evaporate from dry soils, depriving them of already limited moisture.

- Higher temperatures would worsen air quality – recall how photochemical smog increases on hot summer days.
- Diseases now restricted to already warm regions may move into newly warming regions. An illustration is malaria, a major disease spread by mosquito vectors, which infects, sickens, and kills millions each year in warm climates. And, indigenous disease organisms previously killed by winter cold will be better able to survive milder winters.⁷¹
- Coral reefs have limited tolerance for warm waters. They compensate in the short run, but ongoing warming kills them. Because coral reefs are a source of great biodiversity, that diversity will be damaged.
- Atmospheric CO₂ will continue to acidify the ocean with negative impacts on shell-forming species and their ecosystems. The implications of a change in pH are only now unfolding.
- Regions for growing crops and trees will change. However, increased CO₂ and warmer temperatures may have positive effects in some locales. Agricultural crops may respond with increased growth as the concentration of the nutrient CO₂ increases. However, if other nutrients are limited, increased growth may not occur and plants could be stressed.

Taking action beyond Kyoto

Despite these forecasts, GHG emissions have increased in a number of countries. Included among these are countries, formerly in the Soviet Union, that experienced revived economic growth. And, US emissions are projected to be 26% above 1990 levels by 2012. More positively, it is predicted that because of their commitment to Kyoto, about 40 nations will cut GHG emissions 11% below 1990 levels. A strong belief has emerged that if humans are to limit the degree of damage done, they must reduce GHG emissions much more quickly than is now the case and to start doing so quickly. The International Energy Agency (IEA) released a report in 2008 predicting that CO₂ emissions could double in the next 40 years unless governments around the world seriously undertook a massive investment in a “global energy technology revolution” to curb GHG emissions. IEA urged that less-developed countries, especially China and India plan to also meet emissions targets. Some say we already have the technologies to make the major reductions necessary to stop irreversible warming.⁷²

⁷¹ Diseases are already spreading for other reasons, especially due to massive increases in international trade and travel. The West Nile virus in the US may be an example of these latter reasons.

⁷² Pacala, S. and Socolow, R. Stabilization wedges: solving the climate problem for the next 50 years with current technologies. *Science*, **305**(5686), August 13, 2004, 968–972, <http://www.sciencemag.org/cgi/content/full/sci;305/5686/968>.

Delving deeper

Beyond Kyoto: first ponder what has happened recently. At the UN's climate change conference in Bali (December 2007), 180 nations started negotiations for a second phase of mandatory cuts in GHG emissions. As of early 2009 negotiators from around the world were continuing efforts to come to a common agreement that would supersede the Kyoto protocol.⁷³ The EU stated its plans to cut GHG emissions at least 20% below 1990 levels by 2020, and US President Obama also desires significant emission cuts in the United States. Because the United States never became part of the Kyoto Protocol, its active participation is especially important. Among barriers to a new treaty as of early 2009 are some major US legislators who won't endorse a treaty unless China and other less-developed nations also limit emissions. Japan may set ambitious goals, but only with assurances that the United States, China and other less-developed countries make meaningful commitments this time around. However, less-developed countries fear their economic growth will be inhibited if they cut GHG emissions. To participate, they would expect major help with clean "climate-friendly" technologies. China says it would lower its energy intensity, but wants countries that import its products to take responsibility for helping China cut its emissions proportionate to the level of products they import. Brazil, with its immensely important Amazon rain forests has stated a willingness to much reduce deforestation rates.

▪ Clearly, many barriers must be overcome if a post-Kyoto agreement is to be reached. Your assignment: as of the time you are reading this chapter, find out the current state of a post-Kyoto agreement. How likely is humanity to be successful in making meaningful cuts in GHG emissions? Explain why you have come to your conclusion.

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“If all the ozone in the atmosphere were compressed to a pressure corresponding to that at the Earth’s surface, the layer would be only 3 mm [1/8 inch] thick . . . The thin ozone layer has proved to be an Achilles heel that may be seriously injured by apparently moderate changes in the composition of the atmosphere.”

Swedish Academy of Sciences, announcing the
1995 Nobel Prize in chemistry to Mario Molina,
F. Sherwood Rowland, and Paul Crutzen

You are aware of the major pollution problems resulting from combustion, especially of fossil fuels. In this chapter we see a global issue – destruction of stratospheric ozone – which results from *CFCs* and *halons*, synthetic chemicals. Depletion of stratospheric ozone led to the 1987 Montreal Protocol, the first worldwide agreement to protect the environment.¹ The ban on ozone-depleting chemicals is largely working, and the ozone layer is expected to recover, albeit slowly. Before starting Chapter 8: refer to Table 8.1, which presents a summary of what happens during stratospheric ozone depletion.² ■ Section I looks at the atmosphere, and reactions in the stratosphere including CFC destruction, and ozone creation and destruction. It examines ultraviolet (UV) radiation, and asks if all ozone-depleting pollutants are equally potent. And does ozone depletion result in measurable increases in UV radiation reaching Earth? After a brief history of ozone depletion, Section II asks: what are the pollutants of concern, how do they destroy ozone, and what is their environmental fate? Over what sections of Earth does ozone depletion occur? Why is the Antarctic particularly susceptible? What other factors impact ozone depletion? Section III asks: why are we concerned if more UV radiation reaches the Earth? What is the harm to Earth’s life? Section IV examines the Montreal Protocol: what has the world been doing to eliminate ozone-depleting chemicals? It looks at assisting less-developed countries and, briefly at CFCs and halons smuggling. Section V takes us to CFC substitutes, why they were not ideal and why we are now moving toward alternatives to the initial substitutes. It briefly looks at the future.

¹ Scientific assessment of ozone depletion (executive summary). Scientific Assessment Panel of the Montreal Protocol on Substances that Deplete the Ozone layer. *US EPA*, July 31, 2002, <http://www.epa.gov/ozone/strathome.html>.

² Stratospheric ozone home site. *National Oceanic and Atmospheric Administration* (NOAA), 2008, <http://www.ozonelayer.noaa.gov/index.htm>.

Table 8.1 An ozone-depletion snapshot

CFCs¹ are inert chemicals that evaporate into the atmosphere. At ground level almost nothing destroys them. CFCs move with air turbulence into the stratosphere. There the sun's strong ultraviolet (UV) radiation destroys them, releasing extremely reactive elemental chlorine.

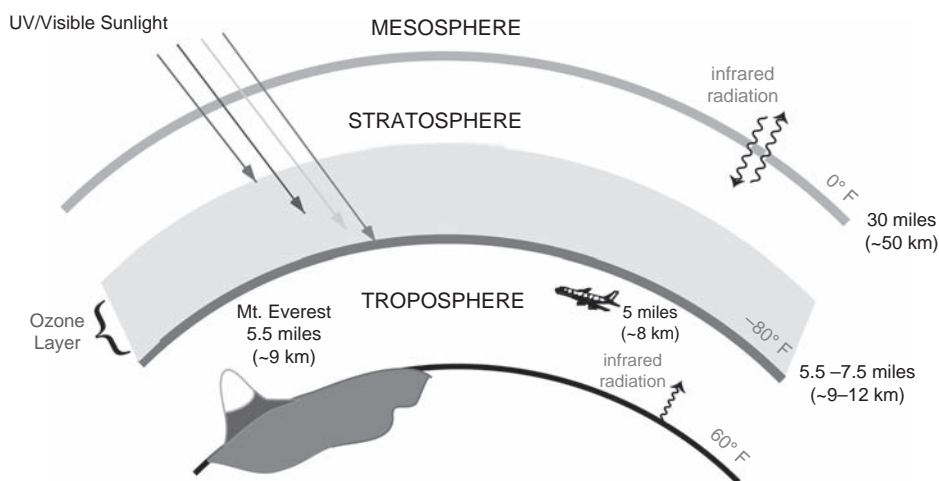
Particles in the stratosphere provide surfaces on which ozone-depleting reactions can take place.

Less ozone in the stratosphere means more damaging UV radiation can reach Earth, increasing the risk of . . .

Damage to plant growth on land and phytoplankton growth in aquatic systems

Skin cancer, eye cataracts, and harm to the immune system in humans

¹ Halons are a family of chemicals related to CFCs. They contain bromine rather than chlorine. The reactions shown for CFCs above also hold for halons.

**Figure 8.1**

Regions of the atmosphere. Credit: NOAA OAR ESRL

SECTION I

The atmosphere³

We examined the troposphere in Chapter 5, the atmospheric layer in which we live, and which contains about 90% of all air molecules. Like the stratosphere above it, the troposphere's depth varies around the Earth, but averages about 6 miles (9.7 km). The stratosphere is about 30 miles in depth (48.3 km) (Figure 8.1). The ozone layer encompasses the entire Earth at altitudes between 6.2 miles and 31.1 miles (10 km and 50 km). Although only 10% of the molecules in the atmosphere are in the stratosphere, it has 90% of the ozone; only

³ Regions of the atmosphere. *NOAA*, March 20, 2009, <http://www.ozonelayer.noaa.gov/science/atmosphere.htm>.

Box 8.1

Questions and answers on stratospheric ozone

1. Stratospheric ozone: questions. *Environment Canada*. <http://www.ec.gc.ca/ozone/docs/UO/faq/en/faq.cfm>.
2. Frequently asked questions. *NOAA*, March 20, 2008. <http://www.ozonelayer.noaa.gov/faq/faq.htm>.
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10% of ozone is in the troposphere. Much of tropospheric ozone is a pollutant, but stratospheric ozone is formed naturally and is necessary to life on Earth because it absorbs more than 95% of the sun's high intensity, UV radiation, which would otherwise reach and damage human, animal, plant and microbial life on Earth. In the stratosphere there is an ongoing natural cycle in which ozone is formed, ozone is destroyed and ozone is reformed again. CFCs and halons damage the cycle by enhancing the second step – destroying ozone.

Making and remaking ozone in the stratosphere⁴

Reactions 1–2 in Box 8.2 show how ozone (O_3) is generated in the stratosphere from oxygen (O_2) with the action of UV light. The amount of ozone is small, but enough to perform a critical function. As UV-C light strikes and dissociates ozone (Reaction 3), the intensity of the UV is lessened, but the destroyed ozone doesn't stay destroyed – it is reformed (Reaction 4). So this natural cycle is constantly reforming ozone over and over again, and maintaining its level.

Ultraviolet radiation

Ultraviolet radiation is divided into UV-A, UV-B, and UV-C (Figure 8.3).⁵

- UV-C has the shortest wavelengths, and is most energy intense, and dangerous. Fortunately it is completely absorbed by ozone, oxygen, water vapor, and CO_2 , and does not reach Earth.
- UV-B is of intermediate energy. It is usually UV-B that is of most interest to us. It is UV-B referred to in discussions of UV radiation reaching Earth's surface. It is here that stratospheric ozone is of great importance: it absorbs most UV-B. (UV-B is also produced by sun lamps.)
- UV-A is not absorbed, but has longer less energy-intense wavelengths. It is just shorter than visible light.

⁴ Burkholder, J. Ozone destruction and recovery, the role of laboratory studies. *NOAA*, December 4, 2008, <http://www.esrl.noaa.gov/research/themes/o3/pdf/OzoneLaboratoryMeasurements.pdf>.

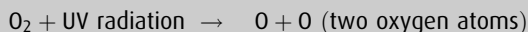
⁵ SunWise Glossary (The SunWise Program . . . aims to teach the public how to protect themselves from over-exposure to the sun.) *US EPA*. January 3, 2008, <http://www.epa.gov/sunwise/glossary.html>.

Box 8.2

Reactions in the stratosphere

Part I. Making and remaking ozone (O₃)

Breaking down oxygen High energy UV radiation from the sun breaks atmospheric oxygen (O₂) into single oxygen atoms (O).



Forming ozone These single O atoms are very unstable and react with O₂ to form ozone (O₃).



Breaking down ozone UV radiation dissociates an O₃ molecule into O₂ and one oxygen atom.



Regenerating ozone Notice that Reaction 4 is the same as Reaction 2

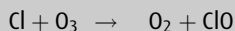
**Part II. Breaking down CFCs and ozone, and regenerating a chlorine atom.**

Also see Box 8.3.

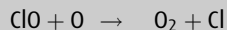
Destroying CFCs UV reacts with CFC molecules to release active chlorine atoms. Also see Figure 8.2.



Destroying ozone Highly reactive chlorine atoms react with ozone to yield O₂ plus the very reactive chlorine monoxide.



Regenerating chlorine Chlorine monoxide reacts with an oxygen atom to yield a chlorine atom⁶



Notice that Reaction 7 is similar to reaction 5 in that once again the highly reactive Cl atom is formed and can destroy another molecule of ozone. This is a chain reaction. It can repeat itself over and over again thousands of times, each time destroying more ozone. Thus, one chlorine atom can destroy thousands of ozone molecules.

Note: stratospheric UV radiation is at work in Reactions 1, 3, and 5. In reaction 5, a fluorine atom is also released, but in a form that doesn't deplete stratospheric ozone. CFCl₃ is the formula of CFC-11.

⁶ Chlorine monoxide has been measured in the stratosphere via satellites. Reactions have also been well studied in the laboratory, under conditions set up to simulate what is happening in the stratosphere.

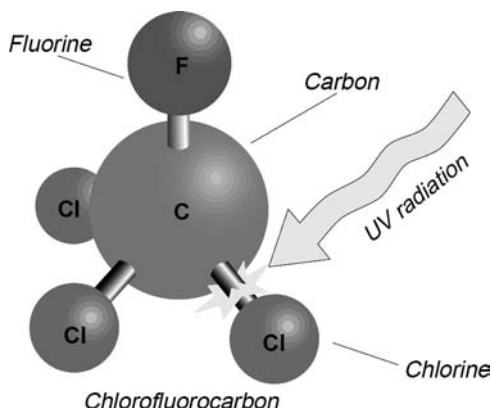


Figure 8.2

A CFC molecule reacting with UV radiation in the stratosphere. Credit: US EPA

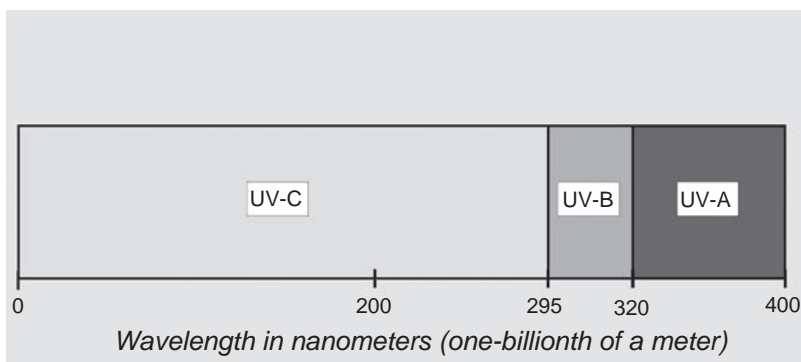


Figure 8.3

The ultraviolet spectrum. Credit: US EPA

Measuring UV radiation

Can the following statement be confirmed? *More UV-B radiation reaches Earth when ozone in the stratosphere has been partially depleted?* Measurements of UV can be straightforward and were first made in the late 1800s. However, in nature a number of variables confuses the situation. ■ Clouds scatter some UV radiation and also absorb part of it. Thicker clouds absorb more. ■ The amount of UV radiation reaching Earth varies with the position of the sun in the sky (time of day) and season of year. UV radiation is greatest in the summer when the midday sun is closest to being overhead. ■ UV radiation varies with latitude: the closer one is to the equator, the greater the amount of UV radiation reaching Earth. Radiation at the equator is about a thousand times greater than at the poles. ■ More radiation reaches Earth at higher elevations as compared to ground level. ■ Snow reflects it. ■ And ground-level ozone absorbs UV radiation, so in polluted areas more UV is absorbed. Other air pollutants also absorb some UV radiation. ■ You begin to see why it has sometimes been difficult to detect small increases in UV radiation.⁷

⁷ See question 17 in: Stratospheric ozone questions. *Environment Canada*, <http://www.ec.gc.ca/ozone/docs/UO/faq/en/faq.cfm>.

Increases in UV radiation are seen most clearly beneath an area where the degree of ozone depletion is great. You may conclude that the best place and time to measure increases in UV radiation are in Antarctica during its spring (August–October) under the region of depleted ozone, “ozone hole.” (The so-called hole refers to the region over the Antarctic where stratospheric ozone is significantly depleted.) Indeed, that is where the greatest increases in UV radiation on Earth are seen: the radiation reaching Antarctica in its spring can be greater than that reaching the ground in San Diego California – a locale which naturally receives more UV because the sun is much higher above the horizon.

- Clear increases in UV can also be measured under the Arctic pole during its spring in March.
- It is more difficult to detect increases in UV radiation under regions with only small amount of ozone depletion. Still, this has been accomplished in many places around the world.
- To increase accuracy, measurements are taken on clear days in areas far from major cities and air pollution.
- Measurements taken by instruments both in satellites and ground based now routinely follow changes in UV radiation around the world, and make corrections for factors such as cloud cover. They confirm that UV-B has increased. Indeed, one can estimate from the amount of ozone depletion what the increase in UV-B radiation on Earth will be.

SECTION II

Destroying ozone with CFCs and halons

A brief history

More than a hundred years ago, the new refrigeration industry used, as coolants, highly toxic gases such as ammonia and sulfur dioxide. Accidental leakage of these chemicals resulted in many human deaths, and in the 1920s, the US Congress attacked manufacturers for producing “killer refrigerators.” Then, in 1928, a young chemist announced the creation of a new coolant. At a later date he demonstrated publicly that he could directly inhale the coolant – so it had low toxicity. When exhaling he used his breath to blow out a candle – so it was not flammable either. This impressive coolant was a chlorofluorocarbon (CFC). In 1931 it was introduced into the market as *Freon*. Its safety made it a godsend and Freon became widely used in refrigerators and, later, air conditioners.

Another property of CFCs (and later the bromine-containing halons) that made them so useful was their lack of chemical reactivity. This stability was their Achilles heel. They persist in the environment, so much so that in the 1970s scientists found CFCs were spreading around the globe. With nothing natural to break them down it was estimated they would survive hundreds of years. Their curiosity piqued by such information, Professors Mario Molina and F. Sherwood Rowland developed a hypothesis that CFCs would lead to significant depletion of the stratospheric ozone layer. Many initially ridiculed

this thesis. Later, Molina also examined the question, why does the greatest ozone depletion occur over Antarctica?⁸

By 1976, some scientists believed that CFCs threatened stratospheric ozone. At that time, two-thirds of manufactured CFCs were used as aerosol propellants. The United States and a number of other governments banned this use in 1979. Thereafter, concern about stratospheric ozone lessened. The quietude ended in the mid-1980s when a group of British researchers, doing ground-based measurements of ozone concentrations above Antarctica, reported a 30% decline as compared to earlier years. These researchers had observed October (spring) depletion as early as 1977, but doubted their own observations. When they reported their findings in October, 1985, the US Aeronautics and Space Administration (NASA) confirmed their observations, measuring stratospheric ozone using satellite and high-altitude balloons. Since then, Antarctica's spring "ozone hole" has been actively monitored.

Characteristics of CFCs and halons

In earlier chapters you learned of organic pollutants such as PCBs and polychlorinated pesticides that persist in the environment. However, CFCs and halons last longer still, and may persist in the atmosphere for more than a century. They are heavier than the air molecules, O₂ and N₂. In fact, skeptics who doubted that CFCs led to ozone depletion argued that CFCs could not reach the stratosphere because of their heaviness.⁹ However, unlike water-soluble compounds such as the components of acid rain, CFCs and halons are not rained out and are very stable. Thus, they survive to mix with turbulent air moving into the stratosphere. They can be detected in the stratosphere by instrumentation aboard balloons, aircraft, and satellites.

Sources of ozone-depleting pollutants in the stratosphere

The sources are chlorine- and bromine-containing chemicals, especially CFCs and halons.¹⁰ These chemicals manufactured by humans escape into the atmosphere from their point of use, or when they are disposed of. ■ CFCs were refrigerants, but were also found other applications as aerosol-can propellants, industrial solvents, cleaning agents, and insulating agents (in which CFCs were blown into foam products or polystyrene cups). ■ CFCs are no longer made, but can still be found in old refrigeration equipment including automobile air conditioners. Freon-12 (CCl₂F₂) was the most widely used refrigerant. ■ *Halons* are related to CFCs, but contain the halogen, bromine rather than chlorine. Halons became important fire-fighting chemicals.

⁸ In 1995 Professors Mario Molina and F. Sherwood Rowland won the Nobel Prize in Chemistry, the first time that a Nobel Prize recognized research into human-made impacts on the environment. They shared the prize with Professor Paul Crutzen, who showed that nitrogen oxides accelerated ozone depletion.

⁹ Skeptics have made a number of arguments against CFCs being able to destroy stratospheric ozone. EPA has responded to several of these: Dispelling the myths of ozone layer depletion. *US EPA*, October 4, 2007, <http://www.epa.gov/ozone/science/myths/index.html>.

¹⁰ Volcano vents release CFCs, but in tiny amounts compared to that produced by humans.

Table 8.2 Atmospheric lifetimes and ozone depletion potentials of selected ozone-depleting gases

Chlorine gases atmospheric lifetime (years)	Ozone depleting	Potential (ODP)
CFC-12 (Freon)	100	1
CFC-11	45	1
Carbon tetrachloride	26	0.73
HCFCs	1–26	0.02–0.12
Bromine gases		
Halon-1301	65	16
Halon-1211	16	7.1
Methyl bromide	0.7	0.51

Not all ozone-depleting pollutants are equally potent¹¹

Synthetic ozone-depleting chemicals Ozone-depleting chemicals are rated according to an *Ozone Depletion Potential* (ODP)¹². See Table 8.2. ■ CFC-12 (Freon), the best-known CFC, has a value of 1. ■ Halon-1301 has an ODP of 16, i.e., it is 16 times more destructive of ozone than is Freon. Halons release bromine in the stratosphere. Bromine atoms destroy ozone much more effectively than chlorine atoms (Table 8.2). So although there is about 160 times more chlorine in the stratosphere than bromine, bromine plays a significant role. ■ A less potent group of synthetic ozone-depleting chemicals is the *halocarbons*, which contain carbon plus at least one halogen.¹³ Ozone-depleting halocarbons include *methyl bromide* a fumigant, *methyl chloride* a specialized refrigerant, and the solvents *methyl chloroform*, *carbon tetrachloride*, and *1,1,1-trichloroethane*. ■ *Methyl chloride*, has an ODP of 0.1 – it is 10 times less destructive than CFC-12. ■ The largest source of ozone-depleting bromine is the fumigant *methyl bromide*. **Natural halocarbons** Marine organisms and forest and grass fires generate methyl bromide; overall about 30% of bromine-containing chemicals in the stratosphere are natural. ■ Most methyl chloride is also natural, about 5 million tons (4.5 million tonnes) as compared to only 26 000 tons (23.5 tonnes) from human activities. Both natural methyl bromide and methyl chloride are produced by oceanic and terrestrial ecosystems ■ However, overall, only about 17% of the chlorine-containing chemicals reaching the stratosphere are natural.

Environmental fate of CFCs and halons

In the stratosphere, CFCs and halons are destroyed by photolysis, light-induced destruction (Figure 8.2). The action of UV light frees highly reactive elemental chlorine from CFCs, and elemental bromine from halons. Elemental chlorine, after conversion to chlorine monoxide

¹¹ Hoffman, D. J. and Montzka, S. S. The NOAA Ozone Depleting Gas Index. *NOAA Earth System Research Laboratory*, <http://www.esrl.noaa.gov/gmd/odgi/>.

¹² Ozone-depleting potentials, a table. *US EPA*, October 4, 2007, <http://www.epa.gov/ozone/science/ods/classone.html>.

¹³ A halogen is any one of the elements in column 17 of the periodic table. Those important in this chapter are chlorine and bromine, although fluorine is in some of the compounds considered here.

(ClO) combines with and destroys ozone. See Part II of Box 8.2. *If each atom of chlorine or bromine destroyed only one atom of ozone, there would be no problem.* But they act as catalysts – one chlorine atom can destroy many thousands of ozone molecules, and one bromine atom is more destructive still. Thus chlorine and bromine destroy ozone disproportionate to their low concentration.

Not all halogen-containing chemicals deplete ozone

Water-soluble chemicals are much less likely to deplete ozone. A major example is hydrochloric acid (HCl), which volcanic eruptions spew in huge quantities. However, a volcanic plume contains about 1000 times more water vapor than HCl. As the water in the plume moves upward, it dissolves the HCl which, subsequently, almost all rains out. ■ Ocean spray also contains high levels of – water soluble – sodium chloride (NaCl, table salt), which does not reach the stratosphere. ■ Other water-soluble forms of chlorine include bleach and chlorine chemicals used to disinfect water or swimming pools. ■ It is the water-insoluble CFCs and halons that survive for years, long enough to reach the stratosphere. ■ Iodine, another halogen is also naturally released from the oceans. It can engage in ozone-depleting reactions, but iodine gases have short lifetimes, and most are removed in the lower atmosphere.

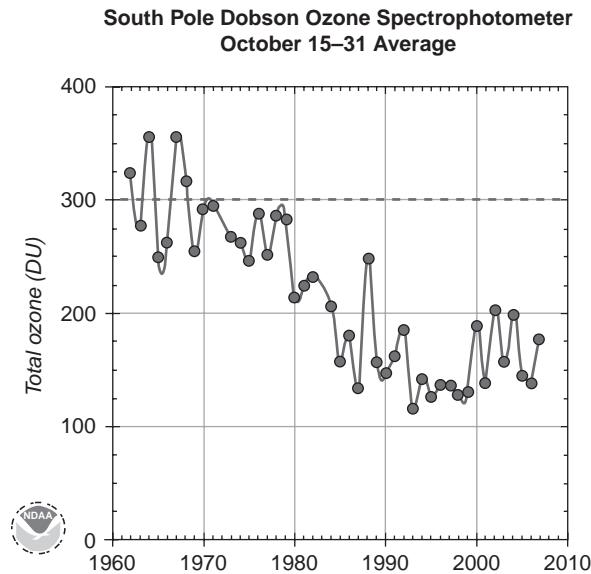
Where on Earth is ozone depletion observed?

Antarctica

- It is over the continent of Antarctica that the largest amount of ozone depletion is seen. Up to 60% of the ozone disappears over some parts of Antarctica during its spring (September-October). Figure 8.4 shows (in Dobson units¹⁴) the stratospheric ozone concentration over the continent starting in the 1960s. Ozone measurements are made both from satellite-based and ground-based instruments, making it possible to map the region where depletion is occurring.
- In Figure 8.5, the region outlined at the bottom of the globe is Antarctica. In 1979, no ozone depletion is seen. By 1986, a shaded area which represents a thinning of ozone (the “ozone hole”) is seen over this continent; the shaded area continues to be obvious in 1991 and in 2008.¹⁵

¹⁴ Southpole ozone spectrophotometer. *National Oceanic and Atmospheric Administration*, 2009, http://www.esrl.noaa.gov/gmd/dv/spo_oz/ozdob.html. Ozone is measured in Dobson Units (DU). The normal ozone layer thickness is about 300 DU. Records of Antarctic ozone date back to the 1920s when Dobson developed the Dobson Spectrophotometer and began making measurements from the ground. Remote sensing of ozone from satellites began in 1960. Currently, ground-based and satellite-based instruments monitor stratospheric ozone levels over the Antarctic, the Arctic, and 80 other sites worldwide.

¹⁵ Ozone hole watch, ozone-hole maps. *NASA*, April 5, 2009, <http://ozonewatch.gsfc.nasa.gov/monthly/index.html>.

**Figure 8.4**

Springtime thinning of Antarctic stratospheric ozone (1960–2008). Credit: US NOAA

Why is Antarctica more vulnerable to ozone depletion than other locales?

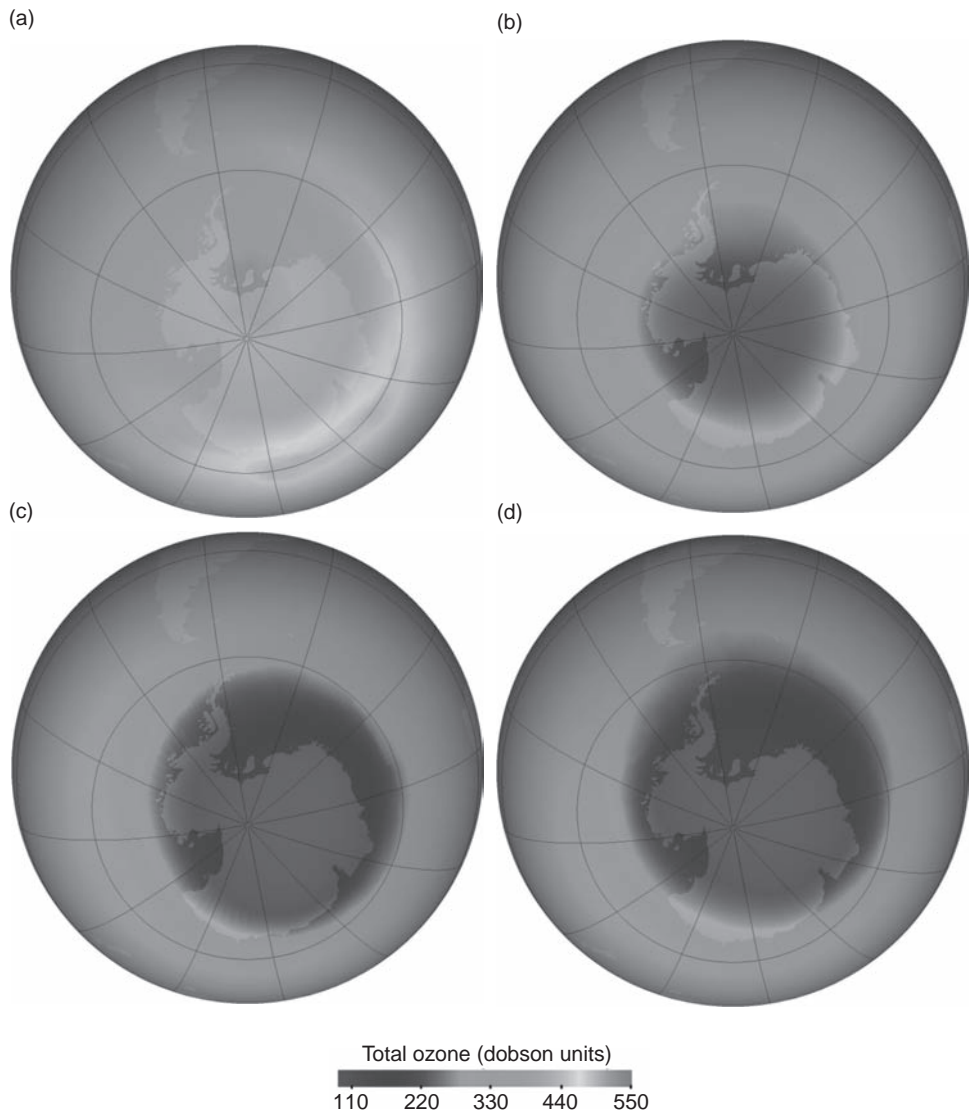
During Antarctica's tremendously cold winters, ice-particle clouds, called polar stratospheric clouds (PSCs) form. PSCs are trapped within a *polar vortex*, strong wind currents circulating around the pole, and preventing air from mixing with the atmosphere beyond Antarctica. PSC ice particles are crucial to ozone destruction because they provide surfaces on which the ozone-depleting reactions of Box 8.2 can take place. Once the spring sun returns with its UV radiation, reactions take place very rapidly and the ozone "hole" appears (ozone thinning). As spring progresses, the atmosphere warms, and the ice particles and the vortex dissipate. The polar air then mixes with air beyond Antarctica again, and stratospheric ozone levels return to normal.

▪ Average ozone loss continued to increase through the 1980s. In the 1990s, average values of ozone were 40–50% below the normal of 300, reaching values, for a week or so each year, as low as 70% below normal.¹⁶ Ozone levels were still well below normal in 2008 (Figure 8.4).

Ozone thinning in locales other than the Antarctic

▪ The Arctic is typically less cold than the Antarctic, so fewer PSCs form, occasionally none, so there are fewer particles on which chlorine gases can be converted to chlorine monoxide. Nonetheless, as much as 30% depletion of Arctic ozone has been seen. This is second only to Antarctic in the late winter/early spring. ▪ Other regions On average around the globe, as

¹⁶ Executive Summary, Scientific Assessment of Ozone Depletion. Scientific Assessment Panel of the Montreal Protocol on Substances that Deplete the Ozone Layer. July 31, 2002, <http://www.epa.gov/ozone/strathome.html>.

**Figure 8.5**

- a** Visualizing Antarctic ozone-thinning (1979). Credit: US NOAA
b Visualizing Antarctic ozone-thinning (1986). Credit: US NOAA
c Visualizing Antarctic ozone-thinning (1996). Credit: US NOAA
d Visualizing Antarctic ozone-thinning (2008). Credit: US NOAA

measured by ground-based and satellite instruments, the amount of stratospheric ozone is about 4% lower than in 1980. This is greater than natural variability. Ozone losses are also seen over middle latitude countries, the United States, Canada, and Europe as well as in middle-latitude countries of the southern hemisphere. ▪ Specifically for Canada, average stratospheric ozone is about 6% below pre-1980 values; scientists estimate that this has resulted in about a 7% increase in the amount of UV-B radiation reaching Earth. ▪ In general: approaching the equator, ozone loss is progressively lower. Approaching the poles, it is progressively higher.

What other factors affect ozone depletion?

Volcanic eruptions

Usually, little hydrogen chloride (HCl) or other materials from volcanic eruptions reach the stratosphere. However, some eruptions such as Mt. Pinatubo in 1991, are violent enough to inject huge quantities of particles and gases including sulfur dioxide (SO₂) into the stratosphere.¹⁷ The SO₂ was subsequently converted into sulfuric acid particles. These apparently serve the same function as ice particles at the poles providing surfaces on which reactive chlorine compounds can destroy ozone. (This has also been shown in laboratory studies simulating stratospheric conditions.) In 1993 a NASA satellite recorded a stratospheric ozone value over Antarctica of 88 Dobson units, the greatest Antarctic “ozone hole” ever observed. This was ascribed to particles injected into the stratosphere during the Mt. Pinatubo eruption. ▪ Because particles settle out of the stratosphere, investigators hypothesized they should be gone by 1994. Indeed, Antarctic ozone levels did partially recover in 1994 reverting to the slower – but still ongoing – depletion rate seen before the volcano erupted.

Other sources of sulfur gases and thus of particles

Two other sources of sulfur dioxide to the stratosphere exist. ▪ One is *carbonyl sulfide* naturally produced in and released from the ocean. Inert in the troposphere, it reaches the stratosphere where photolysis releases the sulfur, which is converted into sulfuric acid particles. ▪ The other source is tropospheric SO₂ (from human pollution), some of which reach the stratosphere. ▪ But alone, particles don’t deplete ozone. It is the interaction of ozone-depleting chemicals with the ice particles or sulfuric acid aerosols that cause the problem.

SECTION III

Why there are concerns about more UV-B radiation reaching Earth¹⁸

Human health impacts

Forget about stratospheric ozone depletion for a moment and ask: can overexposure to normal sunlight be detrimental? Yes, seriously detrimental as sunlight contains some UV-B even with an intact ozone layer. Midday summer sun is the worst especially as one

¹⁷ Aerosols in the stratosphere. *US EPA*, October, 2007, <http://www.epa.gov/ozone/science/myths/aerosol.html>. Also see Volcanoes and global cooling [in the case of Mt. Pinatubo, working against global warming]. *US Geological Survey*, http://vulcan.wr.usgs.gov/Glossary/VolcWeather/description_volcanoes_and_weather.html.

¹⁸ The effects of ozone layer depletion. *US EPA*, October 4, 2007, <http://www.epa.gov/ozone/strathome.html>.

Table 8.3 Weather service UV index

Index value	Exposure level
0–2	Minimal
3–4	Low
5–6	Moderate
7–8	High
9–10+	Very high

approaches the equator, but other parts of the day can also lead to over-exposure; so can exposure that occurs at high elevations. ■ Eyes Overexposure can lead to cataracts. ■ Skin Adverse effects include sunburn, premature skin aging, and skin cancer. Cancer occurs because UV light can damage the DNA within skin cells. Cells repair DNA, but not all breaks are repaired. There is no such thing as a healthy tan.

Because natural levels of UV radiation can be deleterious, any UV increase resulting from stratospheric ozone depletion must be taken seriously. For each 1% increase in UV-B radiation reaching the Earth, there is a projected 2% increase in non-melanoma skin cancers.¹⁹ Skin cancer incidence, including melanoma incidence has increased rapidly in recent decades. One in five Americans develops skin cancer, but the sharp increase started years before stratospheric ozone depletion. Changes in lifestyle are the likely reason: people spend more time in the sun, often around midday, when UV radiation is most intense. Clothing often inadequately protects skin, and perhaps 40% of people wear inadequate sunscreen protection.²⁰ Diet may also contribute to skin-cancer development. Protecting children is particularly important as most of an average person's lifetime sun exposure occurs before age 18. But – even though lifestyle may *now* be the major factor in skin cancer increases – ozone depletion can further increase cancer rates. In 2002, Chilean medical scientists (in that country's southernmost city, Punta Arenas) reported that over a 14-year period of significantly increased ozone depletion (1987–2000), there were significant increases in skin problems including erythema and skin cancers.²¹ Also, a medical doctor working with climatologists found sun blisters appearing on people's skin on the same days that ozone depletion over the Antarctic expanded to southern Chile.

The United States and other national weather services provide a summer UV index used by newspapers, radio, and TV in weather forecasts (Table 8.3). The higher the index value, the more quickly sunburns can occur. The index is calculated for noon, or 1:00 p.m. daylight

¹⁹ Non-melanoma skin cancers are associated with cumulative exposure to sunlight over the years. The more serious malignant melanoma is associated with periods of intense exposure or sunburns that occurred early in life.

²⁰ Sun exposure. *US EPA*, August 20, 2008, <http://www.epa.gov/radtown/sun-exposure.html>. This site includes advice on protecting yourself. When out in the sun, a polo or T-shirt provides little protection. An unbleached cotton, high-luster polyester, or dark material is needed. Specialized fabrics are marketed to those with sun-sensitive skin. A sunscreen with a sun protection factor (SPF) of 15 or higher should be used.

²¹ Abarca, J. F. and Casiccia, C. C. Skin cancer and ultraviolet-B radiation under the Antarctic ozone hole: southern Chile, 1987–2000. *Photodermatology, Photoimmunology & Photomedicine*, **18**(6), 2002, 294–302, <http://cat.inist.fr/?aModele=afficheN&cpsid=14374802>.

savings time. The sunlight at 9:00 a.m. or 3:00 p.m. is only about half as intense as at noon. The farther south a northern hemisphere person lives, the higher the average index value. Light-skinned people or those who sunburn easily are most vulnerable. A high index alerts people to wear wide-brimmed hats, skin covering, and sunglasses that block 99%–100% of UV radiation. To protect against UV-A as well as UV-B, the sunscreen needs an ingredient such as avobenzone.

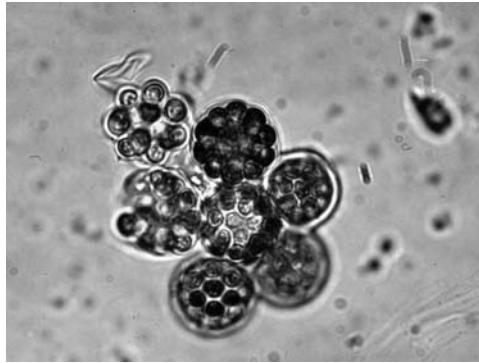
- Because the skin contains immune cells, UV radiation can suppress the immune system. This may be observed as an increase in cold sores during the first sunny days of summer, which result from activation of latent (dormant) herpes virus. An increase in infectious illness is also seen in people with suppressed immune systems already weakened by other illnesses or age. Although immune-system suppression occurs more readily in fair-skinned people, dark-skinned people are susceptible. Increasing radiation resulting from ozone depletion could increase these problems.

- Remember from Chapter 5 that ground-level ozone is also formed in the largest amounts in summer under the sun's strongest UV radiation. So, increased UV radiation could increase ground-level ozone levels. However, ground-level ozone – like stratospheric ozone – also absorbs UV radiation, so ozone pollution is protective to a certain degree; but remember from Chapter 5 the many reasons to avoid ozone exposure.

Harm of UV radiation to other life

UV-B radiation can harm almost any living creature exposed to it including the myriads of phytoplankton (microscopic plants) at the bottom of the ocean food web on which all marine-dwelling animals depend for food, directly or indirectly. ▪ Most phytoplankton (Figure 8.6a) live near the ocean's surface where enough sunlight penetrates the water to allow photosynthesis to occur. In spring phytoplankton begin growing rapidly in Antarctic waters – the same time that stratospheric ozone is depleted over Antarctica, thus increasing the amount of UV-B radiation reaching the ocean. UV-B can penetrate ocean water to depths that cause declines in phytoplankton populations.²² This means less food for the zooplankton, such as krill (Figure 8.6b), a tiny crustacean that eats phytoplankton. Also, fewer phytoplankton means less CO₂ is taken up from the atmosphere in Antarctic waters for photosynthesis. ▪ Other organisms living near the ocean's surface are also impacted. Greater UV-B radiation damages the development to varying degrees of fishes, shrimps, crabs, and amphibians. ▪ A 1985 report projected that, if CFC use had continued at the 1985 rate, a 7% loss of stratospheric ozone would occur by the year 2050. However, at that time CFC usage was rapidly increasing and thus the impact could have been much greater.

²² (1) Davidson, A. Effect of ozone depletion on Antarctic marine microbes. *Australian Antarctic Division*, October 5, 2008, <http://www.aad.gov.au/default.asp?casid=2031>. (2) Litchman, E., Neale, P. J. and Banaszak, A. T. Increased sensitivity to ultraviolet radiation in nitrogen-limited dinoflagellates: photoprotection and repair. *Limnology and Oceanography*, **47**(1), 2002, 86–94, http://aslo.org/lo/toc/vol_47/issue_1/0086.pdf.

**Figure 8.6a**

Phytoplankton (free floating microscopic plants). Credit: US EPA

**Figure 8.6b**

A krill (tiny crustacean that feeds on phytoplankton). Credit: US NOAA

Other damage from UV radiation

UV radiation also damages materials such as plastics and organic materials. Almost everyone has seen the impact on a newspaper of sun exposure. Other synthetic materials have a limited outdoors lifetime because of UV-B's effects.

CFCs and climate

CFCs absorb wavelengths of infrared radiation emanating from Earth not absorbed by other greenhouse gases. CFCs are potent greenhouse gases – indeed, thousands of times more potent than CO₂. ■ On the basis of several factors (not covered here), the overall impact of CFCs is to *cool the stratosphere*.²³ The cooling stratosphere, in fact, may balance out the warming caused by CFC action as greenhouse gases in the troposphere. A colder stratosphere can also contribute to the formation of more polar stratospheric clouds, which may, in turn, contribute to greater stratospheric ozone depletion.

Questions 8.1

1. Some people have asked if we can pump ground-level ozone into the stratosphere to replace lost stratospheric ozone. Assume this is practical. Why would that not solve the stratospheric ozone loss problem?
2. Why are most air molecules in the troposphere?
3. Ozone is heavier than oxygen and nitrogen, but most is in the stratosphere – why?
4. (a) Why does more UV radiation reach higher elevations than lower elevations? b) Why does more UV radiation reach locales closer to the equator than those further away?
5. In response to stronger UV radiation, plankton can move deeper into the water. This being the case, why are we concerned about the effect of UV on plankton?
6. The Montreal Protocol with its ban on ozone-depleting substances is largely a success. Why can't we replicate the success of this treaty with carbon dioxide and other GHG emissions?

SECTION IV

Eliminating ozone-depleting chemicals

The Montreal Protocol

Once stratospheric ozone depletion was confirmed in the mid-1980s, many believed that a quick and complete ban was necessary to avert serious consequences, especially because CFCs and halons have atmospheric lifetimes of decades to centuries. In 1987, most industrialized nations signed the Montreal Protocol on Substances That Deplete the Ozone Layer, an agreement to ban CFC and halons manufacture. This treaty was further strengthened in 1992. The Protocol, now ratified by 190 nations, established legally

²³ Fergusson, A. Ozone depletion and climate change: understanding the linkages. *Meteorological Service of Canada*, 2001, <http://exp-studies.tor.ec.gc.ca/e/ozone/OzoneDepletionClimateChange.pdf>.

binding controls on the production and consumption of ozone-depleting gases.²⁴

▪ Although halons are no longer manufactured, they are still plentiful; they are found in fire extinguishers and are stored in substantial quantities. Halons probably will continue to reach the stratosphere and their levels are likely to remain high for many years to come. ▪ However, the Montreal Protocol is considered a success. It was significant both because it banned ozone-depleting chemicals, and because it represented the first global environmental-protection treaty. In the United States, by 1995, almost all CFC and halons manufacture had ceased.

Less potent ozone-depleting gases

Methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are among the least potent ozone-depleting gases. These are also different from CFCs and halons because a large proportion of their emissions are from natural sources. At the end of the twenty-first century methyl chloride may represent the predominant amount of stratospheric chlorine because the more worrisome CFCs and halons should be largely gone.

Less-developed countries

Production in the United States and other Western countries ceased in 1996, but the Montreal Protocol allowed eight developing countries that produce CFCs a grace period of 10 years. They began phasing out production in 1999. China, in accordance with the Montreal Protocol banned the production and import of CFCs and halons as of June, 2007. The grace period was necessary because *new equipment is necessary for the substitute refrigerants*, and its cost posed a problem to poor countries. ▪ However, ensuring compliance by less-developed countries is essential if the Montreal Protocol is to succeed. Money is a form of assistance that developed nations provide. The World Bank agreed to pay Russian companies to compensate them for ending production of CFCs and halons. More recently the Protocol's Multilateral Fund has helped China and Venezuela to end their production.²⁵ These halts are verified by outside experts who will continue to monitor the situation for some years. ▪ Sometimes, information has been useful in helping the ban to succeed. In the case of halons, poor nations especially had the problem of ensuring fire protection while banning the very-effective safe and affordable halons. The UN Environmental Program assisted by providing published case studies showing how this could be accomplished.

²⁴ Some methyl bromide uses have received a "critical use exemption" under the Montreal Protocol. One such exemption was obtained by the UNITED STATES in 2005 for almost 23 million pounds (10 million kg) of methyl bromide, much more than the rest of the world combined. It is used as a soil fumigant and to fumigate shipping crates. However, even in the UNITED STATES increasing restrictions are slowing the use of methyl bromide as farmers slowly transition to alternatives.

²⁵ China closes ozone-depleting chemical plants. *United Nations Environment Programme*, July 1, 2007. <http://www.unep.org/documents.multilingual/default.asp?documentid=514&articleid=5624&l=en>.

Box 8.3

NASA and the twentieth anniversary of the Montreal Protocol²⁶

The twentieth anniversary of signing the Montreal Protocol was celebrated at a September 2007 conference in Greece. Richard Stolarski of NASA spoke of their Aura satellite, which monitors the chemical make-up of the atmosphere. He also noted the data gathered by NASA's Airborne Antarctic Ozone Experiment, which in 1987 "provided the smoking gun measurements that nailed down the cause of the ozone hole being the increase of CFCs combined with the unique meteorology of the Antarctic." After praising the Montreal Protocol as a "resounding success," Stolarski said, "The effect can be seen in the leveling off of chlorine compounds in the atmosphere and the beginning of their decline." • However, springtime ozone depletion in polar regions continues to be prominent and, another NASA speaker noted: "it's a long process" and CFCs aren't expected to fall below the levels that produced the ozone hole until about 2070. Meanwhile it has become clear that ozone depletion and climate change are linked "in subtle but profoundly important ways." NASA scientists now study climate change as well as the ozone layer.

Smuggling CFCs and halons²⁷

One problem is that some facilities in less-developed countries continue to illegally produce CFCs and halons, and their smuggling has been a serious problem. Contraband CFCs are used to recharge auto air conditioners. Halons are still valued fire suppressors. The substitute chemicals don't cost more than the CFCs they replace. However, expensive equipment must be replaced too. The illegal trade may decrease as more less-developed countries receive assistance from the Multilateral Fund to install new equipment. Also demand for contraband will abate as older cars are removed from the road. Nonetheless, illegal trade is seen as an ongoing threat, which could slow recovery of the ozone layer. This is especially true because, as seen below, the first group of chemicals developed as CFCs replacements are strong greenhouse gases. So, these initial alternatives must in their turn be replaced by chemicals that are not greenhouse gases, but remain safe to ozone.

SECTION V

Developing alternatives for ozone-depleting chemicals

The initial substitutes developed to replace CFCs were the *hydrofluorocarbons* (HFCs) and *hydrochlorofluorocarbons* (HCFCs). These gases have some chemical reactivity and thus

²⁶ Thompson, T. NASA keeps eye on ozone layer amid Montreal Protocol's success. *NASA/Goddard Space Flight Center*, September 14, 2007, http://www.nasa.gov/home/hqnews/2007/sep/HQ_07192_montreal_protocol.html.

²⁷ (1) Illegal trade in ozone depleting substances. *UN Environmental Program*, 2008, <http://www.grida.no/publications/vg/vog/page/1395.aspx>. (2) Environmental investigation agency . . . tackles a threat to global ecological security—depletion of the ozone layer. http://www.eia-international.org/campaigns/global_environment/.



Figure 8.7 One of four balloons launched by NASA during POLARIS, an ozone mission. Credit: Phil DeCola, NASA

have the desirable trait of shorter atmospheric lifetimes than CFCs.²⁸ HCFCs (hydrochloro-fluorocarbons or R-22 refrigerant) are now used in almost all air conditioning systems. However, these chemicals are only short-term alternatives because they still have some ozone-depleting ability; also they are found in the atmosphere at growing concentrations. *And* both HCFCs and HFCs share a worrisome trait: they have thousands of times the global-warming potential of CO₂. Thus, these chemicals are also being phased out under the requirements of the Montreal Protocol.

▪ Substitutes have been developed for many of the industrial halocarbon solvents that have ozone depleting potential (ODP). But many farmers remain unhappy with alternatives available for the fumigant methyl bromide. Because methyl bromide is also produced by the ocean, and forest and grass fires, some argue that the amount used by farmers is not great enough to warrant banning it. However, alternatives have been developed and farmers are testing them. ▪ Good alternatives for fire-fighting halons are not yet available. They could nonetheless be banned because a 30- to 50-year supply remains on hand. The non-halon

²⁸ The major chemical difference between CFCs and HFCs and HCFCs is seen from the “hydro” contained in the names of the substitutes: they still contain some hydrogen. It is hydrogen that makes these molecule susceptible to attack by the hydroxyl (OH) radical, so they suffer the same environmental fate that we saw for organic chemicals in Chapter 5: the OH radical destroys atmospheric organic pollutants. So, most HCFC’s are destroyed before they can reach the stratosphere. With ozone-depletion potentials (ODP) of about 0.01–0.1, HCFCs destroy only a small amount of ozone. The other major replacement, HFCs, contain no chlorine at all, so have zero ODP.

fire-fighting substitutes evaluated either have undesirable properties or are very costly. For example, one iodine- and fluorine-containing chemical showed good fire-fighting properties and had a short atmospheric life, but was too toxic for routine use. So, the search goes on.

Developing alternatives for the alternatives

Especially because of their strong capacity to act as greenhouse gases, efforts are being made to phase out HCFCs and HFCs more speedily than initially intended. Thus, US production of HCFC-22 (R-22) will stop in 2010; however, small amounts will be manufactured until 2020 to allow service of equipment using R-22. ■ **Supermarkets** The US EPA has been working with manufacturers and supermarket chains on evaluating new refrigerants. Supermarkets are important businesses with which to begin the transition to safer substitutes because a typical store has been using about 4000 lb (1800 kg) R-22 in its cooling systems. Each can lose 1000 lb (450 kg) per year through leaks so, along with new alternatives, leak prevention is of importance too. ■ As of 2007, the US EPA approved three products, blends of refrigerants, to replace R-22. These do not deplete ozone and, although they have some warming potential, this will be largely circumvented by prohibiting any intentional leakage of the gases to the atmosphere. ■ **Autos** EU countries, especially Germany, are taking the lead in changing over to new refrigerants for auto air conditioners. As of 2011, German carmakers will substitute carbon dioxide for fluorochemicals. However, CO₂ requires new equipment and most automakers prefer a chemical that can directly substitute for HFC-134a, the auto refrigerant now being used around the world. EU countries will be unable to use any fluorinated gas with a global warming potential (GWP) more than 150 times greater than that of CO₂. The chemical manufacturers, DuPont and Honeywell have developed a hydro-fluoroolefin with a GWP of only 4. ■ Remember the CFCs introduced so many years ago in 1928 were so desirable because they were not flammable, toxic or corrosive. Now chemists and manufacturers continue searching for substitutes that not only have those attributes, but that also avoid ozone-depletion or global warming problems.

The future

A decline in CFCs and a return to normalcy^{29,30}

Together, CFC-11 and CFC-12 represent 50% of all CFCs that were used. *Stratospheric* levels of CFCs increased until 2002. Data supporting this conclusion were gathered from monitoring stations around the globe, including the South Pole and Point Barrow, Alaska. Stratospheric levels are now declining, but only slowly because the lifetime of CFC-11 is 45 years and that of CFC-12 is 100 years. However, concentrations in the *troposphere* peaked in 1992–94 and have declined since then. ■ The Antarctic ozone hole still appears

²⁹ Current state of the ozone layer. *US EPA*, 2007, <http://www.epa.gov/ozone/science/currentstate.html>.

³⁰ von Hobe, M. Atmospheric science: revisiting ozone depletion. *Science*, **318**(5858), December 21, 2007, 1878–1879.

each polar spring with peak depletion in September right after the spring sun returns.³¹ There was concern in 2006 when a record-breaking ozone hole opened over Antarctica in September of about 11.4 million mi² (28 million km²).³² However, in 2007 the peak value fell to 9.7 million mi² (23.8 km²); this value was similar to the average of the previous 15 years. It was similar to 2002 and 2004, which had maximum areas of about 8.3 million and 8.7 million mi², respectively (20.4 and 21.4 million km²). Of course, any one of these values is large compared to the 1970s before ozone depletion existed. The UNEP and the WMO had believed that, given full compliance with the Montreal Protocol, stratospheric ozone level would return to normal about the year 2050. However, NASA more recently stated that stratospheric ozone will not return to normal before about 2070.

Further reading

- von Hobe, M. Atmospheric science: revisiting ozone depletion. *Science* **318**(5858), December 21, 2007, 1878–1879.
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³¹ (1) Hansen, K. NASA data reveals “average” ozone hole in 2007. *NASA*, October 18, 2007, http://www.nasa.gov/vision/earth/environment/ozone_2007.html.

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“The key to reducing dead zones will be to keep fertilizers on the land and out of the sea. For agricultural systems in general, methods need to be developed that close the nutrient cycle from soil to crop and back to agricultural soil.”

Robert J. Diaz and Rutger Rosenberg

Whether animal, plant, or microbe, water is essential to life. Fish and other water-dwelling creatures are vulnerable to polluted water and there are waters in the world so polluted that life has disappeared. In other locales fish and shellfish survive, but are not safe to eat because their flesh is contaminated. Humans enjoy being around water, but contamination with infectious organisms often makes swimming unsafe, and being near water with noxious odors or scum is not pleasant. Clean water – and enough of it – is vital. ■ Laws governing water quality existed in the United States before 1972, but no uniform national law existed. Water pollution was not well controlled and some states, eager to keep or attract industry, were negligent. The Clean Water Act¹ (CWA) of 1972 and the Safe Drinking Water Act (SDWA) of 1974 were laws mandating that water pollution be treated uniformly nationwide; they have been updated over the years. ■ In developed countries, water bodies are generally cleaner. In the United States, some are much cleaner than in 1972, the year that Congress passed the CWA: in 1972, only 30% of US waters were judged fishable and swimmable. By 1994, it was greater than 60%. *Fishable* means that fish living in the water are safe to eat and that the water is safe enough for the fish to live in. *Swimmable* means that the water is safe enough to swim in without fear of infectious organisms or other unhealthy contaminants. However, in 2009, many places are still not fishable or swimmable. Moreover, not all water bodies are regularly monitored – perhaps cannot be regularly monitored – leading to large information gaps. Methods used to monitor water also vary widely, and many consider the statistics unreliable.²

This chapter surveys water pollutants, the problems they cause, their sources, and actions taken to reduce their emissions. Section I introduces *point* and *nonpoint* source water pollution. After first emphasizing the importance of the six *conventional* water pollutants, this section moves on to *priority (toxic) pollutants*, and *non-conventional* pollutants. Section II examines some of the water bodies impacted by pollution, groundwater, wetlands, estuaries and coastlines, including an overview of Chesapeake Bay. Section III discusses

¹ Summary of the Clean Water Act. *US EPA*, February 19, 2009, <http://www.epa.gov/lawsregs/laws/cwa.html>.

² Surface waters (with relevant links, including one to fishable/swimmable). *Net Industries*, 2009, <http://www.libraryindex.com/pages/328/Surface-Water-Rivers-Lakes.html>.

reducing point sources of water pollution through the use of wastewater treatment, and the limits to controlling point releases. It briefly examines the reuse of wastewater, and of alternative wastewater treatments. Section IV overviews the very difficult problem of non-point source runoff. Section V discusses the increasingly serious “nitrogen glut” and approaches to reducing it. Finally, Section VI looks at the sometimes catastrophic water pollution in China and efforts taken to reduce it.

Study suggestions

Early in your study of this chapter: 1. Learn the terminology. 2. Examine Table 9.1 to learn major *sources* of polluted runoff, *contaminants* and common ways to *reduce* runoff. This table is far from comprehensive, but provides the basics. Reviewing Figure 9.1 may also be useful.

Table 9.1 Practices to reduce nonpoint pollution to water bodies and coastal waters

Sources and pollutants produced	Reducing, treating, or absorbing runoff ¹
Agriculture (Growing crops) Contaminants include soil, fertilizers (nutrients), and pesticides. If irrigation is used, salt is in the runoff too.	<i>Buffer strips</i> of vegetation next to water bodies to absorb pollutants <i>No-till farming</i> to limit soil erosion <i>Precision farming</i> to reduce fertilizer use <i>IPM</i> to reduce pesticide use and runoff <i>Grow crops year-round</i> so roots prevent soil from washing away
Agriculture (Animal operations) Contaminants include animal wastes with pathogens, nutrients, BOD, suspended solids	<i>Barriers</i> to prevent leaks from waste lagoons <i>Treat feces/urine</i> from factory farms Provide <i>incentives</i> for family farms.
Timber cutting operations Contaminants include soil, BOD, nutrients	<i>Buffer strips</i> of uncut trees near streams Build logging roads to minimize runoff <i>Construct wetlands</i> to capture and treat it
Construction sites Contaminants include soil, oil/grease, heavy metals, debris	<i>Settlement (detention) pond</i> to trap runoff <i>Hay dam or fabric fence</i> around site Lay out site to <i>follow land's natural contours</i> or modify its contours
Cities/suburbs with paved surfaces ² (roads, parking lots, malls, roofs, etc.) Contaminants include oil, grease, metals, PAHs (from vehicle exhaust), salt, sand, bacteria, eroded soil, animal wastes, and debris.	<i>Buffer strips</i> of vegetation. <i>Permeable paving</i> Re-sculpt streets to <i>direct storm runoff into vegetated road median</i> (not storm drain) <i>Infiltrators</i> placed under parking lots ³ Direct runoff to <i>wetlands</i> . ⁴

Table 9.1 (cont.)

Sources and pollutants produced	Reducing, treating, or absorbing runoff ¹
Mining operations Contaminants include acid (sometimes strong), soil and metals	<i>Plant vegetation</i> on sites to retain soil and pollutants, or seal mine as permanent solution For strip mines: <i>restore</i> damaged land and polluted water

¹ Buffer strip of vegetation (grass or trees) slows down runoff, which is further cleansed as it moves to groundwater.

² 99.9% of water hitting paved or roofed surfaces runs off into storm drains

³ Infiltrators collect and partially clean storm water and allow it to seep down to groundwater.

⁴ After major 1993 floods in US Midwest, some levies were torn down and wetlands constructed.

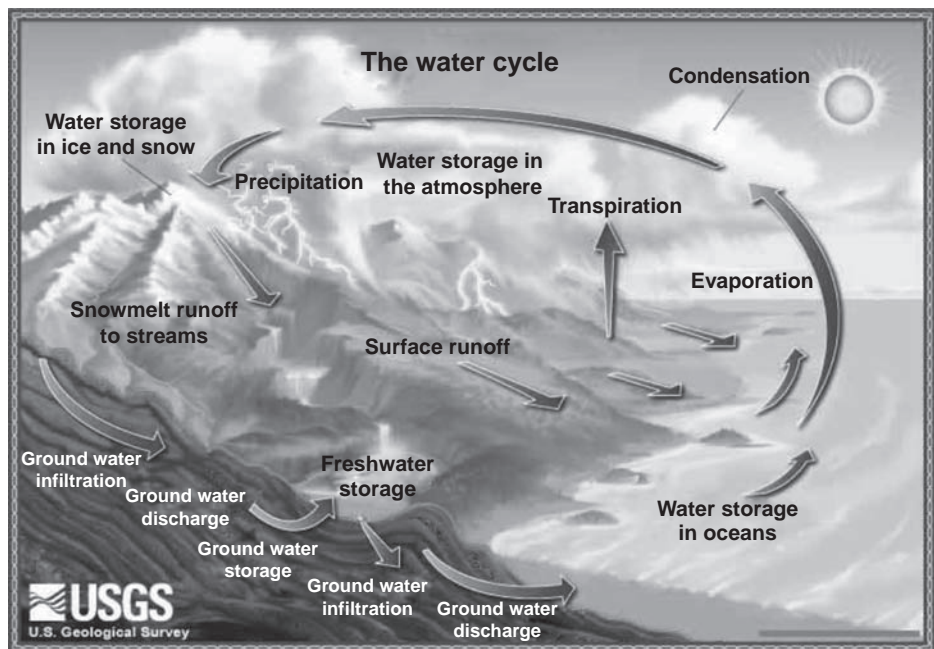


Figure 9.1

Cycling of water in the environment. Credit: USGS

SECTION I

Two major types of water pollution

There are many sources of pollution to water bodies and a number of pathways through which pollutants can move. See Figure 9.2.

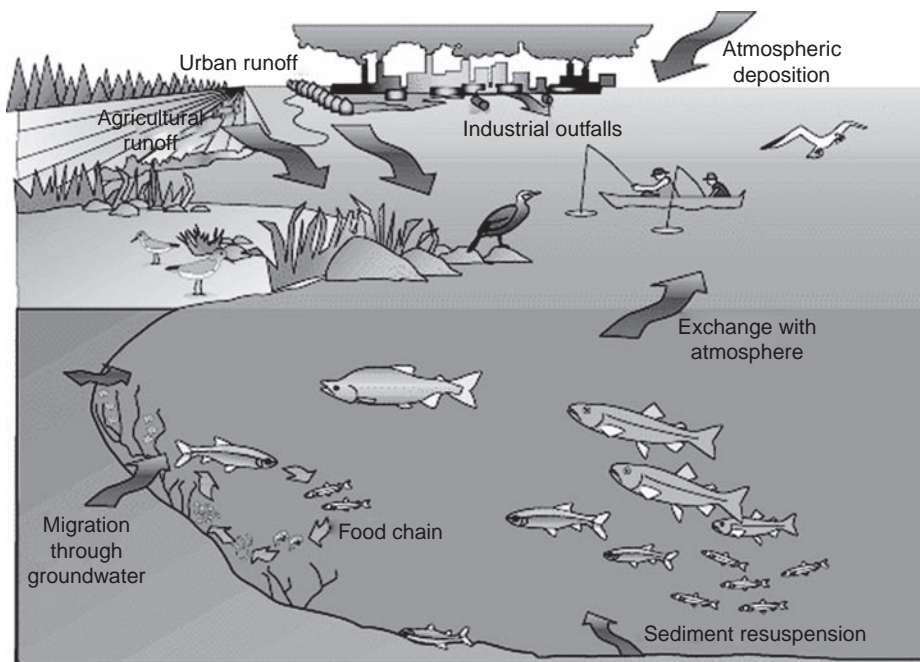


Figure 9.2

Sources and pathways of water pollution. Credit: US EPA

Point source pollution

A *point source* is “any single identifiable source . . . from which pollutants are discharged, e.g., a pipe, ditch, ship, or factory smokestack.” Outlet pipes of industrial facilities or wastewater treatment plants are examples of point sources. Starting in the 1970s, developed countries such as the United States focused their efforts on controlling point sources of water pollution. Point sources originate in large – and easy to trace – facilities. Developed countries control point sources fairly well. However, although the CWA did much to control point sources, its goal was to eliminate pollutant discharges into American waters by 1985. That has not happened.

Nonpoint source pollution³

Nonpoint source (NPS) runoff has sources harder to precisely identify, thus the term non-point. Because of this uncertainty, NPS pollution is harder to control than point source. Just looking at a diagram of a watershed (Figure 9.3) allows you to see the many possible points of origin of a pollutant.

³ (1) What is nonpoint source (NPS) pollution? Questions and answers. *US EPA*, March 7, 2008, <http://www.epa.gov/owow/NPS/qa.html>. (2) Nonpoint source pointers (factsheets). *US EPA*, February 25, 2008, <http://www.epa.gov/owow/nps/facts/>.

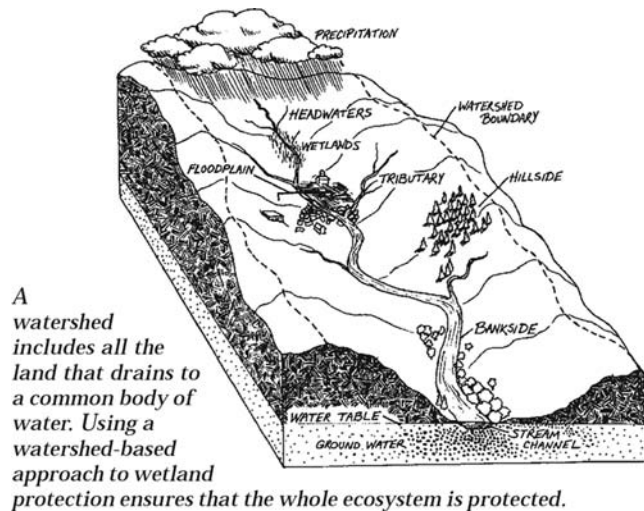


Figure 9.3

Visualizing a watershed. Credit: US EPA

- The word *runoff* indicates rain water or snowmelt carried across land to water. Runoff arises from *nonpoint sources* and can carry oil, grease, dirt, trash, animal waste, micro-organisms, and chemical pollutants such as metals, pesticides, and fertilizers.
- *Urban nonpoint sources* include streets, parking lots, roofs, and construction sites.⁴
- *Rural nonpoint sources* include agriculture, logging, and mining sites. (Table 9.1)
- Think of *watershed*. A watershed is a drainage basin encompassing an area in which rain and other precipitation drains into a particular river or river system (Figure 9.3). It also includes the waters associated with the river – wetlands, aquifers, and estuaries. Basically, all precipitation falling in a watershed flows into one water body. This means that polluted runoff can influence waters distant from its origin.

Polluted runoff is the most serious water quality problem, and is a major problem world-wide. Not all runoff is as obviously polluted as that in Figure 9.4. However, this figure indicates just how heavily some NPS runoff can be. An example of the difficulty of controlling NPS pollution follows: In 1985, European countries decided to reduce excessive amounts of phosphorus and nitrate runoff into the Rhine River. Their goal was to reduce the amount of each nutrient reaching the Rhine by 50% within 10 years. ▪ They succeeded with phosphorus because it came largely from point sources, wastewater (sewage) treatment plants. ▪ However, most nitrate entering water bodies comes via NPS runoff – harder to trace and control. The desired 50% reduction in nitrate has still not been achieved. Table 9.1 notes

⁴ On undisturbed land, rainwater can percolate down through the soil to replenish groundwater. As it moves downward, the soil – providing a natural service – absorbs and detoxifies many pollutants. But on land covered with parking lots, roads, shopping malls, factories, buildings, and homes little soil remains to absorb water. Not only is there no removal of pollutants, there is less replenishment of groundwater, and pollutant-carrying rainwater runs off into water bodies.



Figure 9.4 Visualizing polluted runoff. Note the darker water flowing from the developed area into coastal water (lower right). Credit: US NOAA

major nonpoint sources of pollutants to rivers, lakes and coastal waters and some of the *best management practices* to curb those sources.⁵

Conventional pollutants

Conventional pollutants are a major category of pollutants under the US Clean Water Act. As with the six criteria pollutants, the six conventional water pollutants are often present in large amounts and can have serious, even devastating effects. ▪ The conventional pollutants are *biochemical oxygen demand (BOD)*, *nutrients*, *suspended solids*, *pH*, *oil and grease*, and *pathogenic microorganisms*. ▪ Note Unlike most pollutants described in earlier chapters, *none* of the conventional pollutants are single chemicals. Indeed, microorganisms are living organisms. Each conventional pollutant is dealt with individually below.

Biochemical Oxygen Demand

Microorganisms decompose much of the organic matter in a water body and most require dissolved oxygen (DO) to do so. The amount of oxygen required to decompose a given amount of organic material is the *biochemical oxygen demand* (BOD). Water ordinarily contains some natural BOD such as plant debris and wildlife feces. However, a high BOD

⁵ Polluted runoff, examples of Best Management Practices (BMPs) with photographs. *US EPA*, March, 2008, <http://www.epa.gov/nps/ex-bmps.html>.

often indicates human activity such as emissions from municipal wastewater treatment plants, food-processing operations, chemical plants, pulp-and-paper operations, tanneries, and slaughterhouses. ■ High BOD reduces or depletes the DO in water. In a large water body, fish move away from these *hypoxic* (low oxygen) conditions, but crabs, snails, and sedentary organisms may die. As Professor R. Diaz of the College of William and Mary's School of Marine Sciences noted, "Low oxygen causes more mass fish deaths than any other single agent, including oil spills and it ranks as a leading threat to commercial fisheries and the marine environment in general." Hypoxic water is a problem in the United States and worldwide. Hypoxia can be a chronic problem in a water body or a seasonal occurrence.⁶

Nutrients

Nutrients, although required for life can become toxic when levels get too high (Chapter 3). Manufactured fertilizers (nutrients) contain concentrated *reactive nitrogen*⁷ and phosphorus. Added to agricultural fields, the portion which the plants do not use runs off into water bodies as NPS pollution. Once there, water plants, especially algae absorb the nutrients. This has a cascade of effects (Box 9.2). Although synthetic fertilizer is the major offender, any organic matter has nutrient value. Human activities that discharge organic matter (BOD) into

Box 9.1

Atmospheric deposition as a nonpoint source of water pollution⁸

We typically think of nonpoint source pollution as in water runoff, but atmospheric deposition – also a nonpoint source – can often be prominent.

- Many pollutants can deposit from air. Once deposited, some vaporize again to settle out at yet another place. See Figure 9.5. If they don't become airborne again they may move off in runoff to water. Or seep down through soil to groundwater, being partially or totally detoxified as they go. In groundwater, they move within the groundwater and, in locales where groundwater and surface water mix, may enter surface water.

⁶ A lack of oxygen can suffocate creatures. Moreover, hypoxic conditions – conditions with too little oxygen – can be toxic. Hypoxic conditions appear to transform genetically female fish into fish that look and act like male fish. The implication is that low levels of *dissolved oxygen* (DO) act like an endocrine disruptor, in this case, interacting with the hormones of the reproductive system. See Pelley, J. Dead zones might masculinize fish. *Environmental Science & Technology*, **40**(9), May 1, 2006, 2862.

⁷ Reactive nitrogen is used here as a synonym for "fixed nitrogen" or bioavailable nitrogen. Most plants cannot use atmospheric nitrogen (N₂), however, specialized microorganisms can "fix" atmospheric N₂ into bioavailable chemicals such as ammonia or nitrate. Once "fixed", the nitrogen can be used by plants and algae.

⁸ (1) Air pollution and water quality. *US EPA*, June 19, 2008, <http://www.epa.gov/owow/airdeposition/>. (2) Atmospheric deposition 101. *US EPA*, accessed March 18, 2009, http://epa.gov/oar/oaqps/gr8water/handbook/airdep_sept_2.pdf.

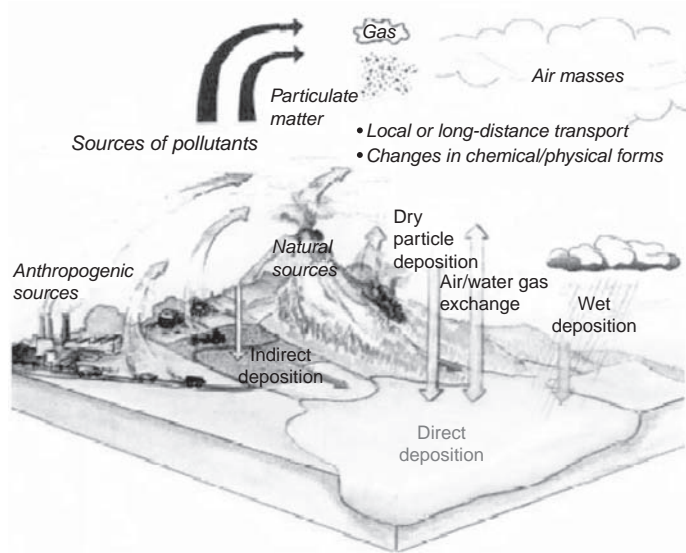


Figure 9.5

Sources and transport of atmospheric deposition upon land and water. Credit: US EPA

- **PCBs** These chemicals (banned in the 1970s) became pollutants when they leaked onto soil from equipment or were discharged from point sources into water bodies. PCBs often become airborne from both water and land, and eventually deposit again onto land and water, sometimes far from their origin. Consider that 91% of the PCBs in Lake Superior, an American Great Lake, were deposited from the atmosphere. And, once in water, PCBs can become airborne again. The cycle continues to repeat.
- **Metals** An estimated 69% of the lead and 73% of the mercury in Lake Superior reached there by atmospheric deposition. Most metals do not become airborne again; mercury is a notable exception.
- **Nitrogen oxides** About 40% of nitrate input into Chesapeake Bay deposits from the atmosphere; the figure is 30% for nitrate input into the Potomac River basin. As an inorganic chemical nitrate doesn't become airborne again (unless caught up in wind-blown dust from land or spray from waters). In this chapter, we see nitrate moving again, this time as a major component of runoff into water bodies.

water were mentioned above. Plant and animal debris and wildlife feces are natural sources of BOD.

Under natural conditions, nutrient input into a water body occurs slowly over a period of many years. This leads to its *eutrophication*, a process “during which a lake, estuary, or bay evolves into a bog or marsh and eventually disappears.” After nutrients reach a certain concentration, the water becomes choked with plant life. Algal “blooms” may form a scum on the water surface, produce offensive smells, give the water a bad taste, and

Box 9.2

BOD and fertilizer nutrients

Nitrate and *phosphorus* (as phosphorus pentoxide) are two nutrients found in commercial fertilizer, which often also contains potash (a *potassium* source). Just as on land, these nutrients *stimulate* plant growth in surface waters. Then, as the vegetation dies, it becomes BOD.

- Nutrients stimulate phytoplankton (algae) growth in water, sometimes enough to cause an algal bloom.
- Zooplankton, tiny animals, eat the proliferating algae.
- As plankton and vegetation, after dying fall toward bottom waters bacteria digest them and also digest the fecal pellets of zooplankton. They use the DO in the water to do so. Thus, if there is much material to digest, oxygen levels fall and aquatic organisms suffer. If most oxygen is depleted, a dead zone can result. Sometimes all DO is depleted.

In estuaries and coastal areas, nitrate is often the major culprit, that is to say that the growth of vegetation is limited by the amount of nitrogen present: add more reactive nitrogen and the vegetation flourishes, especially algae. In freshwater lakes, it is more often phosphorus that limits plant growth.

make it unfit for swimming. ▪ Human activities can put eutrophication on fast forward by rapidly discharging large amounts of nutrients (especially nitrate and phosphorus) into water.⁹ A final step results when the water's DO becomes greatly depleted or eliminated. At that point, it becomes a *dead zone*. Too many nutrients lead to eutrophication and then, increasingly dead zones. Dead zones have been increasing rapidly around the world especially in the northern hemisphere, but are now reported in the southern hemisphere too in less-developed countries. See Section V below for more detail on the nitrogen glut. ▪ Surplus nutrients can impact animals too. For a number of years, frogs have been found with a number of different deformities related to excess nitrogen/phosphorus levels, as described in more detail in the discussion of adverse effects of excess nutrients later in the chapter.¹⁰

pH¹¹

Acid deposition Recall (Chapter 6) that the global problem of acid deposition can lead to water bodies with a pH too low to optimally support life or, sometimes to support life at all.

⁹ The nitrogen in nitrate is reactive nitrogen; plants can use it. When there is more reactive nitrogen than needed, excessive growth of algae occurs. The relatively more rapid growth of algae crowds out the growth of other plant life.

¹⁰ Dunham, W. Frog deformities blamed on farm and ranch runoff. *Reuters*, September 24, 2007, <http://www.reuters.com/article/environmentNews/idUSN2432027920070924>.

¹¹ Extremes of pH can be either acid or basic (alkaline). See Figure 6.2. Too low a pH (excessive acid) is typically the major problem. However, too high a pH (excessively alkaline) can also harm or kill aquatic life as can happen when there is a spill of alkaline "liquor" from a kraft pulp and paper mill.

▪ Mining operations are another source of acid: metal ore and coal deposits often contain metal sulfides, brought to Earth's surface by mining. There, exposed to atmospheric oxygen, sulfide is oxidized to sulfate. If moisture is present, the sulfate is converted to sulfuric acid, which runs off into nearby water. Worsening the situation, sulfuric acid can dissolve the hazardous metals contained in mining wastes, and these too are found in NPS runoff. In the receiving water is a river or stream, the acid may be carried far downstream. If iron is one of the metals present, contaminated streams can turn orange.

Suspended solids

As with other conventional pollutants, suspended solids (SS) are naturally found in water. As always, it is a surplus that is deleterious. Recall that in air, it is the very fine particles which cause the greatest health problems. Similarly, it is the very fine particles in SS, which can cause the most serious problems. ▪ Increased SS content makes water more turbid or cloudy. This limits the sunlight reaching aquatic plants, stunting their growth. ▪ Fine SS can also clog fish gills and harm their respiration and harming the respiration of other aquatic animals. A major source of SS is soil runoff from agricultural fields; row crops such as corn are particular offenders. Forestry and construction activities contribute too. Point sources of SS include facilities that discharge various solids including BOD. ▪ SS entering drinking-water treatment plants can interfere with efficient water disinfection by shielding microorganisms from disinfectant. Surviving microbes enter drinking water.¹²

Oil and grease

Oil spills pose a major problem in near-coastal waters, killing or adversely affecting fish, other aquatic organisms, birds, and mammals. Oil can also kill or injure organisms living in coastal sands and rocks, and the worms and insects that are food to birds and wildlife. If it intrudes into coastal marshes, the oil can damage or kill fish, shrimp, birds, and other animals (Box 9.3). Oil spills can foul beaches used for swimming and recreation. ▪ Despite the sometimes horrendous damage of oil spills, they are seen as a relatively minor problem for fish and the marine environment in comparison to chronic nutrient pollution. Depending upon the amount and type of oil spilled, where it is spilled, and weather conditions, ecosystem recovery can be quick or painfully slow.

¹² Soil particles that are *not* suspended can cause problems too. Heavier particles fall to the bottom of a water body where excessive input can suffocate or damage bottom-dwelling organisms, and change the characteristics of the water body. In the worst cases, it fills in stream beds. Eroded soil carried in runoff from agricultural lands and construction sites has badly impaired water quality in a number of rivers and lakes in the UNITED STATES and elsewhere.

Box 9.3

The *Exxon Valdez*

The Exxon Valdez oil tanker spilled 39 000 tons (35 200 tonnes) when it went aground in Prince William Sound, Alaska, in March, 1989. It was the largest spill in US history, killing hundreds of thousands of birds and marine animals and soiling 1200 miles (1931 km) of coastline. Clean up and reparations cost billions of dollars. By 2006, water, beaches, and animals appeared to have recovered, but oil persists below the surface along about 6.2 miles (10 km) of shoreline.¹³ There is controversy as to whether this still harms animals that live or feed in this beach (in the part exposed during low tide) as when otters dig into the shore. However, one researcher commented, “The oil really is petering out, and it doesn’t look bioavailable.” Regardless of lingering effects, consider the 1993 comments of biologist Rick Steiner describing the spill’s effects. “The essence of the disaster lies in images of once-playful river otters oiled and crawling off to die in rock crevasses along their home streams; bald eagles losing their grip in the treetops, falling dead deep in the forest; orphaned sea otter pups searching for dead parents, shivering through oiled fur in cold water that once seemed warm; seals, sea lions, and whales staring up at a black surface through which they must swim in order to take their next breath, eyes and nostrils inflamed, often then inhaling oil instead of air; diving birds, soaked in oil and unable to fly, with simply nowhere to go but back into the thick of the oil. If nothing else, the *Exxon Valdez* should serve to remind all of us that any true prosperity we seek in this world must also include consideration for the many innocent beings along the way.” Mr. Steiner would probably use similar words to describe the more recent “spills.”

The Exxon Valdez is a notorious example of an oil spill causing major damage¹⁴ (Box 9.3). Other large spills may result from¹⁵ oil line leaks, as has occurred in the Arctic (Alaska and Siberia). Warfare has caused horrendous spills, most recently (2006) when Israel bombed an oil-burning power plant in Lebanon. The largest occurred during the 1991 Gulf war, when Iraq deliberately released 882 000 tons (800 000 tonnes) of crude oil into the Persian Gulf – 23 times the amount spilled by the Exxon Valdez. ▪ How difficult spills are to clean up partially depends on weather; it may be helpful if wind and water currents move the oil out to sea. Viscous and sticky oil is harder to clean up, whereas products such as diesel evaporate and dissipate fairly quickly. Equipment used to contain oil spills includes “booms and skimmers.” Chemicals such as dispersants and gelling agents may be used. Shorelines may be partially cleaned by raking and bulldozing. No method is wholly satisfactory; often the damage cannot be reversed.

Small spills on land result from leaks from vehicles, and oil released during accidents. Rain washes these off roads and into water bodies. Improperly disposed of used oil also washes into water bodies; a portion may seep into groundwater. Direct releases of oil into water bodies also occur: motor and other recreational boats release up to 30% of their fuel,

¹³ Renner, R. Exxon Valdez oil no longer a threat? *Environmental Science & Technology*. **40**(20), 15 Oct 2006, 6188–6189.

¹⁴ Exxon Valdez oil spill. *Wikipedia*, March 15, 2009, http://en.wikipedia.org/wiki/Exxon_Valdez_oil_spill.

¹⁵ Key facts about oil spills. *Reuters*, August 17, 2006, <http://www.planetark.com/dailynewsstory.cfm/newsid/37692/story.htm>.

unburned, into water. ▪ Such individually small, but ongoing events add up to much more oil than is spilled in a dramatic event such as the *Exxon Valdez*. However, the environmental impact of ongoing small events is hard to assess.

Pathogenic microorganisms¹⁶

Most microorganisms do not cause disease.¹⁷ ▪ The problem arises with very specific microbes: *pathogens*. Pathogens can cause infectious disease. A microbial pathogen can be a bacterium, virus, fungus, protozoan, or toxic algal species. In Chapter 10 we will explore pathogens in drinking water. These pose a tremendous health threat. ▪ Infectious microbes found in shellfish (or the toxins that some produce) can halt their harvest as food. ▪ Pathogenic viruses and bacteria in coastal water can infect swimmers. Viruses are abundant in coastal waters, often surviving in salt water longer than bacteria. Infection results through ingesting contaminated water or through broken skin. In the United States, as many as 19 out of 1000 swimmers each year are reported to suffer gastroenteritis caused by swimming in water containing infectious microbes.

Sources of pathogens

- Nonpoint Pathogenic microbes in a water body often result from human activities on land; they arrive via runoff of storm water, from improperly operating septic systems, and runoff from livestock operations. ▪ Eighty-five percent of beach closures in the United States are traced to the presence of fecal bacteria, which arrived in storm water runoff, often from impervious paving in the area. Certain fecal microbes from septic systems near the beach can pass through soil to groundwater and to beach areas – sometimes within hours. ▪ But a bigger problem in coastal areas is the increasing amounts of impervious paving; these have a direct relationship to fecal microbes reaching the beaches. Consider one rapidly growing coastal area in North Carolina: in one subdivision where asphalt and concrete covered 22% of the surrounding watershed, the fecal coliform count was seven times higher than in a nearby subdivision where the figure was only 7%. Impervious surfaces increase in tandem with increasing population and more developed land: “the most polluted beaches and bays in the United States are generally located in densely populated coastal counties.”¹⁸

¹⁶ Water Quality Criteria, Microbial (pathogen). *US EPA*, May, 2008, <http://www.epa.gov/waterscience/criteria/humanhealth/microbial/microbial.html>.

¹⁷ Microorganisms perform useful, often vital functions for humans including assisting the digestion in our guts. We also depend on microbes to degrade organic wastes in the environment, and to biodegrade the organic material in trash and landfills. We use microbes in fermentations to make food products, pharmaceuticals, and other chemicals. They are ubiquitous in our environment, found almost anywhere that one looks. Professors Bruce Levin and Ruston Antia state, “Almost every time we eat, brush our teeth, scrape our skin, have sex, get bitten by insects, and inhale, we are confronted with populations of microbes that are capable of colonizing the mucosa lining our orifices and alimentary tract and proliferating in fluids and cells within us. Nevertheless, we rarely get sick much less succumb to these infections.”

¹⁸ Mallin, M. A. Wading in waste. *Scientific American*, **294**(6), June, 2006, 53–59.

- Point Some pathogens arrive from point sources, especially poorly performing municipal sewage treatment plants. ▀ The situation is worse in many less-developed nations where most sewage may be dumped untreated into rivers and oceans.

Priority (toxic) pollutants

Conventional pollutants often pose the largest and the worst pollution problems with which we must deal, but other pollutants can be significant. *Priority water pollutants*, also called *toxic pollutants* form another category regulated under the CWA. Recall that many pollutants such as lead or chloroform are found in more than one environmental medium, and you won't be surprised to learn that many of the hazardous air pollutants (Chapter 5) are commonly found as water pollutants too. ▀ The US EPA, under the CWA, regulates 126 pollutants, including the metals, arsenic, cadmium, lead, mercury, nickel, copper, and zinc. Thus, these metals are *both* priority water pollutants and hazardous air pollutants (HAPs), see Table 5.4. ▀ Likewise, many organic chemicals that are HAPs are also priority water pollutants too; these include widely used industrial chemicals as benzene, toluene, as well as many pesticides.

▀ A high concentration of a priority water pollutant, commonly a pesticide, may cause acute illness in aquatic creatures or death. In the United States, fish kills continue to be reported as a result of runoff of spilled pesticides or other chemicals. In lower concentrations, many priority pollutants present a chronic health risk as when certain pesticides act as environmental hormones (Chapter 3). Point sources of priority pollutants, such as wastewater treatment facilities can usually be well controlled. Nonpoint sources are more problematic as when pesticides run off from agricultural fields; when organic chemicals runoff from city streets; or when PAHs are deposited from air.

Pesticides

US Geological Survey (USGS) scientists over a 10-year study found pesticides and their breakdown products nationwide in United States streams, usually as mixtures of pesticides.¹⁹ More than 90% of USGS samples contained at least two pesticides (and their metabolic products); 20% contained ten. Organochlorine pesticides banned years ago – DDT, dieldrin, and chlordane – did show *declining* concentrations as compared to earlier years. These results were found in both rural and urban locales, in streams, groundwater, riverbed sediments, and fish tissues. Pesticide concentrations were fortunately low, but could impact aquatic life or fish-eating animals.

¹⁹ Christen, K. Pesticide mixtures ubiquitous in US streams. *Environmental Science & Technology*, **40**(11), June 1, 2006, 3446–3447 [also see <http://pubs.usgs.gov/fs/2006/3028/>].

Banned discharges

The Clean Water Act totally forbids discharges of radioactive chemicals, chemical warfare agents, and biological warfare agents. ▪ Discharge of PCBs is prohibited under the Toxic Substances Control Act (TSCA). In industrialized countries, the manufacture of PCBs was banned in the 1970s, but they still persist in runoff from old spills, waste sites, or leaks from old electrical equipment. As a result of discharges into water that occurred when PCB manufacture was still legal, these long-lived chemicals still survive in sediments where they are more likely found due to their low solubility in water.

Nonconventional and nontoxic pollutants

A third group of water pollutants regulated under the CWA is the *nonconventional and nontoxic pollutants*. Here we find ammonia, chloride (as in sodium chloride), iron, aluminum, total phenols, and color. ▪ Many facilities—textile factories, for instance, discharge colored effluents. The intensity of the discharged color is regulated by law. ▪ Heat is regulated too. Electric power plants especially, but also many industrial facilities discharge heated effluents. This thermal pollution can cause problems but not ordinarily so serious as many other pollutants discussed in this chapter.

Salt Remember that the “dose makes the poison.” Then consider that, as of 2005, the United States had enough impervious paving (blacktopped surfaces) – roads, parking lots and driveways – to cover the state of Ohio. More continue to be built. ▪ Now think that EPA’s limit for salt in drinking water is 500 mg/l. ▪ Then consider that sodium chloride (NaCl) – plain table salt is used every winter to clear snow and ice from American roads in northern climates.²⁰ ▪ Water moving over paved surfaces dissolves the salt – it is very water soluble – and carries it to nearby streams. ▪ More salt is used every year because there are more paved surfaces every year. Thus, the amount of salt reaching northern US streams increases yearly. The result is that streams and groundwater are becoming salinized. ▪ In streams feeding into Baltimore, Maryland, reservoirs, salinity increased from ~10 mg/l to ~50 mg/l between the 1970s and 2004. In Dutchess County, NY, the increase was from 30 mg/l to ~60 mg/l between the 1980s and 2004. These values correspond to about 25% of the concentration of chloride found in seawater. Even in summer, some streams remain up to 100 times more saline than unaffected streams. ▪ University of Maryland researcher, Sujay Kaushal stated, “There is a direct connection between the number of driveways and parking lots and the quality of our water.” There are alternative means to de-ice roads, but they too have impacts. “The problem is the number of roads,” said Kaushal.

²⁰ (1) Kaushal, S. S., *et al.* Increased salinization of fresh water in the northeastern US. *National Academy of Sciences*, **102**, October 3, 2005, 14487–14488, <http://www.pnas.org/content/102/38/13517>. (2) Jackson, R. B. and Jobbágy, E. G. From Icy Roads to Salty Streams. *Proceedings of the National Academy of Sciences*, Published online October 3, 2005. <http://www.pnas.org/content/102/41/14487.full>.

SECTION II

Water bodies impacted by pollution

When thinking about a pollutant, consider the water body it impacts. Is it a river, lake, stream, wetland, estuary or coastal water, ocean or groundwater? This can be important:

- A specified amount of pollutant running off one time into a large fast-running river may have little impact, but the same amount may be noticeable in a slow-moving stream or small lake.
- If the pollutant continues to enter the large river in large quantities – as when reactive nitrogen from fertilizer enters the Mississippi River system – the river itself may still remain undamaged. *But* the locale to which the pollutants are carried may be harmed – consider the Gulf of Mexico dead zone at the mouth of the Mississippi, as you will see in Section V, below.
- Metals are natural components of sea water, and small additional inputs may go unnoticed. But adding the same amount of metals to a freshwater lake, where concentrations are normally low, may lead to problems. Lakes may also have little exchange of water to dilute the metal.
- Or, what happens if an organic pollutant is added to surface water? Microbes, oxygen, sunlight, and wave movement may break it down, or it may evaporate. Conversely, in groundwater there are few means to degrade the pollutant.

Groundwater²¹

More than a quarter of the world's population depends on groundwater for drinking water. In the United States, metropolitan systems usually depend on surface water, but plants in smaller communities often use groundwater. When groundwater is very deep underground, contaminants running off in rainwater may not reach it. However, much of the groundwater used for drinking water is in shallow aquifers and above-ground pollutants may be incompletely removed as they are carried down into groundwater. Once in groundwater then, because of often close connections between shallow groundwater and surface water, the pollution can reach surface water. ■ Because groundwater can come in contact with surface water, its contaminants can reach surface water; the opposite is also true, i.e. surface water pollution sometimes reaches groundwater. ■ Once polluted, groundwater can remain that

²¹ Groundwater is found beneath the Earth's surface in aquifers (porous geologic formations). Sometimes groundwater flows in a channel, but not ordinarily like a surface stream. Rather the formation is composed of permeable rock, gravel, or sand that is saturated with water. Groundwater can flow, but ordinarily more slowly than surface water. On the other hand, groundwater sometimes supplies above-ground springs and wells. (1) Ground water and drinking water. *US EPA*, <http://www.epa.gov/safewater/>. (2) Ground water primer. *EPA and Purdue University*, <http://www.purdue.edu/dp/envirosoft/groundwater/src/ground.htm>.

way for a long time. Especially in slow-moving groundwater, pollutants may persist indefinitely. ▪ Oily chemicals with low water solubility pose special problems. Trapped in soil and rock, they may continue to slowly leach into the groundwater, maintaining contamination indefinitely. ▪ Groundwater can flow albeit often very slowly.

Sources of groundwater pollution

Water-soluble surface pollutants infiltrate soil, often reaching groundwater. Shallow groundwater is most easily contaminated. ▪ How much pollutant reaches groundwater depends on soil type, pollutant characteristics, and the distance to the groundwater. ▪ Contamination sources (Table 9.2) include agricultural and urban runoff, chemical spills, and landfill leachate – anything releasing pollutants that are able to descend through soil into groundwater. Land use affects how much pollution reaches groundwater: intensively used agricultural land can leach out nutrients (reactive nitrogen in fertilizers), pesticides, and microbes; a portion of each of these can reach groundwater. ▪ Likewise, in urban areas highly contaminated runoff, once it reaches surface soil can percolate down to groundwater carrying with it a portion of its pollutant load. ▪ Pathogens, especially viruses which are much smaller than most bacteria, reach groundwater too. Thus, sewage from improperly installed or maintained septic systems can contaminate groundwater; as can nitrate in wastes from confined-animal operations. ▪ Improperly protected landfills can leach contaminants, some of which reach groundwater. This is also true for petrochemicals from leaking underground-storage tanks. Groundwater often has detectable levels of pesticides too. ▪ You begin to see that a great many pollutants can be found in groundwater. Detectable doesn't necessarily indicate a problem, but points out the need for pollution prevention (P²) because cleaning up groundwater is either very difficult or not possible at all.

Pollution prevention and reducing groundwater contamination

- Surface water and groundwater are often closely interconnected, and runoff can contaminate both. Thus, a holistic approach is necessary. The US EPA works with states to

Table 9.2 Sources of contamination to groundwater*

Source	Contaminant
Landfill (improperly built or maintained), old dump, unsecured hazardous waste site	Water-soluble chemicals in trash (metals, salts, some organic chemicals)
Septic systems (poorly built or maintained)	Microorganisms including pathogens
Farms, grassy areas (lawns, golf greens, etc.)	Fertilizer (nutrients) and pesticides
Animal farms (especially large-scale operations)	Nutrients and microorganisms leached from feces
Surface spills	Oil, hazardous chemicals, etc.

* Groundwater is frequently used for drinking water, so humans may be exposed to these contaminants. Also, groundwater can often contact surface water in streams, rivers, lakes, thus allowing any contaminants to reach surface water. Information source: US EPA <http://www.epa.gov/ogwdw/protect/assessment.html>.

develop pollution prevention (P²) strategies to protect watersheds that feed aquifers and wellheads. (A *wellhead* is the immediate area around the intake of a public water supply.)

- P² can help maintain groundwater purity as when regulations specify that only those pesticides with little tendency to migrate into groundwater can be used in a wellhead area, or regulations may specify how to apply pesticides in a way that limits the amount that runs off with rain. ▪ Another P² approach is regulating how land can be used: prohibiting siting of landfills or gasoline stations over groundwater that feeds into a wellhead. Prohibiting large confined-animal operations near vulnerable groundwater, or more strictly, prohibiting farmers from grazing livestock there. ▪ A hazardous waste site is an example where pollution already exists and only control, not P² is possible. However, it is still possible to control the levels of waste site pollutants reaching groundwater.

Groundwater can be hard or impossible to clean up

- Groundwater, once polluted can remain so for years, decades, or indefinitely. ▪ Cleaning up polluted groundwater is extremely costly, often not possible with today's technology. Nonetheless, *pump-and-treat* is commonly used with the goal of restoring the water to drinking-water quality. The groundwater is pumped to the surface, treated to remove pollutants, and then returned to its source. Especially in aquifers with large volumes of water, pump-and-treat may continue for many years without notably reducing pollution. ▪ A US National Academy of Sciences panel, after extensively studying pump-and-treat, concluded that some sites would not reach drinking water quality even if treatment continued for 1000 years. The panel advised against its routine use, instead recommending containing the contaminated water in place until effective treatment technologies become available. ▪ *Containment* involves building an underground barrier to prevent contaminants from migrating off-site. However, this works only for shallow water that is contaminated in a way that it can realistically be contained. ▪ Sometimes groundwater is treated in place, not removed from the aquifer. One such technique involves digging trenches, and installing tons of iron filings mixed with sand in the path of the groundwater. As contaminated groundwater flows through this permeable barrier, some organic pollutants, such as trichloroethylene will react with the iron, and decompose into benign products. ▪ Another in place technique being explored is using anaerobic microorganisms that can degrade the contaminants. (They need to be anaerobic because groundwater has little oxygen.)

Volatile organic chemicals in groundwater

The United States manufactures very large quantities of volatile organic chemicals (VOCs), and has done so for many years. Many are environmentally persistent and are known to be able to migrate in groundwater.²² ▪ Given these facts, it was logical to investigate whether VOCs were contaminating groundwater and drinking water. The US Geological Survey analyzed thousands of samples from aquifers and drinking water wells from around the

²² The types of products produced in which VOCs are used include plastics, adhesives, paints, gasoline, fumigants, refrigerants, and dry-cleaning fluids.

United States, monitoring for 55 different VOCs.²³ They detected 42 in the nation's aquifers. Chemicals often detected included toluene, tetrachloroethylene, trichloroethylene, and MTBE (methyl tertiary butyl ether). ▪ Investigators found that most aquifers throughout the United States *did* contain detectable VOCs, not just those in certain locales. Fortunately, concentrations were all very low and the VOCs were *not* detected at all in about 80% of the home drinking water wells sampled. ▪ It is not reassuring that these chemicals were found. However, the facts that levels were almost all very low, and that the VOCs were not typically detected in home wells is reassuring. Again think P²: prevent further pollution.

Wetlands²⁴

The US EPA describes wetlands as the “link between land and water . . . transition zones,” which are not necessarily wet year around. Chapter 1 noted ecosystem services of wetlands, swamps, bogs, and marshes (coastal and inland). ▪ Relevant to this chapter is the sequestering of pollution in wetlands: they absorb surplus nutrients, sediment, and other pollutants before they reach rivers, lakes, and other water bodies. They also absorb and slow floodwaters, thus alleviating flood damage; and provide habitat for thousands of species of plants and animals. Thus, knowing that an estimated 50% of the world's wetlands have already disappeared means knowing that we have lost a major source of pollution and flood control and have lost wildlife habitat. ▪ Although wetlands can buffer against pollution, they can be overwhelmed and become contaminated enough to harm the animals, plants, and microbes that live within them. Constructed wetlands will be addressed in Chapter 10.

Questions 9.1

1. Remember concepts from Chapter 3. (a) Why should we concern ourselves about very low levels of a pesticide? (b) When multiple pesticides are present, what is the difficulty in determining the total toxicity of the mixture?
2. Consider that the health limit for salt in drinking water is 500 mg/l and the highest value in polluted streams in the example given earlier is ~60 mg/l. So, why be concerned?
3. Levels of VOCs detected nationwide in groundwater were almost all very low. Moreover, they were seldom detected in home wells. This is reassuring, but what else could concern us?
4. Ponder some facts. (1) The population of southeastern Michigan may grow by 6% in the coming 20 years, but the amount of developed land could grow 40%. (2) Nationwide, the average number of persons per household declined from 3.6 to 2.7 over the past 40 years, thus increasing the number of households. (3) The number of vacation homes in the United States is increasing. (4) The amount of shopping space per person has been increasing, usually as more shopping malls. So: (a) How do these facts lead to greater water, air, and land pollution? (b) What can you as an individual do to begin turning this situation around?

²³ Moran, M. J., Hamilton, P. A., and Zogorski, J. S. Volatile organic chemicals in the nation's ground water and drinking water supply wells: a summary. *USGS*, April, 2006, <http://pubs.usgs.gov/fs/2006/3048/>.

²⁴ (1) Wetlands. *US EPA*, January 14, 2009, <http://www.epa.gov/owow/wetlands/>. (2) Wetlands Fact Sheets. *US EPA*, January 12, 2009, <http://www.epa.gov/owow/wetlands/facts/contents.html> (3) Wetlands Overview. *US EPA*, 2004, <http://www.epa.gov/owow/wetlands/facts/overview.pdf>. (4) Functions and Values of Wetlands. *US EPA*, September, 2001, http://www.epa.gov/owow/wetlands/facts/fun_val.pdf.

5. Environmental degradation can be a major urban problem. However, per capita, a person living in a large city such as New York exerts a lower environmental impact than a person in a suburb. How?

Estuary and coastal pollution: the marine environment²⁵

Historically, people believed that we could never fish out our oceans. We also saw oceans as infinitely able to dilute and disperse anything dumped into them.

Why so much coastal pollution²⁶

About 80% of the pollution entering estuaries²⁷ and coastal areas arises from land-based activities as rainwater and snow-melt runoff carries pollutants into rivers and streams and then to the coast.

- A root cause of the pollution is the continuing growth of human population – especially coastal population: a third of humanity lives within a hundred kilometers (~62 miles) of a coastline. Growing in tandem with population are agricultural lands to which large quantities of manufactured fertilizers are applied leading to runoff of the surplus reactive nitrogen and phosphorus applied. At the same time, a non-stop increase in impervious surfaces promotes runoff of a variety of urban pollutants. In the United States, urban sprawl consumes 20 000 acres (8100 hectares) of coastal wetlands a year: these are wetlands that, among their many services could absorb polluted runoff.
- The United States produces at least 10 billion gallons (38 billion liters) of wastewater each day. Although most sewage is treated, about 85% of the treated effluent flows into estuaries and bays. Especially in areas near large cities, this has an impact. The US EPA reported in 2007 that a third of the country's estuaries were in poor shape.²⁸

Coastal waters are increasingly stressed by pollution,²⁹ and fisheries and other coastal resources degraded; wildlife and bird populations continue to decrease due to ongoing

²⁵ (1) Lambert, L. One-third of US estuaries in bad shape: EPA. *Reuters*, June 7, 2007, <http://www.reuters.com/article/environmentNews/idUSN0531143320070606>. (2) Sherman, B. NOAA report on nutrient pollution forecasts worsening health for nation's estuaries. *NOAA Public Affairs*, July 31, 2007, http://oceanservice.noaa.gov/news/pressreleases/july07/supp_073107.html.

²⁶ National Coastal Conditions Reports. *US EPA*, December 9, 2008, <http://epa.gov/owow/oceans/nccr/>.

²⁷ An estuary is where a river reaches the ocean. It is an intertidal zone containing partially fresh and partially salt water. An example is the region where the Sacramento and San Joaquin Rivers empty into a delta on the San Francisco Bay, historically a great maze of channels, wetlands, and ponds, which supported tremendously prolific life. Many estuaries are greatly modified by human activities.

²⁸ Lambert, L. One-third of US estuaries in bad shape–EPA. *Reuters News Service*. June 7, 2007. <http://www.planetark.com/dailynewsstory.cfm/newsid/42456/story.htm>.

²⁹ (1) Halwell, B. Ocean pollution worsens and spreads. *Worldwatch*, 2008, <http://www.worldwatch.org/node/5474>. (2) Wetlands, oceans and watershed. *US EPA*, December 15, 2008, <http://www.epa.gov/owow/>.

destruction of habitat by development, invasive species, and pollution. ▪ In 2004, two separate commissions reported that US coastal waters and oceans are in a state of crisis. And a 2007 National Coastal Condition Report³⁰ rated 25% of US coastal waters as impaired for swimming, 22% impaired for fishing, and 28% as unable to fully support aquatic life. ▪ One major problem, according to a NOAA (National Oceanic and Atmospheric Administration) study is the continued eutrophication of coastal waters. The study expressed pessimism for the future if communities don't begin to control NPS nutrient pollution.³¹ See Section V, the “nitrogen glut.”

Sewage pollution

Shellfish harvesting

At any given time, about a third of US shellfish beds are closed to harvesting because of contamination with fecal microorganisms. ▪ To reduce coastal pollution, the United States bans ocean dumping of industrial waste and sewage sludge, treated or not. The US EPA works with states and cities along marine and Great Lakes coasts to reduce pollution; the hope is to maintain shellfish harvesting, fishing, and swimming or to regain them once lost. Large coastal cities must have stormwater discharge permits which, among other requirements, stem the flow of pollutants into the sea.³² US municipalities are slowly meeting stricter combined sewer overflow regulations that prevent untreated sewage from flowing into water bodies; see Box 9.4. Chapter 10 will come back to sewage pollution in more detail.

Box 9.4

Sewer terminology

- A *sewer* is an underground pipe system that carries wastewater to a treatment plant.
- A *sanitary sewer* carries wastewater from homes, commercial, industrial and institutional establishments to a treatment plant.
- A *storm sewer* carries the street runoff from rainstorms or melting snow.
- A *combined sewer* carries both sanitary wastewater and storm water runoff. Its contents should go to a wastewater treatment plant. However, if a heavy storm exceeds the capacity of the system, it overflows. Then, the combined *sewer overflow (CSO)* containing both untreated sewage and contaminated storm water discharges into nearby water bodies untreated.³³ See Figure 9.6. Combined sewers date from the late nineteenth and early twentieth century, and remain in use in many hundreds of eastern and mid-western US cities.

³⁰ US national coastal condition report. *US EPA*, December 9, 2008, www.epa.gov/owow/oceans/nccr.

³¹ (1) Effect of nutrient enrichment in the nation's estuaries. *NOAA*, 2004, http://ccma.nos.noaa.gov/publications/eutroudate/Exec_summary.pdf. (2) The future looks bleak for US coastal waters. *Environmental Science & Technology*, **41**(19) October 1, 2007, 6637.

³² Stormwater management. *US EPA*, December 24, 2008, <http://www.epa.gov/oaintrnt/stormwater/index.htm>.

³³ Tibbetts, J. Combined sewer systems: down, dirty, and out of date [basic information on wastewater treatment]. *Environmental Health Perspectives*, **113**(7), July 2005, A464–467.

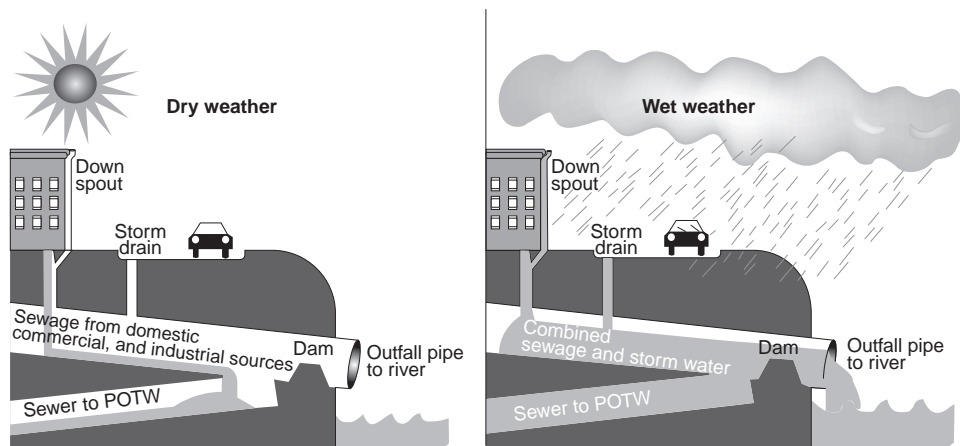


Figure 9.6

How a combined sewer works and what happens in wet weather. Credit US EPA

Closing beaches³⁴

- Storm-water runoff, CSO, and other poorly controlled sewage continue to reach coastlines, and lead to the closure US beaches for swimming. In 2006, there were closures or health advisories at 3500 beaches on the oceans and Great Lakes – up from 1500 in 1998. Closure is due to fecal bacteria such as *Escherichia coli* from animal and human wastes.
 - In southern California alone, 1.5 million (out of about 80 million) swimmers and surfers suffer gastrointestinal symptoms (stomach cramps, diarrhea, and vomiting) after contact with coastal water. Savings in healthcare costs would likely more than offset the costs of preventing beach contamination.³⁵ Not only water is contaminated, beach sand is also infected with fecal bacteria. Indeed coastal waters flush themselves clean before the bacteria in the sand expire.³⁶

Not just sewage pollution

In the 1990s, the US EPA began to regulate or provide guidelines for storm-related events, not just for CSO, but also for storm drains that discharge directly to water, carrying pollutants and trash with them.³⁷ The Natural Resources Defense Council believes that instead of expensive engineering solutions, New York City (one city with major stormwater

³⁴ (1) Beaches: basic information. US EPA, December 1, 2006, <http://www.epa.gov/beaches/basicinfo.html>. (2) Health concerns close record number of US beaches in 2006, August 7, 2007. ENS, <http://www.ens-newswire.com/ens/aug2007/2007-08-07-02.asp>.

³⁵ Polakovic, G. Healthcare savings could offset beach cleanup costs. *Los Angeles Times*, July 18, 2006.

³⁶ Sand can be polluted even with clean water. *The Associated Press*, May 24, 2006, http://www.washingtonpost.com/wp-dyn/content/article/2006/05/24/AR2006052402306_pf.html.

³⁷ Stormwater program. US EPA, April 30, 2009, http://cfpub.epa.gov/npdes/home.cfm?program_id=6.

problems) could use “green” solutions: more trees, roofs with gardens, and porous pavement. These could help to capture storm water where it falls rather than allowing it to runoff and overwhelm sewers.

Coastal pollution beyond the United States

International coastal pollution

In less-developed countries beach pollution can be much worse. Most sewage is dumped into rivers and oceans untreated. The UN Environmental Program (UNEP) stated in 2007 that, “Rising tides of untreated sewage and plastic debris are seriously threatening marine life and habitat around the globe.”³⁸ Developed countries can sometimes be casual about disposing of their sewage too including, surprisingly, Canada. ▪ Not only does about a third of humanity live within a hundred kilometers (62 miles) of a coastline, people increasingly live in megacities – cities with a population of 10 million or greater. Thirteen of the world’s current 19 megacities are coastal cities. Worse, coastal populations are projected to double in the coming 40 years. Sewage pollution will be discussed further in Chapter 10.

Plastics are a major pollutant

A person walking along a coastline even on isolated Arctic beaches can see the accumulated trash on the world’s beaches. One man, hiking on the most isolated of Iceland’s beaches, reported his dismay at finding trash on all of them. David Barnes of the British Antarctic Survey notes that plastic debris is found even the remotest regions of Antarctica, saying “Truly pristine locales no longer exist.” In parts of the Southern (Antarctic) Ocean, the volume of marine debris has tripled in just a decade.³⁹ ▪ Plastic debris is estimated to kill a million seabirds and 100 000 marine mammals and turtles each year as they ingest or become entangled in plastic bags, fishing line and nets, six-pack holders, string from balloons and kites, glass bottles, and cans.⁴⁰ Plastic bags, bottle tops, and polystyrene foam coffee cups have been found in the stomachs of dead sea lions, dolphins, sea turtles and birds. North Sea seagulls had an average of 30 pieces of plastic in their stomachs, according to a 2004 study. Only about 20% of the plastic debris comes from offshore sources, the other 80% from land. Plastics do not biodegrade, but break up into smaller and smaller pieces, and finally microscopic bits. Even tiny one-celled phytoplankton can absorb these bits. Chapter 11 will discuss further the massive amounts of plastics reaching our oceans.

³⁸ Leahy, S. Marine scientists report massive “dead zones,” United Nations report on the marine environment. *Inter Press Service*, October 6, 2006, <http://www.commondreams.org/headlines06/1006-04.htm>.

³⁹ Leahy, S. Marine scientists report massive “dead zones,” United Nations report on the marine environment. *Inter Press Service*, October 6, 2006, <http://www.commondreams.org/headlines06/1006-04.htm>.

⁴⁰ The world’s only snapshot of trash in the ocean and its hazardous effects on ocean life. *Ocean Conservancy*, April 16, 2008, http://www.oceanconservancy.org/site/News2?abbr=press_&page=NewsArticle&id=10773.

Non-plastic debris, oil, and other pollutants

Many other types of debris also present problems. According to the UNEP, “The problem of marine litter has steadily grown worse, despite national and international efforts to control it.” However, there are some success stories. ▪ An international treaty has banned a dozen POPs (persistent organic pollutants) such as DDT and other polychlorinated chemicals. ▪ Input into ocean waters of radioactive waste is also down sharply. This treaty, however does not affect debris (as opposed to chemicals). ▪ Oil spills remain a problem, but there are improvements: the US Oil Pollution Act of 1990 requires double hulls for new or upgraded oil-carrying vessels. Safe transport is a priority for some oil companies. Nonetheless, spills continue because of human error, bad weather, and crowded harbors. Oily waste discharges from industry and cities have also been cut about 90% as compared to the mid-1980s.

Coastal protection

You saw earlier that two commissions reported in 2004 that US coastal waters and oceans were in a state of crisis. Both made recommendations to remediate the problems, but the G. W. Bush Administration took no action. ▪ As seen in the Chesapeake Bay example (Box 9.5), states with coastlines *do* have protective programs, but they also need federal input, money, and coordination of state programs. ▪ Protecting the marine environment from land-based activities is enormously challenging. The UN initiated a program in 1995 involving several of its agencies and involved the governments of 108 countries in this task.⁴¹ ▪ Refer again to the best management practices to capture or prevent runoff noted in Table 9.1.

Box 9.5

Chesapeake Bay⁴²

One-hundred fifty rivers and streams from six states feed into Chesapeake Bay creating the largest estuary in North America. Bay ecosystems once flourished and were major sources of fish and shellfish.

The problems

Human population, industrial and agricultural activities increased over the decades, and impervious (paved) surfaces increased even more rapidly, up 41% just in the 1990s.

⁴¹ The UN agencies' first task was to understand the contaminants and activities contributing to coastal pollution and degradation. It established a clearinghouse to make scientific and technical information easily available to those that need it, and to provide information on financial resources available to help nations attack coastal pollution. Just one international effort among many directed toward reducing coastal pollution was the ban on 12 persistent organic pollutants (POPs) instituted through the Stockholm Convention of 2000.

⁴² (1) Barringer, F. A plan to curb farm-to-watershed pollution of Chesapeake Bay. *New York Times*, April 13, 2007. (2) Blankenship, K. Progress of Chesapeake cleanup. *Bay Journal*, January, 2008, <http://www.bayjournal.com/article.cfm?article=3233>. (3) Phillips, S. Many factors will challenge the recovery of the Chesapeake Bay. *US Geological Survey*, February 11, 2008, <http://www.usgs.gov/newsroom/article.asp?ID=1871&from=rss>. (4) Wyatt, K. Bay governors say progress with Chesapeake is too slow. *Associated Press*, December 6, 2007, <http://www.wtop.com/?nid=25&sid=1305381>.

▪ Nutrients (reactive nitrogen and phosphorus) were and are major pollutants. To understand this, see the description of dead zones in Section V. In addition to NPS pollutants, poorly functioning sewage-treatment plants are point sources of nutrients. ▪ Pathogens come from improperly treated sewage and septic systems, and in runoff of animal waste. ▪ Suspended solids pour in with runoff. ▪ Metal and organic pollutants flow in from industrial point sources and, especially from urban runoff. ▪ Water quality over the years deteriorated so much that fish and oyster populations dropped as much as 80%. Underwater grasses vital to coastal life disappeared. The most severely polluted areas are around urban centers, but the whole bay is impacted.

Starting restoration

The Chesapeake Bay Program,⁴³ a federal–state partnership works with the states on pollution control and P² strategies to protect and restore the estuary and adjacent coastal waters. ▪ *Reducing NPS runoff to the Bay is a major goal* of the effort and the major challenge. Among actions taken, farmers began improving how they applied fertilizer, and managed manure and sludge. ▪ Other actions were to ask pesticide users to enroll in integrated pest management (IPM) programs to help them reduce pesticide runoff. Another action was to begin planting more forest buffers along river banks to absorb runoff. ▪ To reduce Bay microbial contamination, wastewater treatment plants were to be upgraded, and millions of home septic systems controlled. ▪ Plans were developed to reduce input into the bay of 14 high-priority toxic chemicals. ▪ Few of these plans were actively pursued, but some were and early results showed efforts were paying off. Underwater grass beds began to rebound, and more striped bass were found in the bay. (Review Table 9.1 for Best Management Practices.)

A stalled restoration

Each year 13 indicators are assessed for the bay including wetlands, forest buffers, underwater grasses, toxic pollutants, nutrients, water clarity, dissolved oxygen, and populations of crab, rockfish, oyster, and shad. ▪ A score of 100 would represent the pristine Bay that existed before European settlement. In 2001 the score was 27, not much better than the 23 seen in 1983, the year the Bay “bottomed out.” Unfortunately, by 2000 population growth – averaging 150 000 a year – and sprawling development with its loss of farmland and loss of 100 acres (40.5 hectares) of forest a day stalled restoration. There was an ongoing decline in blue crab, and an increase in algae and suspended solids, both blocking the sunlight needed by underwater grasses, and smothering fish and shellfish. It was noted that “The bay remains a system dangerously out of balance.” High nutrient levels in the bay remained the major challenge. In December 2007, the Chesapeake Bay Foundation gave the estuary a grade of D for the ninth straight year, citing poor water quality, habitat destruction, continuing fish kills, and low-oxygen zones. ▪ A more promising development, also in December 2007 was a meeting of three governors from States bordering the Bay. They conceded that the 2000 Bay restoration goals would not be met by 2010. Nonetheless, they optimistically cited such actions as Maryland setting aside \$50 million for the

⁴³ Chesapeake Bay Program: protecting watersheds. September, 2008, <http://www.chesapeakebay.net/news.aspx?menuitem=15845>.

Chesapeake, mostly to reduce the number one problem of farm runoff. Virginia upgraded its sewage treatment plants. Pennsylvania planted 600 miles (966 km) of forest buffers along waterways. The governors noted that many steps had only recently been taken, and may still significantly improve water quality and the local environment.

For Chesapeake Bay to thrive again, reactive nitrogen and phosphorus must be cut in half. One official stated “We will never again see the Chesapeake restored to its pristine state of four centuries ago, but we believe a Bay with an index of 70 is achievable by 2050. We must remember how rich our Chesapeake Bay was, even 40 years ago, and not settle for a small fraction of what we know it can be.”

Questions 9.2

1. How would recovering phosphorus from sewage or animal waste for use in fertilizers be superior to removing it in a way that simply reduces the amount of phosphorus reaching receiving waters?
2. (a) Diagram how releasing BOD (organic matter) to a water body has some of the same effects as nutrients. (b) Why is the reactive nitrogen (nitrate) and phosphorus in synthetic fertilizer more effective at stimulating an algal bloom than that in organic matter?
3. Dr. Stephen Eisenreich of Rutgers University notes that eutrophication is probably the major water quality problem that the United States faces. He noted that although environmental health is critical to ongoing economic development, we seem willing to accept eutrophication and other adverse impacts of urban sprawl rather than change land use practices. (a) How does urban sprawl increase nutrient input to plant life in a water body? (b) Lay out a strategy that you believe could succeed at reducing harmful inputs to an area affected by eutrophication. How could you, personally fit into that strategy?
4. (a) How does surplus nutrient input to a water body change the composition of plant species found there? (b) How does a change in plant species affect aquatic and bird life?
5. Given the extent that worsening pollution problems are directly correlated to increasing population growth in the United States: (a) Why do we so seldom hear about the increasing population of the United States? (b) Are there any policies that the United States could realistically consider to limit population growth?

SECTION III

Reducing *point* sources of water pollution

Wastewater

Wastewater is tap water after it has been used in homes, businesses, and institutions for drinking, bathing, flushing toilets, and other purposes. For a community to have a central treatment plant to treat wastewater coming in from many households requires an expensive

infrastructure. The intent of the US Clean Water Act was to eventually eliminate point sources of pollution. Because elimination was not immediately possible, the EPA issued permits to municipal and industrial facilities, which allowed discharges of a specified amount of specific pollutants. The goal of permits was to lower discharges enough that human health and aquatic life will be protected. A facility must comply with its permit and regularly monitor its discharges to assure compliance.

Wastewater treatment

Municipalities treat their wastewater in a process similar to that seen in Table 9.3.

- **Primary treatment** Screens remove large objects such as sticks and trash from the wastewater, then smaller solids such as sand and small stones. Suspended solids in the wastewater are then settled out by chemical treatment. Most BOD and many pathogenic organisms settle out with the suspended solids. *Removing solids* is the major purpose

Table 9.3 Wastewater treatment process⁴⁴

WASTEWATER

Primary treatment

↓

PRETREATMENT

Aeration allows the release of gases such as hydrogen sulfide.

Physical methods are used to remove the solid materials ⇒ ⇒ Grit

↓

SEDIMENTATION

Suspended solids are allowed to settle out ⇒ ⇒ Primary sludge

Secondary treatment

↓

BIOLOGICAL TREATMENT

Microorganisms digest the organic material in wastewater

↓

SEDIMENTATION

The microorganisms are allowed to settle out ⇒ ⇒ Secondary sludge

Advanced treatment

↓

SPECIALIZED TREATMENT

This is sometimes used to remove remaining contaminants such as phosphorus or nitrogen

↓

WASTEWATER DISINFECTION

↓

DISCHARGE OF EFFLUENT TO RECEIVING WATER

⁴⁴ Primer for municipal wastewater treatment systems, EPA 832-R-04-001. *US EPA*, September, 2004, <http://www.epa.gov/owm/primer.pdf>.

of primary wastewater treatment. Reactive nitrogen and phosphorus are only partially removed in this process. The settled solids – *primary sludge* – are removed leaving the wastewater to move on to secondary treatment.

- **Secondary treatment** Here, soluble organic contaminants in the wastewater are digested by bacteria. Because the bacteria multiply rapidly during this process, major quantities of microbes are produced during treatment. These settle out from the secondary wastewater, and are recovered as *secondary sludge*, see Box 9.6. ■ The final step before discharging the wastewater is to disinfect it, typically with a chlorine-containing chemical.

Box 9.6

Managing biosolids (treated sludge) from wastewater treatment

Large quantities of sludge result from primary and secondary wastewater treatment. In the past sludge was dumped at sea, landfilled, or incinerated. Dumping at sea is prohibited in the United States and a number of other countries. Landfilling is expensive. Europeans increasingly incinerate it as do some American communities, but still must deal with the ash.

Land spreading sludge

In what most see as beneficial reuse, the United States applies about 60% of its treated sludge – *biosolids* – to farms, forests, parks, and golf courses as fertilizer or soil amendment.⁴⁵ Biosolids contain all the elements needed for plant growth, and its organic matter benefits soil, helping to hold moisture and nutrients around plant roots, and allowing rainwater to infiltrate, not run off. ■ To meet standards for land spreading, sludge is sanitized to control pathogens. It is also treated to meet legal standards for hazardous metals and other contaminants. Lime may be added to raise the pH and reduce unpleasant odors. It is hard to argue that sludge, properly treated, is a valuable biological resource that should be land spread. However, some raise objections that it contains harmful levels of metals, and persistent organic chemicals such as PCBs. Concern is expressed too for the health of the workers spreading it and for those living nearby. Communities sometimes protest sludge spreading, fearing its contaminants, its odor, and the flies it attracts. They assert that illnesses, even deaths, have resulted from the use of biosolids.

Heavy metal standards

European countries have stricter standards for heavy metal levels in sludge meant for land spreading than does the United States. They fear that soil to which sludge is applied may build up harmful levels of cadmium, zinc, copper, and other metals. This sometimes happened in earlier years, especially in Eastern Europe. Europeans now consider how difficult, even impossible, it is to remediate metal-contaminated farmland. Thinking ahead 50 or even 500 years

⁴⁵ (1) Land application of biosolids, Technology Fact Sheet EPA 832-F-00-064. *US EPA, Office of Water*, September, 2000, http://epa.gov/owm/mtb/land_application.pdf. (2) Wastewater management, biosolids publications. *US EPA*, October 15, 2007, <http://epa.gov/owm/sectbio.htm>. (3) *Biosolids Applied to Land: Advancing Standards and Practices in Biosolids Management*. Washington, DC: The National Academies Press, 2002, http://www.nap.edu/openbook.php?record_id=10426&page=31.

they ask, what will the soil metal levels be? Some metals in soil are not very bioavailable to plants, but plant roots do take up some metals such as the toxic cadmium. Europe has such strict standards for metals in food that even the low cadmium content now permitted in sludge would result in wheat levels that would exceed standards.

Industrial wastewater

The land spreading of sludge is a means of recycling biological material. This fits into the industrial ecology paradigm where wastes are no longer wastes, but resources. However, there is a need to ensure that wastewater from industrial facilities undergoes prior treatment before sending it to municipal wastewater treatment plants. It was once common practice for industry to pay municipal facilities to treat their wastewater along with its own. This was financially attractive to municipal plants, however some industrial effluents had components the municipal plant could not remove, and these would pass into receiving waters. Municipalities also often wanted to use wastewater sludge for beneficial purposes, and the presence of industrial pollutants could make that impossible. So, the EPA began requiring industrial plants to pre-treat their wastewater before sending it to a municipal plant. Alternatively, some industrial facilities now treat their own wastewater, then release it directly to surface waters themselves. Most environmental organizations support land spreading of sludge done to strict standards. On the other hand, some citizens' groups still strenuously oppose it, convinced that it is harmful. Clearly more work must be done if land spreading controversies are to be resolved.

Standard wastewater treatment removes only a portion of the nutrients – reactive nitrogen and phosphorus – which can be so detrimental to receiving waters. *Advanced treatment* is necessary to accomplish nutrient removal. Moreover, if standard treatment does not adequately remove priority water pollutants, yet additional treatment may be necessary. Non-conventional contaminants such as excessive color may also need to be removed from some wastewaters. ■ Think about an illustration of the effectiveness of point-source control: after receiving poor reports on the quality of its beach water in the mid-1990s, England improved its sewage treatment facilities and took measures to prevent sewer overflows. By 2005 they found that 99% of the water at their beaches was clean. Even when tougher EU standards were applied, almost 75% still met standards. They felt the results well justified the money spent.⁴⁶

Limits to controlling point sources

- Over the years wastewater treatment has become increasingly effective at removing contaminants. Compared to 1972, when the Clean Water Act was passed, some point

⁴⁶ English beach water quality at record high. *Reuters*, November 10, 2005, <http://www.planetark.com/dailynewsstory.cfm/newsid/33401/story.htm>.

emissions have been reduced by 95%, even 99%. By 1994, only about 15% of US water pollution could be traced to point sources. But the original intent of the CWA was to eliminate point discharges – the name of the permit issued to municipalities and industries was the National Pollutant Discharge Elimination System (NPDES). But recall how difficult it is to eliminate a pollutant end-of-pipe (Chapter 2), even with expensive treatment. A spokesperson for the Water Environment Federation, an organization of scientists, engineers, and wastewater managers, observed that many pollutants exist at levels so low that they are hard to quantify and often very difficult to eliminate. He stated, “It would probably cost as much to eliminate the last 5% of a contaminant as to eliminate the other 95% . . . Our philosophy is to move toward smaller amounts of pollutants and analyze the cost of eliminating decreasing quantities versus the benefit of the environmental gain.” ▪ P^2 involves actually reducing the amount of pollutant formed, not trapping it afterwards. This has led some to suggest that society should give the most toxic pollutants a deadline by which time their discharge must be eliminated. This would likely mean societal phase out of those chemicals, which has already happened for some chemicals. An example is the international treaty banning 12 of the worst persistent organic pollutants (POPs). Another (Chapter 15) is the elimination of many uses of lead and mercury leading to greatly reduced emissions in developed countries.

- By the mid-1990s, US water quality was better than in 1970 despite a 25% increase in population and a 50% increase in national economic activity. Yet point sources, municipal sewage treatment plants and industrial wastewater treatment plants, continue to have problems. Maintaining infrastructure is an ongoing challenge. Municipalities have difficulty finding money to modernize or even properly maintain wastewater treatment systems. Many struggle too with CSO: storm water is still sometimes released with untreated sewage during storms. Nationwide, modernization of treatment systems could cost hundreds of billions of dollars.

Reusing wastewater or reducing its volume

Reusing sewage indirectly for drinking water

In many parts of the world, water, especially clean water, is increasingly scarce. But – for communities that can afford it – it is possible to treat sewage to a purity that allows its use as drinking water. ▪ This happens in the space station where urine (not urine mixed with feces) is purified so thoroughly that it can be used for drinking, food preparation, and washing. Recycled wastewater is also used in Israel, Singapore, and parts of Europe. ▪ Several American communities approach this issue indirectly. A Virginia community takes purified wastewater and adds it to a stream that feeds into its drinking water reservoir. In water-poor Southern California an off-and-on drought combined with ongoing population growth led to the Advanced Water Purification Facility. This takes industrial and household sewage and produces 70 million gallons (265 million liters) of drinkable water per day, about 10% of the water needs of 2.3 million residents. The water goes through an elaborate purification

procedure that treats organic chemicals, pathogens, and other contaminants including pharmaceuticals. But the product, at least as clean as drinking water, is not directly used. Rather, it goes into a percolation pond situated over permeable soil that allows the water to slowly percolate down to recharge the groundwater, being further purified as it moves. Taking at least six months, it finally reaches the intakes of drinking water wells. This water is carefully tested for hundreds of contaminants and meets or exceeds all drinking water standards.⁴⁷ Yet, at least one community in Australia has rejected such a possibility despite ongoing drought and a severe water shortage.

Reducing the volume of wastewater

Households, businesses, institutions

Gray water is all wastewater except that flushed down toilets. Gray water usually goes down drains to the sewage line. But now, some water-scarce areas are beginning to use that gray water. It is recovered by separate pipes, and used to flush toilets, wash cars, or to water yards.

Cities

Wastewater reclamation is a major issue in arid urban areas with increasing populations and increasing water demand. In reclamation, treated wastewater is not discharged, but used as cooling and process water for commercial washing, ornamental fountains, fire fighting, golf-course irrigation, creation of artificial wetlands, and groundwater recharge. The major concern, but not the only one, is surviving pathogens. But, because the reclaimed water is not used for drinking, pathogens need only be reduced, not eliminated. Many embrace water reuse, but caution that more monitoring is needed.

Reusing wastewater inappropriately?⁴⁸

In many cities of less-developed countries, farmers use raw wastewater or wastewater diluted in streams to irrigate their crops, commonly vegetables and rice grown on urban agricultural land. This often happens in cities in China, India, Vietnam, sub-Saharan Africa and some Latin American countries. One example is Accra in Ghana, where each day about 10% of the people in this city of 2 million buy produce grown on ~250 acres (100 hectares). These practices may be unhealthy, but it produces much needed food and provides livelihoods to farmers. A researcher for the International Water Management Institute said “In the face of water scarcity generally and a lack of access to clean water, urban farmers will have no alternative except to use diluted or untreated wastewater or polluted river water.”

⁴⁷ Kemsley, J. Treating sewage for drinking water, new California plant cleanses water to replenish supply. *Chemical & Engineering News*, **86**(04), January 28, 2008, 71–73.

⁴⁸ Cox, A. Scores of cities using untreated wastewater-study. *Reuters*. August 18, 2008, <http://www.alertnet.org/thenews/newsdesk/LG151453.htm>.

The organization did mention that sometimes it's possible to build on farmers' own practices: in several countries, farmers store wastewater in ponds and allow suspended solids to settle out.

Wastewater treatment for homes and small communities

Wastewater treatment plants are expensive to build and operate. Another major cost is building the underground pipes connecting homes to the plant. To save money, homeowners and businesses in less-populated areas often build individual less-costly onsite systems.

Home treatment

Underground septic systems are best known (Figure 9.7).^{49,50} ■ Properly built and maintained onsite systems treat wastewater in an ecologically sound manner and return the water to the environment. But improperly installed and maintained systems fail. Indeed, the US EPA estimates that at any one time 10–30% of septic systems are failing. EPA guidelines for septic system operation note that, to assure proper building and maintenance, local governments may track onsite systems by issuing building permits, which must be periodically renewed. Before renewal the homeowner must show that the system has been properly maintained. If a homeowner has a private well too, then a malfunctioning septic system not only contributes to NPS runoff, but *also* contaminates their own groundwater, their drinking water. ■ Treated household wastewater leaves behind a concentrated *septage*, which must periodically be pumped out of the tank, and transported to a traditional wastewater treatment plant for treatment.

Small and very small communities, and industrial operations

- Communities or industries with enough land sometimes use artificial (constructed) wetlands to treat wastewater.⁵¹ The wastewater is directed to the wetland. There, suspended solids drop out. Wastewater nutrients are used by plants and microorganisms, which also often degrade organic chemicals. Metal pollutants are absorbed by the soil and are contained in place.

⁴⁹ (1) Water quality information for consumers: septic systems and wastewater. *Cornell University Cooperative Extension*, February 24, 2009, <http://waterquality.cce.cornell.edu/septic.htm>. (2) Septic (on site) systems. *US EPA*, March 16, 2009, <http://cfpub.epa.gov/owm/septic/index.cfm>.

⁵⁰ Home•A•Syst Program, an environmental risk-assessment guide for the home and farm. Ithaca New York: Regents of the University of Wisconsin System, Cooperative Extension. See <http://www.uwex.edu/homeasyst/index.html>. Related programs include Farm•A•Syst: Cooperative Extension contacts are given for each US State.

⁵¹ Natural treatment design guidelines, *Irvine Ranch Water District*, June, 2007, <http://www.naturaltreatmentsystem.org/PDF-DesignGuidelines/NTS-DesignGuidelines.pdf>.

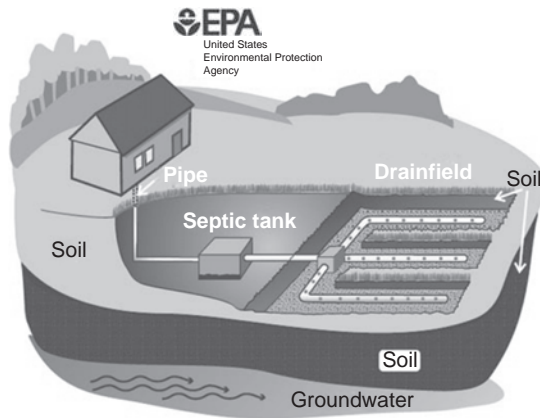


Figure 9.7

Home septic system. Credit: US EPA

- Even in cold climates, small communities can construct their wetlands in greenhouses especially set up to treat wastewater. The use of greenhouses can be an attractive technology for very small communities. The greenhouse has a complete ecosystem, including slow-moving streams. It has flowers, ferns and other vegetation, and aquatic life such as fish, worms, and snails. After screening and grit removal, the wastewater is fed to bacteria, algae, zooplankton, and plants. These remove nutrients, reduce suspended solids and BOD, and otherwise carry out the functions of a wetland. They are attractive operations. One author described one as having “the smell of a freshly tossed garden salad and the glassy look of a botanical museum.” The effluent can be used for plant irrigation, flushing toilets, and for groundwater recharge. Mature plants grown in the greenhouse can be sold.
- Chrysanthemums are among the plants found to be useful in these systems.⁵² Aerobic (oxygen dependent) microbes that grow on chrysanthemum roots use, for their own nutrition, 40–80% of the wastewater’s reactive nitrogen and phosphorus. The system reportedly removes 95% of the suspended solids and 91% of the BOD. The chrysanthemums can be harvested and processed to obtain the natural insecticide *pyrethrin*.

SECTION IV

Reducing *nonpoint* sources of water pollution

You are aware of the challenges of reducing nonpoint source pollution. You have learned the sources of polluted runoff, and the contaminants within it. In Table 9.1, you learned some best management practices to lessen runoff. Homeowners also need to learn and practice

⁵² Report on deliberations of Third International Conference on plants and environmental pollution (ICPEP-3) 12 (1), February, 2006, <http://www.isebindia.com/icpep/icpep-3-report.html>.

these approaches.⁵³ ▪ In the United States, the first stage of cleaning up rivers, lakes, and streams was straightforward: point sources were contained through laws and regulations. Commercial and municipal sources of pollution – as identified by effluent pipes – became fairly well controlled. ▪ The remaining problem was and is much more difficult: how to contain or, better, prevent runoff from roads, parking lots, paved and roofed urban surfaces, farms, and timber operations.

Reducing agricultural runoff

Agriculture is a major cause of NPS runoff of soil, pesticides, fertilizers, and animal wastes into rivers, lakes, and other water bodies. See Table 9.1 as an introduction to reducing NPS pollution.

- Plant grass or trees as buffer strips next to water bodies to absorb the runoff.
- When possible, use no-till farming in which crop residues are not tilled into the ground, but left on soil. This greatly limits soil erosion and runoff. A disadvantage is that more herbicide is needed to manage the weeds that are no longer plowed into the ground.
- Farmers ordinarily apply more fertilizer than needed. Crops cannot capture or use it all and, when it rains, the surplus run off into surface water or infiltrate down into groundwater. One way to lessen runoff is to apply smaller amounts more frequently to help keep fertilizer in the soil.⁵⁴ In some instances, agricultural specialists work with farmers to analyze land nutrient needs, section by section, and enter the results into a computer within a tractor. The computer lets the farmer know whether a particular section needs fertilizer, and how much, before any is applied. Less fertilizer applied means less fertilizer runoff into water.
- Contour strip-cropping (planting rows of different crops) helps to lower both chemical runoff and soil erosion.
- Minimize pesticide runoff by using *integrated pest management* (IPM). In IPM, farmers evaluate their fields regularly, and use a pesticide only when a pest population reaches a certain level. This contrasts with applying pesticides according to a schedule regardless of need. Reduced applications mean less pesticide in runoff from treated fields.
- Get chemical companies to place priority on developing herbicides that can kill weeds in much smaller amounts. Newer herbicides are often less water soluble and bind more tightly to soil, both characteristics that can lower pesticide runoff.
- Confined animal feeding operations with large numbers of confined animals produce runoff, which contaminates both surface and ground water with potentially infectious bacteria, viruses, or protozoa (especially *Giardia* and *Cryptosporidium*). Methods exist to

⁵³ Lake and watershed protection: dos and don'ts for individual homeowners and farmers to reduce nonpoint runoff. *Woodstock Conservation Commission*, January 13, 2009, http://www.woodstockconservation.org/watershed_dos_and_donts.htm.

⁵⁴ Engelhaupt, E. Biofueling water problems. *Environmental Science & Technology*, **41**(22), November 15, 2007, 7593.

minimize runoff, but some mammoth operations do little more than allow animal waste solids to settle out in a detention pond. P² could mean a return to smaller family farms with fewer animals at one locale, and encouraging people to eat less meat.

Changing farming methods to reduce agricultural runoff can present major challenges to farmers. They need to be willing to educate themselves on methods to reduce runoff. Taking action can mean significant changes in farming methods, and require more time, and often additional costs. Providing incentives or assistance can make a difference. A P² story A cooperative venture among Wisconsin dairy farmers, the University of Wisconsin, and the US Department of Agriculture provides an example of reducing runoff of pesticides, fertilizers, and eroded soil to waterways. Cooperative Extension Service agents visited participating farms each week of the growing season for three years. They worked with farmers to monitor pest populations in the crops they grew to feed cows with the intent of using fewer pesticide applications. They encouraged farmers to plant nitrogen-fixing legumes to enrich the soil, thus reducing the need for artificial fertilizer. Farmers did reduce pesticides and fertilizer use and reduced volumes of contaminated runoff. Participating farmers also saved several dollars for each dollar invested. Eighty percent of farmers continued with these methods after the program ended. ▪ However, most farmers do not use such methods, and groundwater and many surface water bodies continue to have high or sometimes increasing levels of reactive nitrogen. The situation is worse in Europe, which is more populous than the United States. It is especially bad in Asia where attention is focused on the immediate problem of producing enough food for growing populations.

- Growing crops for biofuels The US National Research Council warns of the consequences of growing more corn and other crops for biofuels without environmental protection.⁵⁵ When corn is grown to produce ethanol, more pesticides and herbicides are applied per acre than for soy or mixed-species perennial grasses. More water and fertilizer is also used. The overall result is more eroded soil and more pesticides carried away in runoff. ▪ Farmers need to rotate between corn and soy crops (soy to replenish nutrients naturally), to apply fertilizer in smaller amounts (but more frequently so there will be less runoff), and to learn when in the growing cycle fertilizer can be applied with less runoff. ▪ More generally, life-cycle assessments need to be carried out on the environmental consequences of the various crops grown to produce biofuels.

Reducing urban runoff

Because runoff from paved surfaces is a major problem, attempts are slowly being made to address the problem. Runoff can be reduced even from paved roads, using *low impact design*.⁵⁶ The first step is to realize that the ways we traditionally handled water are

⁵⁵ Water implications of biofuels production in the United States. National Research Council, October, 2007. http://dels.nas.edu/dels/rpt_briefs/biofuels_brief_final.pdf.

⁵⁶ Lubick, N. Using nature's design to stem urban storm-water problems. *Environmental Science & Technology*, 40(19) October 1, 2006, 5832–5833.

environmentally harmful – as seen in the runoff problems noted here. A number of different approaches have been started since the late 1990s.

- The city of Seattle is redesigning its streets to function more like a natural drainage system. They meander along like a stream, no longer straight; some spots are left unpaved to allow stormwater to infiltrate into the ground; other places are designed to simply keep the water from running off, allowing it to evaporate later. Street retrofitting costs ~\$300,000 per block. ■ Benefits: the need to treat or store storm water is eliminated; there is less flooding of local streams and less soil erosion. People living on these streets enjoy them and contribute by planting and caring for vegetation along the new streets. But retrofitting is more costly than designing in such solutions before streets are built.
- In Prince George’s County, Maryland, low impact design includes streets that use vegetation and holding ponds to enhance stormwater drainage into the soil.
- Alleys in the city of Chicago cover an area equivalent to “five midsize airports.” Chicago is now working to transform them into “green” alleys.⁵⁷ Whenever an alley needs repaving or sewer improvements, they take up the old paving and lay down a stone bed. This is covered with permeable paving (either concrete or asphalt). When it rains, stormwater filters through the paving and stone bed, and infiltrates the soil and recharges groundwater. The pavement also reflects sunlight and so is cooler on hot days and warmer on cold days. The alleys also are provided with more energy-efficient lighting. Professor Michael Martin of Iowa State University praises Chicago: “The alley is not only functional, but an educational green landscape that is helping a city experiment with design and different ways to handle water.”
- Regulations to prevent stormwater runoff are stricter in Europe and designers use methods such as public plazas with waterworks that also function to store water. All these methods decrease stormwater runoff, but also recharge aquifers underneath the cities.

Reducing nonpoint source runoff from other activities

In Table 9.1 notice that many sources of runoff are controlled in similar ways. ■ Providing buffer zones of grass or trees near water bodies onto which runoff can flow is a control common to many sources of runoff. ■ Building detention ponds or constructed wetlands into which runoff can flow for natural treatment is another technique. ■ Some methods are unique to specific sources such as sealing off an open mine that is the source of runoff. ■ For large construction sites or logging roads, reducing runoff may mean laying out the sites in a way that makes use of or modifies the land’s natural contours, see Box 9.7.

⁵⁷ Chicago has other ongoing programs including retrofitting old buildings to reduce energy usage, rooftop gardens to collect rainwater, 90 miles (145 km) of landscaped road medians, a half million new trees, and 200 acres (81 hectares) of new parks and open spaces. Saulny, S. In miles of alleys, Chicago finds its next environmental frontier. *New York Times*, November 26, 2007, <http://www.nytimes.com/2007/11/26/us/26chicago.html?n=Top/Reference/Times%20Topics/People/S/Saulny,%20Susan>.

Box 9.7

Reducing phosphorus and reactive nitrogen pollution

Reducing *point* source phosphorus pollution: treatment, P², and industrial ecology

Wastewater treatment plants do not routinely remove phosphorus and reactive nitrogen. Examples of approaches to reduce phosphorus include:

- **Control** The US EPA in 2007 said that it was now possible for treatment plants, at a reasonable cost, to remove phosphorus to levels below 10 µg/l.⁵⁸
- **P²** To prevent some phosphates from even reaching treatment plants, the State of Washington outlawed automatic dishwasher detergents that contain phosphates. This means less phosphorus in sewage to be removed. As of 2008 the initiative is going nationwide.⁵⁹
- **Industrial ecology (IE)** Most of the world's arable land lacks enough phosphorus for optimal plant growth. Thus, phosphorus is also a component of fertilizers. However, good ores, from which phosphate is extracted, are expected to run out within 100 years. Attention is being given to recovering phosphorus from excrement – make sewage treatment plants an alternate source of phosphorus.⁶⁰ Currently, study is ongoing to recover phosphorus from wastewater in a form concentrated enough to use in fertilizer. Study is ongoing too on how to recover phosphorus from the massive amounts of livestock waste produced by intensive animal farms.

Reducing reactive nitrogen pollution through emissions trading

Recall from Chapter 6, the sulfur dioxide (SO₂) trading scheme whereby one electric power plant, which is exceeding its permit for SO₂ emissions could buy credits from another power plant, which is releasing less SO₂ than its permit allows. Similar efforts are underway for nutrients emitted by wastewater treatment plants: a plant that releases a greater weight of nutrients to a waterway than its permit allows buys credits from a plant releasing less than its permit allows. The plant buying credits is thus able to put off expensive upgrading of its equipment. Both sides save money. • However, it is *much more difficult to trade between point and NPS* nutrients. Whereas it is straightforward to calculate the amount arriving in a water body from a wastewater treatment plant, a point source, it is much harder to calculate the amount arriving via runoff or from atmospheric deposition. However, there has been some successful trading of point with nonpoint, and efforts to do so will continue.⁶¹

⁵⁸ Advanced wastewater treatment to achieve low concentration of phosphorus. US EPA, April, 2007, [http://yosemite.epa.gov/r10/water.nsf/Water+Quality+Standards/AWT-Phosphorus/\\$FILE/AWT+Report.pdf](http://yosemite.epa.gov/r10/water.nsf/Water+Quality+Standards/AWT-Phosphorus/$FILE/AWT+Report.pdf).

⁵⁹ An exception will be made for industrial and institutional settings where phosphates are critical to good cleaning.

⁶⁰ Christen, K. Closing the phosphorus loop, *Environmental Science & Technology*, **40**(7), April 1, 2007, 2078.

⁶¹ Lubick, N. Advancing water-quality credit trading. *Environmental Science & Technology*, **41**(20), October 1, 2007, 6882.

Reducing water use to reduce NPS pollution

The EPA has noted, “The high demand for and overuse of water can contribute markedly to nonpoint source pollution.” This happens in many ways.

- When farmers use more water than necessary to irrigate their land, this increases runoff, which carries with it sediment, nutrients, and salts.
- Homeowners who overuse water to maintain yards and gardens increase runoff carrying soil, nutrients, and pesticides.
- When households with septic systems overuse water, this contributes to system failure with resultant nonpoint source runoff carrying microbes and nutrients.⁶²

Reducing atmospheric deposition

Methods to reduce atmospheric deposition are specific to given pollutants and are noted throughout this book. Reducing acidic deposition, for example, was discussed in Chapter 6.

SECTION V

The “nitrogen glut” and dead zones

The major increase of reactive nitrogen in the environment is often called the “nitrogen glut.” In this book’s second edition, the “nitrogen glut” was described as “one of the world’s biggest environmental headaches.” The headache has become life-threatening. Humans have at least doubled the rate at which reactive nitrogen is delivered to plant life. ■ An 8-year study finished in the late 1990s indicated that human activity had increased inputs of reactive nitrogen into coastal regions three-fold in North America, six-fold in Europe, and 11-fold in Europe’s North Sea.⁶³ You might hypothesize just from a re-examination of Figure 3.2 that such sharp increases could have adverse effects, and that is proving to be the case.

The nitrogen (N₂) in the air we breathe is a very stable chemical and is biologically inert to most living organisms. Until the twentieth century, people fertilized their crops by applying nutrient-containing manure or compost (decaying leaves, grass, and other organic materials). They also periodically planted fields with legumes; legumes have root nodules, which contain bacteria that convert nitrogen into bioavailable reactive nitrogen, thus boosting

⁶² How does excessive water use affect water quality? *US EPA*, July 31, 2009, http://www.epa.gov/watersense/water/save/water_quality.htm.

⁶³ Howarth, R. W. An assessment of human influences on fluxes of nitrogen from the terrestrial landscape to the estuaries and continental shelves of the North Atlantic Ocean. *Nutrient Cycling in Agroecosystems*, **52**(2–3), 1998, 213–223, <http://www.springerlink.com/content/v2381059700171t1/>.

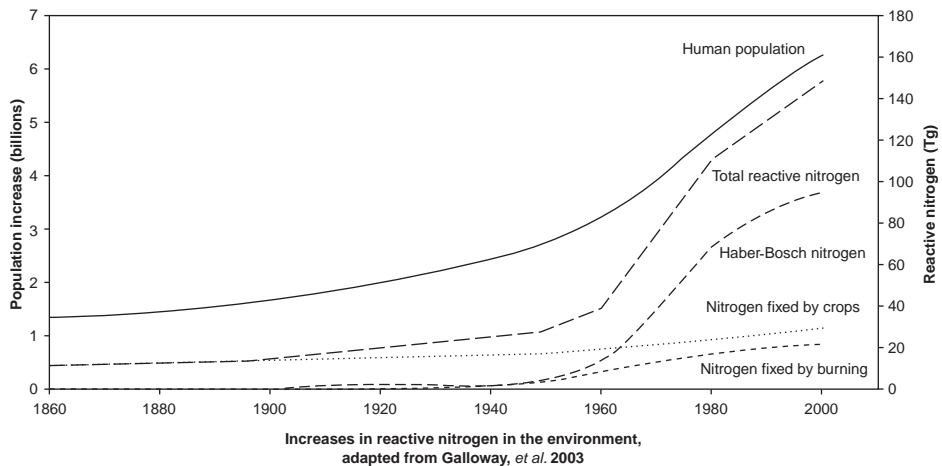


Figure 9.8 Increase in reactive (fixed) nitrogen in the environment (1860-present). Copyright: American Institute of Biological Sciences⁶⁴

amounts in the soil. ▪ However, no concentrated sources of bioavailable nitrogen were available. This changed in 1913 with the invention of the Haber-Bosch process: with the input of much energy, this process *fixes* atmospheric nitrogen into the bioavailable nitrogen chemical – ammonia. Ammonia can be used directly as a fertilizer or, more usually converted into the solid nitrate. Nitrate is found in fertilizer mixtures that also typically contain phosphorus and potassium.⁶⁵ Synthetic fertilizer is credited for allowing humanity to increase food production to keep pace with twentieth-century population increases. Over half of all fertilizer employed in human history was used in the last 20 years of the twentieth century. The amount of synthetic fertilizer now used equals the amount of naturally available reactive nitrogen, and its use continues to grow, see Figure 9.8.

Adverse effects of excess nutrients⁶⁶

The first impact of surplus reactive nitrogen in a water body is eutrophication, which uncorrected can lead to *dead zones* in coastal water. Both eutrophication and dead zones were noted briefly earlier as adverse impacts of nutrients, and will be further described below. Dead zones have primarily occurred in northern hemisphere countries where fertilizers are liberally applied, but the problem is spreading to coasts of less-developed countries as well. It has become a planet-wide problem. ▪ Although reactive nitrogen is emphasized here, too much phosphorus also causes problems, especially in fresh-water bodies. ▪ Perhaps

⁶⁴ Galloway, J. N., Aber, J. D., Erisman, J. W. *et al.* The nitrogen cascade. *BioScience*, **53**(4), April 2003, 341–356. http://www.initrogen.org/fileadmin/user_upload/N_Cascade_BioScience.pdf.

⁶⁵ Fertilizer mixtures also often contain other essential nutrients (calcium, sulfur, magnesium). Sometimes trace elements (metal micronutrients) are added.

⁶⁶ Diaz, R. J. and Rosenberg, R. Review: spreading dead zones and consequences for marine ecosystems. *Science*, **321**(5891) August 15, 2008, 926–929.

surprisingly, nutrients can be indirectly toxic to developing frogs. For a number of years, deformed frogs – too many or too few limbs or displaced limbs – have been found in many locales with no explanation as to how their deformities occurred. These deformities were traced to excess nitrogen and phosphorus in lakes and ponds. The nutrients stimulate the growth of a parasitic flatworm, which burrows in large numbers into tadpoles at the points where limbs are developing. This causes cysts that lead to developmental deformities.⁶⁷ Below algal blooms are first considered and then dead zones.

Algal blooms

Surplus nitrate and phosphorus from fertilizers, atmospheric deposition of nitrate, and nutrients in sewage and manure are associated with eutrophication. In coastal areas nitrate is the major culprit, whereas in freshwater lakes, it is more often phosphorus. ▪ Of major importance, high nutrient levels trigger heavy growth of phytoplankton (algal blooms). In turn, these trigger rapid growth of the zooplankton that eat the phytoplankton. As all these organisms die and sink toward the bottom they contribute to BOD: oxygen-requiring bacteria degrade them and the move toward hypoxia, conditions with too little oxygen begins.

- If the bloom is severe or if conditions persist, hypoxia and eutrophication results. Algal blooms have other ill effects – crowding out other plants and covering the water surface so thickly that sunlight is prevented from reaching the underwater grasses that provide food, shelter and a spawning ground for crabs, fish, and other aquatic creatures, habitat for their offspring, and food for water fowl. If the hypoxic area is in an estuary, fish can swim away. However, sedentary creatures die if they don't have enough oxygen. ▪ As you may surmise from this description, too many nutrients in a water body change the composition of species. This change moves through the food web to affect plant, bird and animal diversity. ▪ A bloom can create esthetic problems too – scum and unpleasant smells.
- *Harmful algal blooms* (HABs) produce the problems just noted and *also* produce toxins. The bloom of one dinoflagellate, *Gonyaulax* appears as red tide in marine coastal water. Red-tide organisms produce a toxin that accumulates in the fish and shellfish that eat them. Fish may become ill and suffer impaired reproduction and damaged immune systems. Some humans eating the contaminated shellfish suffer from paralytic shellfish poisoning. ▪ Thus, a red tide leads to banning the eating of shellfish from the affected areas. Water birds and other sea life may also suffer ill effects.⁶⁸ Other algae toxins have been associated with a variety of other ill effects including tumors in sea animals such as turtles.

⁶⁷ Dunham, W. Frog deformities blamed on farm and ranch runoff. *Reuters*, September 24, 2007, <http://www.reuters.com/article/environmentNews/idUSN2432027920070924>.

⁶⁸ The diatom *Pseudo-nitzschia australis* also generates a noxious HAB producing the neurotoxin, *domoic acid*. In a 1987 case, 140 people on Canada's Prince Edward Island were poisoned after eating mussels that had ingested this diatom. Three died, and others suffered memory loss that was still apparent in 2000. In California the 1998 deaths of 400 sea lions was convincingly tied to their eating of anchovies that had eaten the domoic acid-producing algae.

Sources of reactive nitrogen

- Natural reactive nitrogen Bacteria in the root nodules of legumes (peas, beans, and related plants) can fix atmospheric nitrogen into bioavailable nitrogen, which is released to plant roots. ▪ *Cyanobacteria* in water bodies also fix atmospheric nitrogen. ▪ A small amount of atmospheric nitrogen is also fixed by lightning.
- Reactive nitrogen from human sources The major chemical form of reactive nitrogen running off to rivers, streams, lakes, and coastal areas is nitrate. The largest source of nitrate is fertilizers applied to agricultural fields; smaller amounts come from yards and greens. Fertilizer use is projected to continue to increase, especially in Asian, African, and South American countries, which now use relatively little. With increased fertilizer use, more nitrate is expected in the runoff that reaches coastal areas. Very often, *excess* fertilizer nitrogen is applied to crops, i.e., more than the crops can use, and often more than the soil can hold. To capture nitrate from runoff, a grass or tree buffer zone or a wetland can be placed between farm fields and water bodies, see Table 9.1. ▪ Fossil fuel burning is a lesser, but important source of reactive nitrogen. Nitrogen oxide (NO_x) emissions worldwide have quintupled in the twentieth century. The result is that nitrate (oxidized from NO_x) now represents a quarter of the reactive nitrogen from human sources. Just as fertilizer nitrate arriving on a coast may come from far up-river, atmospheric nitrate can come from afar. Unlike nitrate from fertilizer, atmospheric NO_x cannot be trapped in buffer zones: after its conversion to nitrate or nitric acid, it directly deposits from the atmosphere. Sewage, poorly treated or untreated, is a source of nutrients too as is runoff of animal manure. More generally, biological matter has nutrient value. The reactive nitrogen in these sources is not concentrated.

Study Figure 9.8: notice that the amount of reactive (fixed) nitrogen has grown over the years.

- Top line: as human population grows, reactive nitrogen likewise increases.
- Second line: total reactive nitrogen in the environment – natural and synthetic – began growing in the early twentieth century, then much more rapidly toward the end of the century.
- Third line: increase in Haber-Bosch nitrogen explains much of this increase in reactive nitrogen as more and more is applied to crops.
- Fourth line: nitrogen fixed by legumes is also increasing because more legumes are grown.
- Bottom line: nitrogen fixed by burning is increasing as we increase our burning of fossil fuels.

Livestock operations

Reactive nitrogen in manure is much less concentrated than in synthetic fertilizer but often thousands of animals are kept in confined-animal feeding operations (CAFOs) producing large amounts of waste. Waste runoff is a nutrient source. At any one time, the United States

has 60 million hogs, 47 million beef and dairy cows, and 7.5 billion chickens. In confinement, they produce about a billion tons (0.9 billion tonnes) of manure and urine a year. This is often stored in waste lagoons. In a 1995 incident in North Carolina, a lagoon leaked 25 million gallons (95 million liters) of hog waste into the New River, leading to an algal bloom, which depleted the water of oxygen, and killed off fish and other aquatic organisms. ▪ Other ways that CAFOs release nitrogen pollution include chronic seepage from animal-waste lagoons, and runoff from fields onto which lagoon liquids have been sprayed. Both surface water and groundwater contamination occurs. ▪ In Colorado, groundwater nitrate concentrations of towns near large beef cattle feedlots are double the EPA human-health standard. Livestock operations also emit the pungent gas, ammonia into the atmosphere. Rained out, ammonia is converted to nitrate in the soil contributing to acidification. In North Carolina, ammonia in rain increased 25% between 1990 and 1995, coincident with increased hog operations. ▪ The Netherlands has intensive pig farms too. This very small country produces almost a quarter as much pork as does the much larger United States and it has similar problems. However, its government places the most stringent controls in the world on CAFOs; it also mandates a limit to the pig population, and has a system to account for all nutrients entering or leaving its borders. These actions reduce, but do not eliminate, escaping nutrients. Probably because of this careful regulation, some owners of intensive pig farms have chosen to set up operations in the United States where regulations are more lenient. Worse, corporations also set up industrial-size livestock operations in less-developed countries, which cannot handle the resulting pollution.

Dead zones resulting from surplus nutrients

Once dissolved oxygen levels in a water body or portion of a water body are depleted, life disappears. Creatures living there have either died or swum away. At this point it is a dead zone. There are many areas in the world that have undergone eutrophication (that still support some life) and have not yet progressed to dead zones. The dead zone is the final stage of damage. However, note how rapidly the situation is worsening: the number and extent of areas with hypoxia, worldwide, increased from 46 in 1995 to at least 400 in 2008.⁶⁹ This may happen even more frequently as massive inflows of nutrients into coastal area continue. Two dead zones are described below.

The US Gulf of Mexico⁷⁰

In the bottom waters of the US Gulf of Mexico (beyond the mouth of the Mississippi River system) a dead zone occurs each summer. At its largest, its size is equivalent to the state of New Jersey. River waters draining into the Gulf contain massive amounts of nutrients from 31 states, representing about two-thirds of the area of the continental United States (starting

⁶⁹ Diazl, R. J. and Rosenberg, R. Worldwide spreading dead zones and consequences for marine ecosystems. *Science*, 321, August 15, 2008, 926–929

⁷⁰ Rabalais, N. Hypoxia in the Gulf of Mexico. *Louisiana Universities Marine Consortium*, <http://www.csc.noaa.gov/products/gulfmex/html/rabalais.htm>.

in Minnesota and including every state between the Rocky and the Appalachian Mountains). The nutrients stimulate algal blooms in the gulf leading to hypoxic water. As oxygen becomes scarce, fish move elsewhere. Creatures unable to leave, including crabs and brittle stars, suffocate. As expressed by Elizabeth Carlisle,⁷¹ “Hypoxic waters appear normal on the surface, but on the bottom, they are covered with dead and distressed animals, and in extreme cases, layers of stinking, sulfur-oxidizing bacteria.” This dead zone occurs in a region that provides 40% of US seafood. Fishing boats must move across it before finding fish.⁷² ■ Nonpoint sources of pollutants Corn and soybean crops are the largest contributors of reactive nitrogen to the Gulf. An estimated 16% of nitrate fertilizer applied to crops in the Mississippi River watershed runs off and is delivered to the gulf. The largest source of phosphorus is animal waste carried in runoff from animal pastures and from confined animal feeding operations. There is also point-source pollution from municipal wastewater treatment plants.

Reducing nutrients runoff to the Gulf Studies of Gulf sediment show that nitrate levels increased three-fold since 1960 and phosphorus two-fold.

- Prior to 2007, reactive nitrogen was estimated to account for two-thirds of the nutrient problem and phosphorus for the rest. However, further EPA analysis pointed to phosphorus as making a greater than one-third contribution. A new EPA assessment recommends lowering both reactive nitrogen and phosphorus in the Mississippi River by at least 45%.
- An earlier 31-state plan proposed paying farmers to reduce fertilizer use, restore wetlands, plant trees or grass buffers between crops and streams, and take measure to reduce manure runoff. It also recommended assisting municipal sewage treatment plants to install equipment capable of removing nutrients.
- Other research indicated that 9 of the 31 states involved contribute 75% of the two nutrients. This is leading to greater focus on those nine states.⁷³
- Other work found that the adverse effects of algal blooms on the marine ecosystem carry over from year to year making the results of the hypoxia (low oxygen) or anoxia (no oxygen) increasingly hard to correct.
- Moreover, the United States is growing ever more corn for biofuel production, a crop requiring large amounts of fertilizer.⁷⁴ This leads to increasing amounts of reactive nitrogen runoff. As has been pointed out: providing subsidies and other economic incentives to farmers that favor corn-based ethanol “are at odds with the goals of hypoxia reduction.” But farmers point to the investigations indicating that phosphorus is more of a problem than previously realized. They take this information to mean that nitrogen runoff

⁷¹ Carlisle, E. The Louisiana environment, the Gulf of Mexico dead zone. *Louisiana Universities Marine Consortium*, 2000, <http://www.tulane.edu/~bfleury/envirobio/enviroweb/DeadZone.htm>. (Although written in 2000, this article provides a good description of the problem.)

⁷² Achenbach, J. A “dead zone” in the Gulf of Mexico, scientists say area that cannot support some marine life is near record size. *Washington Post*, July 31, 2008, A02, <http://www.washingtonpost.com/wp-dyn/content/story/2008/07/31/ST2008073100349.html?hpid=topnews>.

⁷³ Targeted cuts can ease Gulf dead zone. *Chemical & Engineering News*, **86**(05), February 4, 2008, 20.

⁷⁴ Hogue, C. Gulf of Mexico: Shrinking the dead zone, draft report faults corn-based ethanol. *Chemical & Engineering News*, **85**(41), October 8, 2007, 11.

from corn and soybeans is less important, and point to phosphorus-releasing wastewater treatment plants.⁷⁵

From this Gulf of Mexico dead zone example, you see how difficult it is to revive a dead zone or even, sometimes to know *how* to revive it.⁷⁶ First scientists and agencies must carefully define the problem and decide what needs to be done. The next step is harder still, getting responsible parties, governments, farmers, livestock operations, municipalities and others to take the necessary steps. As Professor Laurence Mee notes: “reducing nutrient runoff . . . requires major changes in agricultural practices and wastewater treatment efforts. Most programs have achieved only partial cuts . . . To shrink nutrient loads, comprehensive plans (at the scale of an entire river catchment system) must be put in place.”⁷⁷

Reviving the Black Sea dead zone

The Black Sea dead zone had an area equivalent to that of Switzerland. This sea is an almost landlocked body of water in Eastern Europe bordered by Bulgaria, the Republic of Georgia, Romania, Russia, Turkey, and Ukraine. In these and other upstream countries intensive use of fertilizers on agricultural lands and CAFOs began in the 1960s leading to much increased runoff of reactive nitrogen and phosphorus to the Danube River. In addition, there were point sources of industrial and urban sewage emptying into the Danube. As all these reached the Black Sea, levels of reactive nitrogen and phosphorus doubled between the 1960s and the 1980s. This led to what has been called a Black Sea catastrophe. Year-round severe eutrophication and hypoxia developed, and the incidence of red tide blooms greatly increased. Sixty million tons (54 million tonnes) of creatures living on the bottom of the sea (benthic life) perished from hypoxia. A final blow came in the early 1980s when an exotic (foreign) species, the Atlantic Jelly Comb was accidentally released. This jelly bloomed so ferociously that it became the dominant Black Sea species. It destroyed native fish species, and 20 of 26 commercial fish species became extinct. Finally, the jellies almost wiped out the zooplankton on which they themselves fed, which led to the collapse of their own population. ■ A major change occurred after 1990 when the Soviet Union regime, which had provided fertilizer subsidies to support intensive agriculture collapsed. Thereafter, fertilizer use fell by more than half and many huge animal farms closed. ■ Nutrient runoff to the Black Sea fell between two- and four-fold. It was obviously recovering by 1994 and, by 2005 it appeared normal, although species had not completely recovered. ■ Potential problem As economic conditions improve, fertilizer use could again increase. However, the governments involved, with aid from the UN Global Environment Facility, started an initiative to maintain nutrient runoff at levels no higher than those of the mid-1990s. Farmers began adding buffer zones around agricultural fields to absorb runoff, and wastewater treatment practices improved. ■ Obviously, these changes must be

⁷⁵ (1) Dead zone plan adrift. *Environmental Science and Technology*, **42**(10), April 2, 2008, 3485–3486. (2) Ferber, D. Ocean ecology: dead zone fix not a dead issue. *Science*, **305**(5690), September 10, 2004, 1557.

⁷⁶ Engelhaupt, E. Trouble killing the dead zone? *Environmental Science and Technology*, **41**(23), December 1, 2007, 7956–7957.

⁷⁷ Mee, L. Reviving dead zones. *Scientific American*, **294**(11), November, 2006, 79–85.

maintained. Again quoting Professor Mee: “Coastal dead zones remind us that humanity cannot simply expect natural ecosystems to absorb our wastes without severe, often unexpected consequences. We now know how to revive dead zones, but ultimately the steps required to do so depend on our recognition of the ramifications to the environment of waste disposal and the degree to which we value the world’s marine ecosystems.”

Reducing the “nitrogen glut”

Professors Diaz and Rosenberg have noted that “there is no other variable of such ecological importance to coastal marine ecosystems that has changed so drastically over such a short time as dissolved oxygen” (see Further Reading).

- Agriculture Implementing practices to reduce nutrient and manure runoff is difficult. Farmers believe they will get a lower yield if they use less fertilizer, and it takes resources to set up buffer zones. Owners of CAFOs often fight attempts to require them to change their handling of animal waste. ■ People eating less meat would reduce the problem not only because this could lead to fewer CAFOs, but because animals eat several pounds of grain per pound of meat produced. Eating meat means that more grain is grown – and more fertilizer used – than if humans eat the grain themselves. In poor sections of the world, when people’s incomes increase, they eat more meat. About 40% of the world’s grain now goes to food animals. ■ Another approach to reducing nitrogen in manure is to feed food animals a diet that results in less reactive nitrogen excretion; that too is expensive.
- Power plants Methods exist to reduce emissions of NO_x by power plants beyond what they are presently doing. Moreover, NO_x emissions could be trapped and converted into fertilizer, but this is costly compared to using synthetic fertilizer. And, although producing synthetic fertilizer is energy intensive, its use continues to increase. ■ On a more positive note, Europe expects soon to reduce NO_x emissions more than 40% by 2010 as a result of the Gothenburg Protocol, a 1999 treaty.
- Motor vehicles In the United States, NO_x emissions from vehicles and fertilizer runoff are still poorly controlled. As one observer commented: “We are not making the lifestyle changes needed to cap nitrogen inputs.” Moreover, the sources of reactive nitrogen are often far from the coastal areas impacted (the Gulf of Mexico), and people balk at taking responsibility for distant impacts. However, results from the Black Sea have been positive. Professors Diaz and Rosenberg, writing a review on dead zones⁶⁴ note, there are other success stories of eliminating, or almost eliminating dead zones including those in the Mersey and Thames estuaries in England. Mostly, these reversals in hypoxia have been small scale. These authors espouse a goal of reducing nutrient inputs to levels seen in the middle of the twentieth century. Some believe that the major problem is that “people haven’t recognized the global nature of nitrogen and that human activity is altering the nitrogen cycle.” That recognition may be slowly occurring. UN studies have projected that reactive nitrogen will soon be a global problem. The US National Research Council has urged the government to develop a strategy to combat both reactive nitrogen and phosphorus pollution.

SECTION VI

China's water pollution

China has the largest population in the world. Its rapid economic growth and development is occurring at the expense of its environment. Reports from the UN Food and Agriculture Organization, the World Bank, the World Resources Institute, and China's State Environmental Protection Administration (SEPA) all stress the gravity of China's environmental degradation including severe water pollution. Water pollutants include agricultural runoff, massive quantities of domestic sewage and wastes from oil refineries, chemical plants, and paper mills. Agricultural runoff, untreated human sewage and animal waste have led to excessive BOD, suspended solids, and microbial contamination in rivers. China has a water scarcity problem too, made worse by the fact that so much of the water is polluted.

Pollution's impact on China's water bodies

Rivers,⁷⁸ lakes, and coastlines

- **Rivers** Significant portions along the length of China's seven major rivers including the Yellow and Yangtze no longer support fish life. Some fish species have become extinct taking with them a valuable food source. Pollution is especially bad in the industrial north. In places, the water is unsuitable even for industrial use let alone irrigation or drinking water. A drought worsened the pollution in recent years because during a drought, the same amount of pollution may enter the rivers, but with less water to dilute it. ■ China's state media describes the Yangtze, China's longest river as "cancerous with pollution." In 2000, SEPA reported that 23 billion tons (21 billion tonnes) of sewage and industrial waste were discharged into the Yangtze and its branches. Wildlife is severely impacted and the number of animal species living in the river fell from 126 in the mid-1980s to 52 in 2002. The Yangtze may be completely dead within a few years.⁷⁹ ■ Likewise, billions of tons of wastewater flow into China's second longest river, the Yellow River so that sewage may be as much as a tenth of its volume.⁸⁰ The Yellow River has lost a third of its fish species. About 70% of its length is considered unfit for drinking or swimming; yet it provides water to 150 million people and irrigates 15% of China's farmland.
- **Lakes** About 75% of China's lakes are highly polluted. More than 60% of its large lakes are eutrophic, and suffer algal blooms that kill fish, make water undrinkable and sometimes have sickening odors.

⁷⁸ (1) Polluted China rivers threaten "sixth" of population. *Reuters*, August 27, 2008, <http://www.abc.net.au/news/stories/2007/08/27/2016373.htm>. (2) Tremblay, J. -F. Efforts to clean the Huai fail again. *Chemical & Engineering News*, **85**(36), September 3, 2007, 28.

⁷⁹ Pollution risks Yangtze's "death". *BBC News*, May 30, 2006, <http://news.bbc.co.uk/2/hi/asia-pacific/5029136.stm>.

⁸⁰ China's Yellow River ten percent sewage. *Reuters*, May 14, 2007, <http://www.reuters.com/article/environmentNews/idUSPEK26151720070511>.

- Coastlines⁸¹ A group of Chinese authors describe the coastal waters of seaside towns in the east China provinces of Jiangsu and Shandong as “massive dumping grounds” with filthy water and vanishing fish. Fishermen are giving up and going elsewhere to look for work. Coastal pollutants include reactive nitrogen, phosphorus, and oil products. Large quantities of waste come from fish and shrimp farms along the coast while, at the same time villagers in Shuigou find dead and dying fish in their nets. Sometimes nets, laden with rubbish and black oil are almost too heavy to pull up. Clam beds are dead or dying. This village and many other coastal communities are disintegrating.

Drinking water

In 2007, the Organization for Economic Cooperation & Development (OECD) reported that water in half of China’s major cities does not meet drinking-water quality standards: ~300 million people drink contaminated water and 70 million drink water containing enough arsenic and fluoride to put their health at risk. An estimated 190 million people contract water-related illnesses every year, especially diarrhea. People who can afford it drink bottled water.

Severe water pollution and working to reduce it

Why water pollution is so severe

China’s population of ~1.3 billion continues to grow as does industrialization and urbanization. Although the majority of industrial wastewater is treated, only half is treated to government standards. Unregulated pollution pours from about 7 million small village businesses, this although China shut down many thousands of the worst. Farmers use inappropriately large amounts of pesticides and fertilizers, much of which run off into surface water or infiltrates groundwater. The central government struggles to at least stabilize the pollution. Its highest decision-making body, the State Council says a major reason is that lower-level government bodies do not enforce national standards.

Reducing China’s water pollution

In late 2007, China, with a new urgency passed the Water Pollution Prevention and Control Law^{82,83} which allows for stiff fines against companies that foul water. China also has

⁸¹ Chen, Y., Bin, L., Chuanmin, Y. *et al.* Dark water: coastal China on the brink. *Southern Metropolis Daily*, April 8, 2008.

⁸² China launches vast water clean-up. *ENN*, March 19, 2009, http://www.enn.com/top_stories/article/39464.

⁸³ China cracks down on water polluters with new law. *Reuters*, February 28, 2008, <http://www.enn.com/ecosystems/article/31965>.

developed a detailed plan to restore its lakes to their original state by 2030:⁸⁴ the State Council ordered strict regulation of wastewater releases to lakes and improved sewage-treatment plants. Because of the major quantities of waste coming from fish farms, the government ordered their removal from the country's three largest lakes by the end of 2008; it also issued regulations as to where fish farms could be placed. It will close heavily polluting factories near lakes. It furthermore banned the use of certain pesticides near its large lakes, and detergents containing phosphates. ■ China has also released a three-year master plan to manage environmental degradation more generally, and plans to spend ~\$300 billion on air, water and solid waste control.⁸⁵ Of this, \$85 billion will go to reducing water pollution. Because the State Council believes that a major problem is the lack of enforcement by lower-level government bodies, it decided to start auditing how well local governments enforced standards.

Delving deeper

1. See Nonpoint Source Success Stories, *US EPA*, February 23, 2009. http://www.epa.gov/nps/success/pdf/319_cat1.pdf. Choose one story of interest to you, e.g., one in which individuals are actively involved, one in which a business chose to do the right thing, or one involving an agency working with a community. After you understand the story, write a brief paper or make a brief report to the class regarding what made it a success and what larger lessons can be drawn. How could individuals or companies, sometimes just by maintaining awareness prevent such an occurrence?
2. Examine the many possibilities listed on The Chesapeake Bay Program, Help the Bay in Your Backyard. <http://www.chesapeakebay.net/inyourbackyard.aspx?menuitem=16888>. Then, consider what possibilities you see for an individual such as yourself to use this information to develop a project on NPS pollution. Or how you realistically could change your own lifestyle.
3. We are most aware of acid deposition, but many pollutants are deposited from the sky. Read the references in Footnote⁸⁶ or other relevant references. Summarize this issue including addressing its importance.
4. Examine the two "Citizens' Guides" references in Internet Resources. Prepare a report on their relevance to you, and how to make these issues more relevant to your fellow citizens.
5. Investigate permeable concrete and porous asphalt. What are its advantages? Is it available locally? How much does it cost relative to ordinary concrete and asphalt? What goes under the concrete or asphalt and why?

⁸⁴ Bradsher, K. China offers plan to clean up its polluted lakes. *New York Times*, January 23, 2008, <http://www.nytimes.com/2008/01/23/world/asia/23china.html?ex=1358744400&en=2aef30682eb8b69b&ei=5088&partner=rssnyt&emc=rss>.

⁸⁵ Tremblay, J. –F. China releases new cleanup plan. *Chemical & Engineering News*, **85**(49) December 3, 2007, 12.

⁸⁶ (1) Air pollution and water quality. *US EPA*, June 19, 2008, <http://www.epa.gov/owow/airdeposition/>. (2) Atmospheric deposition 101. *US EPA*, March 18, 2009, http://epa.gov/oar/oaqps/gr8water/handbook/airdep_sept_2.pdf.

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“The wall between us and microbes, is beginning to crumble.”

American Academy of Microbiology

Most of us in developed countries take clean and plentiful water as a given not just drinking water, but water for household, yard, and other uses. Yet, says the American Academy of Microbiology, “Microbiologically safe drinking water can no longer be assumed, even in the United States and other developed countries, and the situation will worsen unless measures are taken in the immediate future – the crisis is global.” Treating drinking water to kill pathogens is given much credit for increasing the life span of US people from 47 years at the turn of the twentieth century to 77 years. But the twenty-first century begins with a fifth of humanity still without clean drinking water. Even poor-quality water is becoming scarcer and even scarcer for sanitary needs. ▪ The UN estimates that in the near future, at least 40% of the world’s people will live in countries where they cannot get enough water to satisfy basic needs. Wildlife is increasingly deprived of water. Domestic animals may go wanting. Demand for fresh water increased six-fold in the twentieth century, more than twice the rate of population growth.¹ Reasons for water scarcity include an increasing human population that wants and needs more water. Industrial use of water has increased. However, most of the increased water use has arisen from irrigating farm land.

Less than 3% of the water on Earth is fresh and only about a third of this is available for human – and wildlife – use because the other 2% is frozen into polar ice sheets and glaciers. ▪ Ninety-seven percent of Earth’s water, including ocean water is too salty to drink. ▪ Brackish water is less salty than ocean water, but usually not potable. Some groundwater is also too brackish to drink as is some non-marine surface water such as Utah’s Great Salt Lake. However, an increasing amount of freshwater is too polluted to drink. Human activities that pollute water were described in Chapter 9. Surface water is more likely to be significantly contaminated with pathogens, but contaminated groundwater is an increasing concern.

The emphasis in Chapter 10 is on pathogens, monumental drinking-water pollutants in less-developed countries. Section I addresses drinking-water protection in developed countries. Primary and secondary water standards are examined. Two primary pollutants are emphasized, microbes and nitrate, which can have immediate impacts on health. Drinking-water treatment, disinfection, and disinfection by-products are examined, as is fluoride in

¹ Increasingly there are predictions of competition over water resources leading to violent international conflict. “A looming crisis that overshadows nearly two-thirds of the Earth’s population is drawing closer because of continued human mismanagement of water, population growth and changing weather patterns” (former UN Secretary Kofi Annan speaking on World Water Day, March 22, 2002).

drinking water. We see another drinking-water pollutant, arsenic, which is wreaking havoc in several countries where it contaminates water from the tube wells that replaced pathogen-contaminated surface water. Section II discusses the close inter-relationships between clean water and human waste, and the ongoing major problems that waterborne pathogens pose to human health and life. Alternative toilets and ways of treating sewage are noted. Section III looks at methods that can be used to reduce pathogens in drinking water of less-developed countries including point-of-use methods.

SECTION I

Primary and secondary drinking water standards²

US communities began treating their drinking water supplies in the early twentieth century. The primary purpose of treatment initially was to destroy pathogens. Over the years, treatment evolved to include clarifying water and removing components contributing to unpleasant taste, odor, or water hardness and, since the 1970s, to the removal of anthropogenic contaminants.

Drinking water in the United States is regulated under the Safe Drinking Water Act (SDWA) first passed in 1974.³ Both primary and secondary contaminants are discussed below.

The SDWA sets national health-based *primary standards* for microorganisms and toxic substances considered a health risk. Safe levels – remember how risk assessment works to determine safe levels – of these contaminants are enforceable by law to ensure uniform health standards nationwide. Table 10.1 has examples of the nearly 100 chemicals for which primary standards are set. Footnote ⁴ has a full list of regulated drinking water contaminants and of regulated microorganisms. Because most chemicals are present in amounts too small to be an acute health risk, the major concern is potential chronic health effects that might result after years of drinking the water. It is because of potential chronic effects that metals such as lead and cadmium, and organic pollutants such as solvents, and pesticides are regulated.

▪ The EPA sets *primary standards* for many of the pollutants just mentioned. Setting standards involves two steps: 1. The EPA determines a *maximum contaminant level goal* (MCLG), a level not expected to cause adverse health effect over a lifetime of exposure; 2. Because achieving the MCLG is not always possible, the EPA also sets an achievable *maximum contaminant level* (MCL). The MCL is set as close to the MCLG as possible. The *MCL is an enforceable standard*. ▪ Some regulated drinking-water contaminants are natural, including fluoride (Box 10.1), arsenic, and the radioactive elements, radon and radium.

² National primary drinking water regulations. *US EPA*, March 18, 2009, <http://www.epa.gov/safewater/contaminants/index.html>.

³ The history of drinking water treatment (Fact sheet based on EPA report “25 Years of the Safe Drinking Water Act: history and trends.”) *US EPA*, February, 2000, <http://www.epa.gov/safewater/consumer/pdf/hist.pdf>.

⁴ Drinking water contaminants. *US EPA*, March 18, 2009, <http://www.epa.gov/OGWDW/contaminants/index.html>.

Table 10.1 Primary drinking-water standards for chemicals

Contaminant	MCLG (mg/l)	MCL (mg/l)	Sources of contaminant
Volatile organic chemicals (VOCs)			
Benzene	0	0.005	Some foods, gas, drugs, pesticides, paint
Carbon tetrachloride	0	0.005	Solvents and their degradation products
<i>p</i> -Dichlorobenzene	0.075	0.075	Room and water deodorants, mothballs
Organic chemicals			
Atrazine	0.003	0.003	Runoff from use as herbicide
Chlordane	0	0.002	Leaching from soil treatment for termites
Chlorobenzene	0.1	0.1	Waste solvent from metal degreasing
PCBs	0	0.0005	Coolant oil from electrical transformer
Benzo[<i>a</i>]pyrene	0	0.0002	Coal tar coatings, burning organic matter
Inorganic chemicals			
Arsenic	0	0.010	Natural deposits; runoff from several sources
Barium	2	2	Natural deposits, pigments, epoxy sealants
Cadmium	0.005	0.005	Galvanized pipes, natural deposits, batteries
Nickel	0.1	0.1	Metal alloys, electroplating, batteries
Nitrate	1	1	Animal waste, fertilizer, natural deposits

The above pollutants are examples of the nearly hundred contaminants for which the US EPA has set primary standards. See complete list at <http://www.epa.gov/OGWDW/mcl.html>.

When natural sources of regulated substances exist, the EPA takes these into account when setting standards. ▪ Removing contaminants If a chemical is detected at a concentration greater than its MCL, its level must be reduced using the *best available technology* (BAT). Absorption, using activated carbon can be used to reduce levels of a number of these. See list of technologies in footnote ⁵. Two contaminants—*bacteria* (and other pathogenic microbes) and *nitrate*—can pose an immediate, an acute, threat to health or life if primary standards are exceeded.

Box 10.1**Fluoride in community drinking water**

Background Fluoride is added to drinking water in about half of US communities to lower the incidence of tooth decay among children. It is added at 0.7–1.2 ppm, the level considered optimal to prevent caries. EPA's MCL for fluoride is 4 ppm, higher than this because some sources of drinking water are naturally rich in fluoride. Natural fluoride levels are usually low, but about 0.5% of the US population have supplies with levels greater than 2 ppm. In a few people who ingest more than 2 mg/l stained or pitted teeth develop over time. Moreover, a few cases are known of people who, for many years drank water naturally containing more than 8 mg/l fluoride; as a result some developed crippling skeletal disease.

⁵ Removing multiple contaminants from drinking water: treatment technologies. *US EPA*, December, 2007, http://www.epa.gov/OGWDW/treatment/pdfs/poster_treatment_technologies.pdf.

Controversy

After more than 50 years of use, fluoridation remains controversial because some believe it is harmful. Critics assert that lax monitoring leads to fluoride ingestion at levels high enough to harm human health. In one (now old) example, a grape juice for babies was found to contain 6.8 ppm fluoride. People ingest fluoride from food and beverages that were processed with fluoridated water. Fluoride is also sometimes found in tooth paste, which children may swallow.

Government position

In 2006, on the basis of a report from the National Research Council (NRC), the CDC affirmed the use of fluoride in drinking water to prevent dental caries.⁶ The report's emphasis was on addressing the safety of high *natural* levels of fluoride in water (2 ppm or more). It did not question using lower levels to prevent tooth decay. However, the CDC advised the EPA to lower the MCL for fluoride because natural levels of up to 4 ppm (and sometimes greater) were associated, after lifetime exposure, with an increased risk of bone fractures and, rarely, severe skeletal fluorosis. Babies and children Severe tooth enamel fluorosis has occurred in some babies and children up to 8 years of age from exposure to high natural levels. However, at less than 2 ppm, the NRC committee noted that severe fluorosis was near zero. The CDC recommends that, if water systems have fluoride levels greater than 2 ppm, parents of young children give them an alternative source of drinking water.⁷

Pathogens

Destroying pathogenic agents – bacteria, viruses, protozoa – remains the primary reason to treat drinking water. Microorganisms are naturally present in water.

- However, fecal coliform bacteria in the water may indicate human or animal wastes because these bacteria inhabit the intestines of humans and other vertebrates. Coliform bacteria do not necessarily cause disease themselves, but are an indicator of fecal material, which may contain pathogens. They are used as an indicator because simple inexpensive methods are available to detect them. If coliform are detected, the water is further tested for the presence of organisms known to be pathogens. Examples are: *Legionella* bacteria are responsible for the respiratory disease, Legionnaire's disease.
- Enteric viruses are pathogens which can cause gastrointestinal distress.
- Two protozoa causing serious intestinal illness are *Giardia lamblia* and *Cryptosporidium parvum* (Figure 10.1).⁸

⁶ CDC statement on the 2006 NRC report on fluoride in drinking water. CDC, Division of Oral Health, September 24, 2008, http://www.cdc.gov/fluoridation/safety/nrc_report.htm.

⁷ Community water fluoridation overview. CDC, May 15, 2008, <http://www.cdc.gov/fluoridation/>.

⁸ *Cryptosporidium* and *Giardia*. US EPA, October 30, 2007, http://www.epa.gov/nerlcwww/cpt_gda.htm.

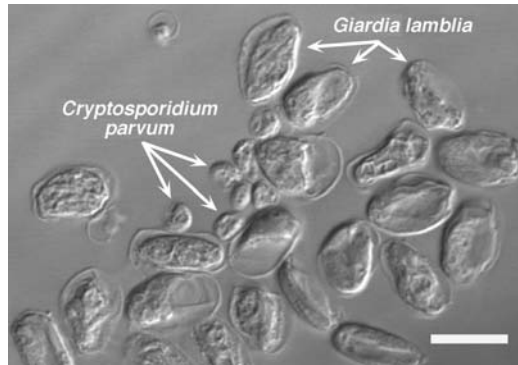


Figure 10.1

Two parasitic protozoa. Credit H. D. A. Lindquist, US EPA (Bar = 10 microns) EPA

Sources of pathogens

Pathogen sources include poorly treated sewage, malfunctioning septic systems, runoff of animal manure, and other storm water runoff. Pathogenic agents can also come from fish, water birds, and wild animals. Before the twentieth century, pathogens frequently contaminated drinking water causing epidemics of cholera, typhoid fever, amoebic dysentery, and other diseases. Small children in particular, often died from waterborne diseases and a great many still do in less-developed countries. As communities began disinfecting drinking water in the early twentieth century, these diseases fell dramatically. Nonetheless, pathogen contamination did not disappear. A 1985 CDC report estimated that 940 000 Americans become ill each year from infectious organisms in drinking water, and about 900 die. Those at greatest risk are infants, elderly people, and individuals with immune systems compromised by other illnesses. ▪ An especially serious incident occurred in 1993 when about 400 000 people in Milwaukee, Wisconsin, became ill after drinking water contaminated with *Cryptosporidium*. More than 100 already ill people died. The US EPA already required water utilities to remove at least 99% of *Cryptosporidium* from their drinking water; this regulation became stricter as of 2006 for certain utilities.⁹

Killing microbes in drinking water

Disinfection is often vital to obtain safe drinking water.¹⁰ The most common and technologically simple means of disinfection is with chlorine-containing chemicals, *chlorination*. Unfortunately, chlorination produces its own contaminants, *disinfection by-products* (DBPs). These result from the reaction of chlorine with organic material present in water.

⁹ *Bad Bug Book: Foodborne Pathogenic Microorganisms and Natural Toxins Handbook*. US FDA, June 18, 2009. <http://www.fda.gov/Food/FoodSafety/FoodborneIllness/FoodborneIllnessFoodbornePathogensNaturalToxins/BadBugBook/default.htm>.

¹⁰ Water and disinfection. *Centers for Disease Control and Prevention*, 2008, <http://www.cdc.gov/Features/DrinkingWater/index.html>.

Higher chlorine concentrations produce higher levels of DBPs, especially if significant quantities of organic material are present. High levels of chlorination can also produce an odor and affect taste.

Disinfection by-products

Chloroform is the DBP produced in the largest amount. At high doses, chloroform is an animal carcinogen. ▪ The EPA has established an MCL for total *trihalomethanes* (THMs), a family of DBPs found in chlorinated water, so THMs are a primary water pollutant. Epidemiologic studies suggest that drinking chlorinated water for many years increases the risk of bladder and rectal cancer.¹¹ This raises a dilemma because disinfection is critical to killing harmful microorganisms; moreover, disinfectant levels must be high enough to accomplish this. Some argue that chloroform levels and, more generally, total DBPs are not of concern, especially balanced against the risk of infectious diseases. ▪ Removing DBPs Removing DBPs from drinking water is an end-of-pipe process, and sometimes costly. A P² approach is to remove as much organic material as possible from water before chlorination, which results in lower levels of DBPs. Better, ensure that water comes from a clean source such as the Catskill Mountain watershed for New York City.

Alternative disinfectants

These produce smaller amounts of DBPs than does chlorine. However, all disinfectants form some DBPs, which may pose problems too. What are these disinfectants?

- *Chlorine dioxide* is more effective at destroying pathogenic microbes than chlorine; it also produces much smaller quantities of DBPs. However, it does produce *chlorite*, an EPA-regulated DBP; and without careful handling ClO₂ is dangerous. An increasing number of United States communities use chlorine dioxide.
- *Chloramine* is effective too and produces fewer DBPs. ▪ However, chloramine has produced a major problem in some situations – it leaches out the dangerous pollutant lead from old plumbing.¹² ▪ Moreover, chloramine can lead to the formation of *nitrosamines*, which are much stronger carcinogens than are THMs.¹³ This is ironic because one reason for switching to chloramines was that THMs from chlorine are associated with an increased bladder-cancer risk.
- *Ozone* (O₃) disinfection works even better than chlorine, and also helps to remove poor tastes, color, and odors from water. Ozone decomposes into oxygen (O₂) and a free oxygen atom O. With its unpaired electron, this oxygen atom is a free radical and

¹¹ Another epidemiologic study had raised concern that DBPs in chlorinated tap water might also increase the risk of miscarriage in pregnant women. However, a well regarded 3-year, \$3.5 million study of pregnant women exposed to THMs found no greater risk of miscarriage than in less-exposed women. Renner, R. DBPs not associated with miscarriage. *Environmental Science & Technology*, **39**(20), October 15, 2005, 416A.

¹² Renner, R. Chloramine's effect on lead in drinking water. *Environmental Science & Technology*, **40**(10), May 17, 2006, 3129–3130.

¹³ Lubick, N. More nitrosamines in drinking water. *Environmental Science & Technology*, **40**(24), December 15, 2006, 7454.

extremely reactive.¹⁴ It reacts with and degrades many water contaminants. However, O₃ cannot maintain disinfection just because it does so readily break down; thus, to maintain disinfection a small amount of chlorine must be added before piping the water to users; so small amounts of THMs form. Many consider ozone the ideal disinfectant. However, if the water contains *bromide*, ozone oxidizes it to the DBP, *bromate*; bromate is a strong animal carcinogen and a regulated pollutant. Ozone disinfection is about 10% more expensive, and needs better trained operators. Nonetheless, cities planning new drinking-water treatment plants are moving toward ozone if they have the financial resources. Another major positive for ozone is that it destroys the serious protozoan contaminant *Cryptosporidium*, whereas chlorine is considerably less effective.

- *Ultraviolet light* (UV) kills pathogens. However, because it is expensive, it has been used primarily to treat small volumes of water. Like ozone, UV light also can destroy *Cryptosporidium*. As with ozone, small amounts of a chemical disinfectant must be added before piping water to users. However, cities able to afford the added cost seriously consider UV light. Plants using UV light cost more, but less expensive UV operations are being developed. Small-scale inexpensive versions are also being explored for less-developed countries.
- *Distillation* of water can purify it and the distillate has no DBPs. However distillation is costly and the distilled water lacks minerals and taste.

Reducing the need for disinfection

Disinfection is critical for impure water. But if a community conscientiously works to reduce infectious microorganisms in its water supply, it needs less or no disinfection. The US EPA and a number of states have watershed protection programs to maintain the purity of water sources. Recall the New York City P² example: spend money to buy and protect land bordering on the water bodies that supply drinking water. ■ At the individual level, those with private wells can make sure there is no source of pathogens that can reach the groundwater serving the well. See Table 9.1 for approaches used to reduce polluted runoff. As population continues to increase and development pressures grow, maintaining water purity becomes both more important and more difficult.

Nitrate: a second threat to health

The second contaminant able to pose an acute threat to health – if above its MCL of 1 mg/l – is *nitrate*. Recall that nitrate is found in runoff from fertilizer-treated fields and from areas with large amounts of manure (animal operations). This happens because rainwater can dissolve the nitrate, which then runs off into surface water. It can also infiltrate into soil and groundwater and sometimes contaminates rural wells. Infants are most vulnerable because

¹⁴ In the water treatment plant ozone is a very useful agent, but in the environment it is a major pollutant (Chapter 5). Its reactivity can damage the mucous membranes of the eyes and lungs and can harm crops and trees.

nitrate is converted to *nitrite* in infant stomachs more readily than in adults or older children. After absorption into the bloodstream, nitrite reacts with the iron in the infant’s hemoglobin to produce *methemoglobin*, which cannot carry oxygen. The result may be “blue baby” syndrome.¹⁵ Excessive nitrate ingestion has resulted in infant deaths in the Midwestern United States.

Arsenic¹⁶: “the largest mass poisoning in history”

Arsenic is a primary drinking-water pollutant¹⁷ that is becoming “the key environmental health problem of the twenty-first century.” Public health personnel make this statement because of what is happening in portions of Bangladesh, West Bengal, India, Vietnam, and a number of other countries. In Bangladesh, more than a hundred million people drink water contaminated with more than 50 µg/l of arsenic – this although the World Health Organization (WHO) advises a maximum permissible level for arsenic in drinking water of 50 µg/l, and recommends 10 µg/l. In some Asian wells levels exceed 3000 µg/l. Why is this happening? Surface water in Bangladesh and in many other impoverished countries is so polluted with pathogens (and sometimes with industrial chemicals) that it cannot serve as drinking water. So, more than 30 years ago the UN International Children’s Emergency Fund (UNICEF) began funding the drilling of wells to provide clean drinking water. Once well water became available, infant deaths from diarrhea dropped dramatically. The wells seemed a major success. However, organic matter is buried in the sediments into which the wells were drilled; its decay leads to chemical events that result in arsenic release into groundwater, and thus into wells.

Arsenic toxicity¹⁸

Although arsenic levels in Bangladeshi wells are high, they are not acutely toxic. Chronic toxicity is the problem. This meant that awareness of the poisoning was slow in coming. People began showing symptoms after drinking the water for 5 to 10 years or more. In one region of Bangladesh where 59% of nearly 11 000 well-water samples contained more than 50 µg/l arsenic, nearly a quarter of the villagers examined had skin lesions. ▪ Early symptoms are changes in skin coloration or many hard corns on the palms, soles, and torso. Drinking water with arsenic levels greater than about 300 µg/l resulted in skin lesions (Figure 10.2). Later, skin cancers also began appearing. ▪ Over decades, as people

¹⁵ Nitrate and nitrite, human health fact sheet. *Argonne National Laboratory*, August, 2005, <http://www.ead.anl.gov/pub/doc/nitrate-ite.pdf>.

¹⁶ ToxFAQs™ for arsenic. *ATSDR*, August, 2007, <http://www.atsdr.cdc.gov/tfacts2.html>.

¹⁷ (1) Arsenic in drinking water. *US EPA*, September 14, 2006, <http://www.epa.gov/safewater/arsenic/index.html>.
(2) Arsenic in drinking water, basic information. *US EPA*, March 26, 2007, <http://www.epa.gov/safewater/arsenic/basicinformation.html>.

¹⁸ Mead, M. N. Arsenic: in search of an antidote to a global poison. *Environmental Health Perspectives*, **113**(6), June 2005, A378–A386.

**Figure 10.2**

Keratosis on feet from chronic arsenic poisoning. Credit: Arsenic Foundation

continued drinking the water, lung, liver and bladder cancers developed. ▪ Other major toxic effects include gangrene because arsenic is toxic to the nervous system, including the long nerve fibers to the limbs. Notice below that the MCL for arsenic in US drinking water is 10 $\mu\text{g}/\text{l}$.

Reducing the risk of arsenic

Nutrition

At the earliest stages of the poisoning, skin changes can be reversed by drinking clean water and eating nutritious food. However, a great many poisoned people are poor and have access to neither. Recall from Chapter 3 that people with nutritious diets are less susceptible to poisoning; in fact, even drinking water with arsenic levels of 400 $\mu\text{g}/\text{l}$ may not lead to lesions. In contrast lesions occur at quite low levels in people who have poor nutrition, drink large quantities of contaminated water, or drink it over a long time. In Bangladesh alone 85 million people are at risk of developing cancer. This poisoning is a stunning tragedy.

Pregnant women and their babies

Studies showed adverse impacts showing up after many years in people whose mothers drank water with high levels of arsenic when pregnant. One researcher noted that, if no other action is taken, pregnant women should receive low-arsenic water.

Other personal actions to reduce risk

Contaminated wells have had their handles painted red to warn people. Nonetheless, if uncontaminated water is located far from their homes, some people continue to drink from arsenic-contaminated wells. ■ Recall (Chapter 3) synergism: studies find that the lung cancer risk of smokers who also drink water high in arsenic was 32 times that of non-smokers with low levels of drinking-water arsenic. Compare this to a six-fold greater risk for lung cancer resulting from smoking alone.

Removing arsenic from water¹⁹

An intense effort has been underway to find ways to cheaply remove arsenic from water. Technologies already existed, but were too costly for impoverished countries. When a million dollar prize was offered for methods to inexpensively reduce arsenic levels below 50 µg/l, a number of good technologies were developed: the winner produced a simple, inexpensive system for filtering arsenic from well drinking water. It uses buckets of river sand, pieces of cast iron, and charcoal. At the time the prize was received in 2006, some of these devices were still being successfully used after five years in Bangladeshi villages. In some cases, drilling deeper wells is appropriate. However, close oversight over their installation must be provided because of potential corruption.

Arsenic in wealthier countries

In the United States, the MCL is 10 µg/l (as of 2006); previously it had been 50 µg/l. The 10 µg/l resulted from epidemiologic studies finding association between low-dose exposures to arsenic and increased risks of vascular disease, diabetes, and some cancers. Laboratory studies on animal cells indicated that at low doses, arsenic is an environmental hormone (endocrine disrupter): it disrupts the action of *cortisol*, a steroid hormone involved in regulating blood glucose levels and blood pressure.²⁰ ■ However, the United States too has many water wells containing greater than 50 µg/l arsenic. A great many more contain at least 10 µg/l. But the MCL regulation does not apply to private wells many of which have not been tested.

¹⁹ Ritter, S. K. Sustainable technology: chemist wins gold in million-dollar arsenic challenge, *Chemical & Engineering News*, **85**(7), February 12, 2007, 19.

²⁰ Arnette, R. Low dose arsenic is an endocrine disruptor. *NIEHS*, January 2008, [http://www.niehs.nih.gov/news/ newsletter/2008/january/arsenic.cfm](http://www.niehs.nih.gov/news/newsletter/2008/january/arsenic.cfm).

Table 10.2 Secondary drinking-water standards

Contaminant	Suggested levels	Contaminant effects
Aluminum	0.05–0.2 mg/l	Water discoloration
Chloride	250 mg/l	Salty taste and corrosion of pipes
Color	15 Color units	Visible tint
Manganese	0.05 mg/l	Taste or staining of laundry
Sulfate	250 mg/l	Salty taste, laxative effects
Total dissolved solids	500 mg/l	Bad taste or may damage plumbing or limit effectiveness of detergents
Odor	Threshold odor	Rotten egg, musty, or chemical smell
pH	6.5–8.5	Low pH: bitter metallic taste, corrosion High pH: slippery feel, soda taste, deposits

See complete list at <http://www.epa.gov/OGWDW/mcl.html>.

Secondary drinking-water contaminants

Secondary standards are designed to protect *public welfare*. The contaminants involved are those that can influence taste, odor, or color. See Table 10.2. These are primarily aesthetic concerns. The EPA has guidelines for these substances but they are not enforceable unless individual states treat them as enforceable. A full list of secondary contaminants is found on the US EPA website noted in footnote ²¹ (following the list of primary drinking-water contaminants).

Emerging drinking-water contaminants

Recall (Section V of Chapter 1) “The tyranny of small decisions.” Think of all the shampoos, cosmetics, personal care products, and other household chemicals that go down the drain. Plus the metabolic breakdown products of pharmaceuticals that go down the toilet. Sometimes people deliberately dump the whole of unused prescriptions down the toilet. They end up at small levels in surface waters, sometimes re-emerging, albeit at tiny levels, in our drinking-water taps. Among the chemicals being disposed of this way, the ones of most concern are environmental hormones and antibiotics. ▪ Hormones The metabolites of hormones that we ingest, e.g., birth control pills become, once they are released into the environment, environmental hormones. Recall that although most environmental hormones have weak activity, the downside is that hormones are active at tiny concentrations. This is reason enough to be concerned that these substances are reaching water bodies. ▪ Antibiotics

²¹ Drinking water contaminants. *US EPA*. See table following list of primary drinking-water contaminants in this file, <http://www.epa.gov/OGWDW/contaminants/index.html> (August, 2008).

Perhaps of the greatest concern are the antibiotics released into the water. These can contribute to the development of resistance to antibiotics.²² ▪ These contaminants are not regulated. The American Water Works Association has assessed 18 possible treatments that US water purification facilities could use, and suggested several treatments that can remove these micro-contaminants including ozonation (see description above), activated carbon, and reverse osmosis.²³ The good news is that ozonation is already being adopted by an increasing number of facilities for other reasons, and activated carbon is also often used to absorb other contaminants.

Questions 10.1

1. (a) How do microorganisms get into groundwater? (b) Viruses move in groundwater more quickly than do other microbes – why?
2. How can diarrhea cause death?
3. Considering the problems associated with DBPs, why is chlorination still often used, indeed promoted in less-developed countries?
4. Many individuals obtain drinking water from home wells. (a) Where should wells be sited in order to avoid pathogen contamination? (b) To avoid contaminating the wells with fertilizer or pesticides, where should they be located? (c) How might the ages of wells affect the risk of groundwater contamination? Explain.
5. Think about a community that obtains its drinking water from a well. What are practical steps that it can take to educate its citizens to protect the source of their water?

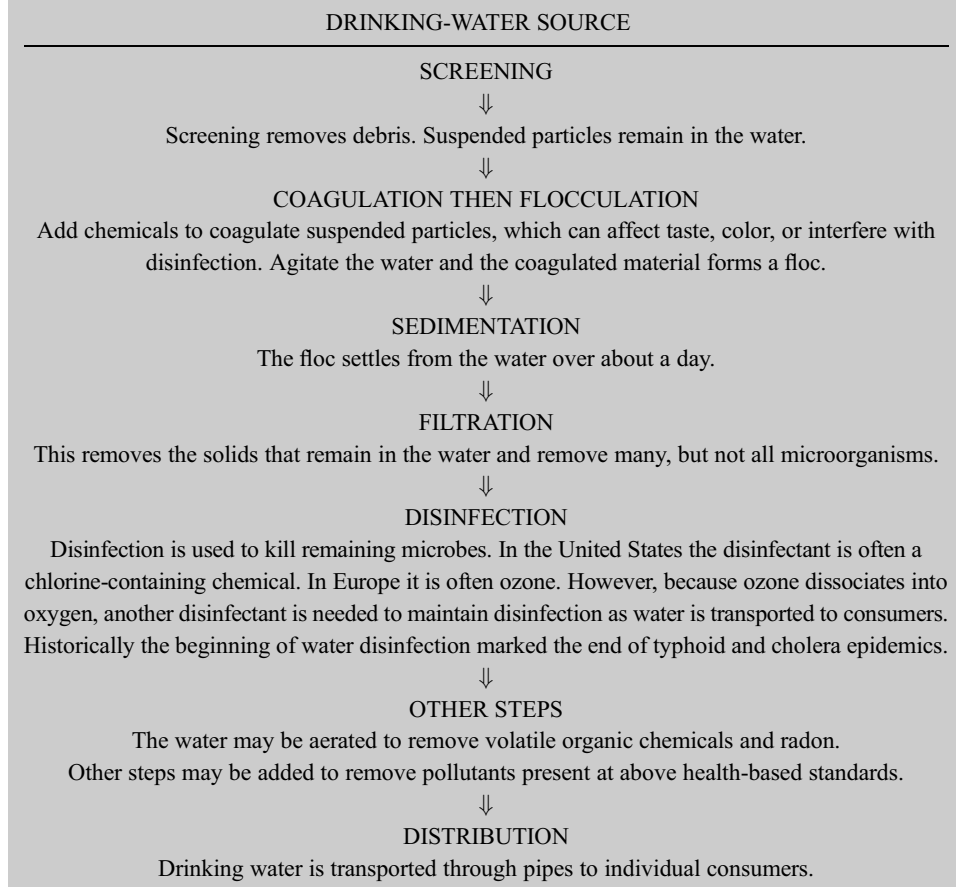
Maintaining drinking water safety

See Table 10.3 for typical steps taken to treat water to bring it to drinking-water standards.

In the United States, the EPA requires states to evaluate the performance of their water supply systems, but many fail to do so due to limited resources. Many water-treatment systems are aging, or lack the modern technology needed for optimal performance. ▪ Most US public water systems are small, serving 25 to 3300 customers. At one time, small systems had only to meet standards for water clarity, bacteria, and nitrate levels. After 1986 they were required to meet the same demanding regulations that larger systems meet. ▪ Nonetheless, the cost of drinking water to US citizens is low; it was an average of \$0.51 per m³ (\$35.3 ft³) in 2000 as compared to \$1.15 in the United Kingdom and \$1.82 in Germany. Still, Americans pay as much for water as Europeans because they use much more water. ▪ Europe has many of the same concerns as the United States, including pollution resulting from pesticide and nitrate runoff from agricultural lands and

²² One product that we can completely control is *triclosan*. Triclosan is not an antibiotic (which is ingested), but an antibacterial product found in nearly all liquid hand cleansers and many other products. Triclosan is used outside the body. However, many believe that triclosan could also be stimulating resistance to antibiotics.

²³ Snyder, E.M., Pleus, R.C. and Snyder, S.A. Current Issues. Pharmaceuticals and EDCs in the U.S. Water Industry: An Update. *AWWA*, 97(11) November 2005, pp. 32–34, 35, <http://www.awwa.org/Resources/content.cfm?ItemNumber=1140&showLogin=N>.

Table 10.3 Drinking water treatment process Credit: US EPA

livestock operations. Europeans also express concern that exposure to and health effects of water pollutants have not been properly assessed.

Other issues

- High population densities already exist in a number of European countries. The United States is still land rich, but with its population growing 1% a year, some locales are increasingly crowded, which makes it more difficult to maintain the purity of drinking water-sources.
- Sensitive groups The United States and other industrialized countries have begun to evaluate what to do about those populations that are especially sensitive to contaminants including the aged with deteriorated immune systems, and infants and small children whose immune systems are immature. Others have immune systems impaired by AIDS, cancer, radiation therapy, organ transplants, or serious chronic diseases. These persons may be advised to boil drinking water or drink bottled water to avoid pathogens that may

have survived to reach tap water. Another group of people routinely advised to drink bottled water is those who travel to poor countries where microbes may be in tap water (Box 10.2).

Box 10.2
Bottled drinking water²⁴

Over a billion people lack any access to clean drinking water, but others buy bottled water in places well served by treatment plants that produce high quality drinking water. US municipalities spend \$43 billion a year to provide clean drinking water. Moreover, the water quality standards that the US EPA sets for tap water are more stringent than those set by the US Food and Drug Administration (FDA) for bottled water. In Europe as well as the US, more regulations govern the quality of tap water than of bottled water.

People believe bottled water is purer than tap water, or prefer its taste. The Natural Resources Defense Council, a US environmental organization, had 103 brands tested. Results revealed that about a quarter of the brands were simply tap water; some had been further treated. Some brands had contaminant levels exceeding those allowed by state or bottled-water industry standards, but most appeared safe and clean. • Similar situations are reported in other countries. A University of Geneva (Switzerland) study found that a bottled-water category called “purified” was drawn from rivers, lakes, or underground springs and treated. Its quality was usually good, but some samples differed little from tap water and had the same contaminants. • Similarly, a University of Winnipeg (Canada) study examined 40 domestic and imported bottled water brands. It found some brands in which total dissolved solids, chloride and lead exceeded the Canadian Water Quality Guidelines for drinking water. • In these three countries, bottled water is much more expensive – costing from 240 to 10 000 times more than tap water. For instance, in San Francisco, residents can purchase 1000 gallons (38 000 liters) of tap water for the same amount spent on 1 gallon (3.8 liters) of bottled water. Worldwide, the industry is worth about \$100 billion a year.

The environmental impact²⁵ of producing bottled water includes drawing down some local streams and aquifers to obtain the water. There are the energy costs and environmental pollution of producing, bottling, packaging, storing, and shipping bottled water. To manufacture the 29 billion plastic bottles that the US uses each year for bottled water takes the equivalent of ~17 million barrels of crude oil. Bottled water is often shipped long distances which, of course, requires fossil fuel. And US drinkers recycle less than a quarter of the bottles; they become garbage or litter. Municipalities, often the same ones that produce valuable tap water, end up with the cost of landfilling the bottles. • US cities have been responding. Chicago, tired of paying landfilling costs, placed a 5 cent tax on each bottle of water sold in the city; the intent is to cut consumption. San Francisco has barred its city departments, agencies, and

²⁴ Aslam, A. Bottled water: nectar of the frauds? February 5, 2006, *OneWorld.net*, <http://www.commondreams.org/headlines/06/0205-01.htm>.

²⁵ Zabarenko, D. Report finds bottled water has high environmental costs. *Reuters*, May 11, 2007, <http://www.alertnet.org/thenews/newsdesk/N10484560.htm>.

contractors from using city funds to serve water in plastic bottles when tap is available. New York City reminds its citizens that its tap water is naturally filtered in the well-protected Catskill Mountains (See Chapter 1). In Louisville, Kentucky, the water utility provides free “sports” bottles to citizens, urging them to fill them with “Pure Tap.” Many other local governments are also taking action. ▪ The industry defends itself saying that water is healthier than sugary beverages served in the same type of bottles (and with the same environmental impact). Moreover, they defend the rights of citizens to buy whatever they want. ▪ However, the promotion of bottled water consumption is seen by many as a back-door approach to the privatization of water. In less-developed countries, people who can afford it drink bottled water to avoid water contaminated with pathogens and other pollutants. But increasingly, governments around the world are saying that governments should have a primary role in improving access to safe drinking water.”²⁶

- **Emerging problems** In the 1990s several infectious-disease outbreaks were traced to drinking water in North America. The worst by far was the outbreak described above of *cryptosporidiosis* in Milwaukee, Wisconsin. Another cryptosporidiosis outbreak in Walkerton, Ontario (Canada), sickened 13 000. In response, the US EPA began to more strongly focus on ambient water quality criteria, and will establish pathogen monitoring protocols, guidelines for septic system operations, and requirements for water reuse applications. The EPA is also developing a risk assessment protocol for waterborne infectious diseases, as well as examining pathogens in sediments.

SECTION II

Clean water and human waste are closely intertwined²⁷

In Chapter 9 you learned that pathogens are a conventional water pollutant. In this Chapter you have learned that pathogenic microbes in drinking water can pose an immediate threat to health or life if primary standards are exceeded. In both these cases – wastewater and drinking water – the source of the pathogens are human and animal excreta. ▪ “The WHO estimates that *80% of all sickness in the less-developed countries of the world is attributable to unsafe water and sanitation.*²⁸” Thus the most important point to remember in this section is the great unmet need for clean water and sanitation around the world. In 2007, the British Medical Journal surveyed its readers as to what they considered the “greatest medical

²⁶ Mulvey, K. Water ought to be a public good, not a commodity. *Star Tribune*, March 20, 2006, <http://www.commondreams.org/views/06/0321-25.htm>.

²⁷ Montgomery, M. A. and Elimelech, M. Water and sanitation in developing countries: millions suffer from preventable illnesses and die every year. *Environmental Science & Technology*, **41**(1) January 1, 2007, 17–24.

²⁸ Malaria is transmitted by mosquitoes, which lay their eggs in stagnant water.

milestone since 1840.” Among more than 11 000 readers that responded, the overwhelming choice was “improved sewage disposal and clean water supply systems.” Access to these greatly reduces the chances of developing disease from a waterborne microbe.

“One of the biggest threats to human health”

Upon hearing the words “water pollution,” chemical pollution may first come to mind. Yet the major problem of people in impoverished countries is pathogen-contaminated drinking water. If industries are also present and releasing poorly treated or untreated effluents, or if there is agricultural runoff containing pesticides and fertilizers, then chemical pollutants add to the burden posed by pathogens. ▪ Aggravating the problem is too little water in many locales.²⁹

The UN estimates that 1.1 billion people don’t have access to clean drinking water. Intertwined with this problem is that 2.6 billion people in less-developed countries lack access to sanitary facilities and, increasingly due to water shortages don’t have water for basic sanitation procedures such as hand washing. This often leads to pathogens in water, food, and environment, and to passing on those microbes to other people. Water-resources expert Peter Gleick refers to water-related diseases as perhaps the greatest failure of human development. ▪ The WHO reports that millions die each year in less-developed countries from drinking water contaminated with infectious microorganisms or parasites³⁰, or insufficient water (Table 10.4).

Table 10.4 Infectious organisms in the water supply

Organism	Diseases and agents	Symptoms
Bacteria	Typhoid, paratyphoid, bacillary dysentery, gastroenteritis, cholera	Headache, diarrhea, abdominal cramps, fever, nausea, vomiting occurring several hours to days after ingestion. Severity varies depending on organism.
Viruses	Viral gastroenteritis (up to 100 types in raw sewage [§]) Also polio and hepatitis A	Symptoms seen depends on the specific virus
Parasites	Protozoans causing disease include <i>Giardia lamblia</i> and <i>cryptosporidium</i> Parasitic worms include tapeworms, roundworms, hookworms	Protozoa: Mild to severe diarrhea, including bloody diarrhea. Worms: Symptoms vary depending on specific worm: abdominal pain, anemia, fatigue, weight loss

See complete list at <http://www.epa.gov/OGWDW/mcl.html>

[§] The human immunodeficiency virus (HIV) is *not* spread by water.

²⁹ The WHO reported in 2005 that half of the world’s hospital beds are filled with people suffering from water-related diseases, not just diarrhea, but cholera, typhoid, guinea worm, diarrhea, and polio. Malaria is also spread by mosquitoes that breed in water, and trachoma is related to water scarcity, spreading where people have little water to use for cleanliness.

³⁰ Green, S. T., Small, M. J. and Casman, E. A. Policy analysis: determinants of national diarrheal disease burden. *Environmental Science & Technology*, **43** (4), February 15, 2009, 993–999.

Most deaths, 80%, occur in children under 5, who frequently die from diarrhea associated with waterborne pathogens. In India alone, diarrhea kills about 500 000 small children a year. Globally³¹ diarrhea is the sixth largest cause of death. A 2005 World Bank document reported “four billion cases of diarrhea a year” and other water-related diseases. Indeed the WHO reports that at any one time, up to half the world’s people are ill due to infections resulting from contaminated drinking water.³² ▪ Two of the UN’s Millennium Development Goals (MDGs) are to cut in half the number of people without safe drinking water and without improved sanitation by 2015. The WHO, as part of this effort established a Household Water Treatment and Safe Storage Network.³³ ▪ The developed world’s methods of treating wastewater are expensive. Also, despite laws and regulations, there are still some point sources contaminating waterways as well as nonpoint source runoff from problems such as combined sewer overflow.

Polluted water and water scarcity

In less-developed countries as much as 98% of human waste goes into rivers and streams untreated. “Rivers are often open stinking sewers.” In China, an estimated 300 million people drink contaminated water. In Buenos Aires, Argentina, only 2% of sewage is treated. Sometimes developed countries can be casual about disposing of their sewage including, surprisingly, some major Canadian cities. In India, less than a third of people have access even to basic sanitation, let alone improved sanitation or flush toilets. Yet cities in impoverished nations continue their rapid growth with ongoing lack of basic services. Especially affected by a lack of sanitation, according to the UN Environmental Program (UNEP) are the almost 2 billion people living along the coasts of South Asia, northwestern Pacific, and West Africa. In addition to impacting human health, the livelihood of people working in fishing and tourism is increasingly impacted. ▪ Given this information, you might correctly guess that an important reason for drinking water scarcity is that the water is often too polluted to drink. ▪ And drinking water is expensive: On average, the poor in less-developed countries pay 12 times more for drinking water than do better-off people with homes connected to municipal water supplies; yet, despite the cost, the water they buy is often contaminated. People are advised to boil water for 10 minutes before drinking it. However, in, for example, Bangladesh it would cost the poorest people more than 10% of their income to buy the fuel to boil water. Thus, water is often not boiled.

³¹ Cohen, J. Pipe dreams come true. *Science*, **319**(5864), February 8, 2008, 745–746. A big investment in sewer connections in Salvador, Brazil, led to a steep decline in diarrhea in young children. Said water engineer, Sandy Cairncross: “Diarrhea kills more children than AIDS, tuberculosis, and malaria put together. Yet there isn’t a global fund for diarrhea. All politicians would like an airport or a train station named after them but not a sewage plant.”

³² Go to Table 2.1. Notice that contaminated drinking water and untreated human waste are major human health threats.

³³ Household water treatment and safe storage. *World Health Organization*, 2009, http://www.who.int/household_water/en/.

Deliberately polluting surface waters

Why deliberately pollute water with human waste?

Those in developed countries take for granted toilets connected to an underground pipe system with sewage transported to a facility for treatment, disinfection, and finally released to receiving waters. However, some find it strange to deliberately pollute receiving waters with human waste, albeit treated. Indeed, US President Teddy Roosevelt said 100 years ago that “civilized people ought to know how to dispose of the sewage in some other way than putting it into the drinking water.” Such disposal raises a number of problems:

- Dealing with the sludge produced by wastewater treatment.
- Flush toilets consume significant quantities of water, although more efficient toilets are increasingly used.
- Pharmaceutical chemicals and their metabolites enter wastewater in feces and urine. Many are not removed by treatment systems. Hormones and antibiotics pose particular concerns.
- Wastewater treatment plants discharge reactive nitrogen and phosphorus.
- As human populations grow, so do the problems associated with treating increasing quantities of human waste.

Alternative toilets

There are alternative means to handle human waste, but none are widely used. ▪ Electric or gas-fired incinerating toilets³⁴ incinerate waste products deposited in a holding tank; the ash can be disposed of in the trash. However, it adds to energy usage and destroys useful nutrients and organic matter. ▪ Composting toilets³⁵ can be used inside or outside, but require some maintenance and a system to disperse odors. In some composting toilets, the underlying compost chamber is solar or electrically heated to assure that microbial action continues regardless of season. These toilets are used most often in isolated locations.

Treating sewage as a valuable resource

- Consider. phosphorus is now produced from mining phosphate rock, an increasingly limited resource,³⁶ and mining phosphorus is often environmentally destructive.

³⁴ Incinerating toilets. Water efficiency technology fact sheet. *US EPA, Office of Water*, September, 1999, <http://www.epa.gov/owm/mtb/incinera.pdf>.

³⁵ Composting toilets. water efficiency technology fact sheet. *US EPA, Office of Water*, September, 1999, <http://www.epa.gov/owm/mtb/comp.pdf>.

³⁶ Phosphate recovery. *Natural History Museum*, September–October, 1998, <http://www.nhm.ac.uk/research-curation/research/projects/phosphate-recovery/p&k217/steen.htm>.

Phosphate rock is high in cadmium, a heavy metal taken up by plants. (2) Manufacturing nitrogen fertilizer is an energy-intensive process, which converts (fixes) atmospheric nitrogen into reactive nitrogen.

- Also consider: urine is an especially rich source of nitrogen, phosphorus and potassium – the three main ingredients of fertilizer. The urine cannot be used separately with current sewage systems because urine and feces are mixed. ▪ To address these issues, the Swiss developed a technology to separate urine from feces; only feces being carried to a central plant. This uses 80% less water than that needed to flush even a water-saving toilet. If this technology was used, wastewater treatment plants would be small and less sludge produced, and reactive nitrogen and phosphorus would not be released to waterways.
- Urine could be temporarily stored and separately collected. After collecting and sterilizing the urine and removing pollutants and odor, a rich fertilizer would be left. And urine is a renewable resource. Homeowners would use less water.

However, setting up a new system would be very expensive, which would deter most communities from considering this scheme at least for the present.

Ecological sanitation^{37,38}

The Chinese have used human excreta as fertilizer for thousands of years. Many Chinese still do. However, some Chinese (and others) use *ecological sanitation*, collecting urine and feces separately for use as fertilizers. This can be done safely. The latrine includes a structure sitting over a raised sealed vault, which diverts urine and feces into two separate chambers within a vault below. Urine is sterile as it comes from the body and only becomes contaminated outside the urethra. The urine, after dilution with water can be used immediately to fertilize crops. The feces remain in their separate chamber for a number of months to allow pathogens to die; thereafter it can be handled safely and applied to crops. It is not so rich a source of nutrients as urine, but is rich in organic matter and serves as a soil amendment. Having a sealed vault prevents groundwater pollution. ▪ A similar system is used in Sweden by over 100 000 people in Sweden, a developed country; they call it urine diversion³⁹ or NoMix. The urine is given to farmers for use, after dilution, on fields. Decent sanitation for the billions without it has now become a subject of intensive study and work. At the First International Conference on Ecological Sanitation in 2001,⁴⁰ the system that developed countries primarily use is seen as “in the long term an unsustainable sanitation model” even for rich countries: there is a great need for “safe and efficient no-flush sanitation systems” in well-to-do countries too. ▪ Meanwhile, in less-developed countries even a

³⁷ George, R. Wasted waste ecological sanitation. *International Herald Tribune*, February 27, 2009, <https://www.istockanalyst.com/article/viewiStockNews/articleid/3075874>.

³⁸ Ecological sanitation. *Wikipedia*, January 23, 2009, http://en.wikipedia.org/wiki/Ecological_sanitation. This article introduces not just the two chamber toilet described here, but other ecologically viable alternatives as well.

³⁹ George, R. Wasted waste ecological sanitation. *International Herald Tribune*, February 27, 2009, <http://www.istockanalyst.com/article/viewiStockNews/articleid/3075874>.

⁴⁰ Report on First International Conference on Ecological Sanitation, Nanning, China, November 5–8, 2001, http://www.ecosanres.org/pdf_files/Nanning_Conf_report_final.pdf.

simple pit latrine is better than streets, gutters, or bushes. Latrines often have strong odors and flies, but a ventilated and sheltered one allows odors to escape, prevents flies from entering, and provides privacy. Getting such latrines to the many millions without them could fulfill a major need while reducing pollution. At the same time, there is the related need for enough water so people can wash their hands.

SECTION III

Reducing pathogens in drinking water of less-developed countries

It would cost an estimated \$68 billion worldwide and a 10-year effort to provide clean drinking water to all in the world who need it. This is about 1% of the amount that the world spends on military expenditures. In 1992, *Agenda 21* that emerged from the Earth Summit in Rio de Janeiro in 1992 spelled out universal access to safe drinking water as a goal. Subsequent efforts had partial success in increasing access to clean drinking water. However, population growth and lack of adequate funding has left at least 1.1 billion people without clean drinking water at the beginning of the twenty-first century, and 2.4 billion without adequate sanitary facilities. ■ At the 2002 World Summit in Johannesburg, 10 years after Rio, the world's nations again made commitments. They pledged that by 2015, they will half the proportion of people without access to safe drinking water, and half the proportion of people who do not have access to basic sanitation. Unfortunately, especially in sub-Saharan Africa it appears increasingly doubtful that they will succeed by 2015.

Point-of-use methods to purify drinking water

Especially in cities there is a great need for clean inexpensive water that is directly piped into homes after being treated at a central facility. At the same time, there is ongoing research and implementation of *POU* (point of use) purification of drinking water. In 2007, the Bill and Melinda Gates Foundation granted \$17 million to further the development of simple POU water treatments. In return, they want a determination as to which devices were worth being mass produced and knowledge of how to market them. Several devices and chemical approaches are described below. In all the methods, the water may become contaminated again so it is necessary to maintain disinfection.

- Ceramic filter⁴¹ (fired clay filter): the water to be purified is allowed to percolate through the filter, which can be made from local materials, and sold for \$5–15. It is already in use

⁴¹ Lubick, N. Ceramic filter makes water treatment easy. *Environmental Science & Technology*, **42**(3), February 1, 2008, 650–651.

in a number of locales. It can remove 98% or more of *Escherichia coli* from the water; if coated with a fine layer of silver it can remove 100%.

- **PUR⁴²** (Purifier of Water) is a well regarded POU treatment developed by Procter & Gamble working with the US CDC. It is a powder containing calcium hypochlorite as disinfectant. Iron sulfate is the flocculating agent, which aggregates the solids in the water (dirt, organic matter, etc.) into a floc. The floc is filtered out of the water through a cotton cloth leaving purified water behind. PUR is sold in individual packets, each treating 2.6 gallons (10 l) of water. It cannot be produced locally. Initially Procter & Gamble intended to break even in terms of cost. When that proved impossible, it started giving the packets away or selling them at about a third of cost.
- **Solar treatment⁴³** can be simple and cheap. The easiest method is to fill transparent plastic bottles (PET, polyethylene terephthalate bottles) with water, and place them on a black-painted roof or a roof with a piece of dark roofing underneath the bottles. The water must not be turbid. To assure disinfection – by solar rays and by heat – the bottles are left all day (or two days under a cloudy sky). A chlorine-containing tablet can be added to maintain disinfection. One Tanzanian village woman commented, “We no longer suffer from stomach illness.” She is also grateful there is no longer a need to collect firewood, start a fire, and boil the water.
- **Safe Water Solution (SWS)⁴⁴** was developed by the US CDC. It is a bottle of a chlorine-containing solution, which can be produced locally. It provides clean water for a family of six for about a penny a day. First the water is treated with the SWS (dilute sodium hypochlorite). Subsequently, as with other POU methods, the disinfected water must be stored in a way that makes it unlikely to become re-contaminated. Like solar treatment, it cannot treat turbid water well. Also, certain protozoan cysts resist the chlorine.
- **Water Treatment Tablets** Use of these tablets is a variation on SWS. The tablets are very inexpensive calcium hypochlorite tablets that cost about a half cent and treat 5.3 gallons (20 L) of water.⁴⁵ Tablets are more easily transported, stored, and have a longer shelf life than SWS.

⁴² (1) Amato, I. Making troubled waters potable. *Chemical & Engineering News*, **84**(16), April 17, 2006, 3940. (2) Short, P. L. Keeping it clean. *Chemical & Engineering News*, **85**(17), April 23, 2007, 13–20, <http://pubs.acs.org/cen/coverstory/85/8517cover.html>. This article describes a number of ways of purifying water, including the removal of arsenic.

⁴³ (1) Hasslberger, S. Low-tech solar water purification: it works. *Solar Water Disinfection*, March 24 2006, http://www.newmediaexplorer.org/sepp/2006/03/24/lowtech_solar_water_purification_it_works.htm. This is a POU method for water treatment at the household level. (2) Migration of organic components from polyethylene terephthalate bottles to water. *SANDEC*, Report 429670, June 20, 2003, http://www.sodis.ch/files/Report_EMPA.pdf. The study found that levels of plasticizers were no higher than in water not exposed to plastic.

⁴⁴ Best practices in social marketing, a safe water solution for household water treatment: lessons learned. *Population Services International Field Programs*, March, 2007, <http://www.ehproject.org/PDF/ehkm/LessonsLearnedFinal.pdf>. This project was supported by the US Agency for International Development and others involved in developing safe water programs in developing countries. This *Safe Water System* (SWS) for household water treatment (and subsequent safe storage) was originally designed in response to cholera outbreaks in Latin America. The use of a chlorine solution ensures that water will remain disinfected.

⁴⁵ The web site <http://www.ehproject.org/PDF/ehkm/LessonsLearnedFinal.pdf> focuses on treating water with a chlorine solution. However, Population Services International also works with a manufacturer of chlorine tablets.

- Commercial products These are available on the web for campers, hikers, etc.⁴⁶

The basics of POU

An overview of several methods is found at a WHO website showing the four basic steps in purifying water.⁴⁷ As you examine Figure 10.3, compare it with Table 10.3. Notice the similarities, and notice that the fourth step in Figure 10.3 is disinfection. Making it the last step heightens the chances that the water will still be disinfected when drunk. Nonetheless, once purified, the water must be protected from re-contamination. The International Network to Promote Household Water Treatment and Safe Storage, and WaterAid⁴⁸ is among those working with water storage practices. Those who promote POU programs also campaign for proper hygiene, including hand-washing with soap and water-use practices. All these POU products and methods cut diarrhea significantly, but work remains to determine by what percentage in each case. For example, Johns Hopkins researchers found that people using PUR were one-eighth as likely to contract diarrhea as those drinking untreated water. Even better, children under 5 were one-twelfth as likely to get diarrhea.⁴⁹

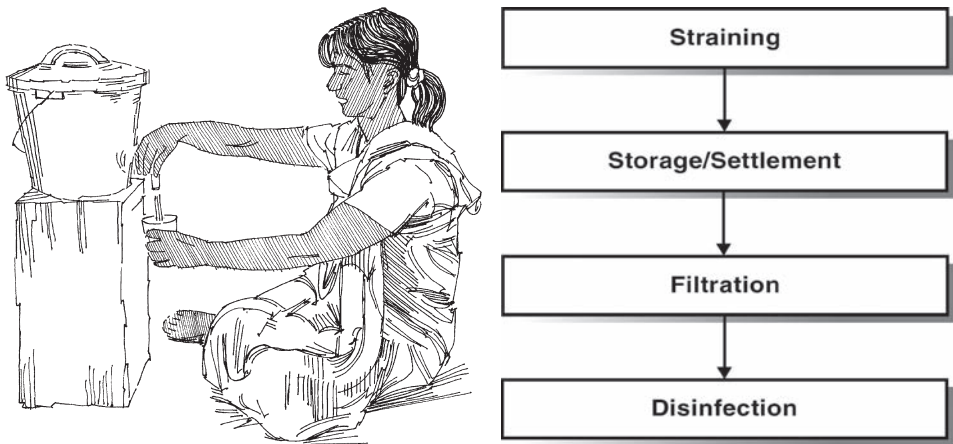


Figure 10.3

Steps in point-of-use water purification. Credit: UN World Health Organization

⁴⁶ See, for example, Water Treatment Tablets & Purification Kits at <http://www.safetycentral.com/wattreattab.html>.

⁴⁷ Emergency treatment of drinking water at point-of-use (POU), technical note for emergencies No. 5. *UN World Health Organization*, July 1, 2005, http://www.who.int/household_water/resources/emergencies.pdf.

⁴⁸ (1) Household water treatment and safe storage. *WHO*, http://www.who.int/household_water/en/. (2) Combating waterborne disease at the household level. *The International Network to Promote Household Water Treatment and Safe Storage*, http://www.who.int/household_water/advocacy/network.pdf. (3) WaterAid, <http://www.wateraid.org/uk/>.

⁴⁹ Montgomery, M. A. and Elimelech, M. Water and sanitation in developing countries: millions suffer from preventable illnesses and die every year. *Environmental Science & Technology*, **41**(1) January 1, 2007, 17–24.

Questions 10.2

1. Latin America had been free of cholera (caused by the bacterium *Vibrio cholera*) for a hundred years. Then, in about 1991, Peru's capital city, Lima ceased chlorinating the city's water after reading an US EPA report indicating that the DBPs left by chlorination could cause cancer. Lima's water supply was later contaminated by *Vibrio cholera*. Over the years hundreds of thousands became ill with cholera in Latin America and about 10 000 died. Cholera is now endemic to that region. Think back to risk assessment described in Chapter 4 before answering the question: how does the risk of DBPs differ from the risk of impure drinking water?
2. What is the difference between a bore well and a dug well? Which is most likely to have clean water? You may need to go to the web to answer this question.
3. The "arsenic eaters" were Austrian smugglers who found that arsenic increased their physical endurance during difficult journeys across high mountains.⁵⁰ They began by ingesting about 10 mg twice a week, eating it with bacon to increase absorption into their bodies. As their bodies acclimated, they ended up eating doses perhaps 40-fold greater than those, which could kill sensitive people. With this information in mind, consider Bangladesh. People here are ingesting low doses of arsenic compared to the arsenic eaters. What are possible reasons for the fact that they don't adapt in the same way as the Austrian smugglers?

Delving deeper

1. Think about how water is treated to make it safe for drinking. Visit or speak with your local drinking water treatment plant. Are there specific contaminants that are of concern locally? How are they removed? What concerns do you have at present regarding the status of drinking water in your community? What future concerns do you or your local treatment plant have about safe drinking water and enough of it? Do a presentation to your class or to a local school.
2. Go to "Safe Drinking Water Is Essential," www.drinking-water.org. View documentaries on how households in poor countries without tap water can purify their own water. Assume you are working on a project to provide safe drinking water. How would you go about coming to a decision on an effective solution?

Further reading

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“Pollution is a symbol of bad design.”

William McDonough

Municipal solid waste (MSW) is the waste we know best. However, MSW is only one among many wastes: construction and demolition debris, municipal sludge, combustion ash, mining and drilling debris, agricultural wastes, industrial process wastes including sludge, hazardous waste, and others. The United States alone produces more than 12 *billion* tons (10.9 billion tonnes) a year of waste.¹ MSW, which includes home, business, and institutional waste, is less than 3% of that great stream, but it is directly important to us – its composition and amount is the result of our behavior. Moreover, move back one step – look at the whole life cycle of each product – and we observe much more than 3%. We see the extractors of raw materials, the manufacturers and businesses producing, selling and transporting the products that eventually end up as MSW. We begin to see many more of those billions of pounds of waste.²

Section I of Chapter 11 asks why we generate so much waste. It examines the composition of MSW and why it is of concern. Section II looks at the waste management hierarchy (WMH). Source reduction (pollution prevention) sits atop the WMH. Section III examines various means of reducing waste including environmentally preferable buying, extended producer responsibility and design for the environment. It also looks at what is happening in our oceans as we continue to irresponsibly dispose of waste, especially plastics. The section also examines reuse – and its similarity to source reduction – and the recycling of both common and less common materials. Incineration and landfilling are also overviewed. Section IV moves onto the major problems that MSW poses in less-developed and impoverished societies. It ends with the story of a city, Curitiba, Brazil.

SECTION I

Why do we generate so much waste?

As one illustration of why we and our society produce so much waste, consider a metal. To obtain it, an ore is mined. However, the metal is but a small portion of an ore, so most of the

¹ Wastes, A-Z subject index. *US EPA*, February 26, 2009, <http://www.epa.gov/epawaste/topics.htm>.

² Wastes: information resources (with links to other information resources). *US EPA*, February 18, 2009, <http://www.epa.gov/epawaste/inforesources/index.htm>.

Table 11.1 How much waste is produced when producing chemical products?

Industry	Tons of products/year ^a	Waste/product (by weight)
Oil refining	10 ⁶ –10 ⁸	~0.1
Bulk chemicals	10 ⁴ –10 ⁶	<1–5
Fine chemicals	10 ² –10 ⁴	5–50
Pharmaceuticals	10 ⁰ –10 ³	25–>100

^a 1 ton is equivalent to 0.9 tonnes

Source: Sheldon, R. A. *ChemTech*, March 1994, 38; Poliakoff, *et al.*, *Science*, August 2, 2002, 807–810.

mined material becomes waste. And the *overburden* – soil disturbed during mining – becomes waste too, as does the disturbed rock. Not properly handled, these are damaging materials. ▪ Refining and smelting of the ore produce more waste. So does manufacturing a product from the refined metal, and the product's recycling or disposal. ▪ Or, consider the book in front of you. Starting in the forest, it produced waste when the wood was harvested to make it, when the wood was transformed into paper, and yet more when the book was printed. ▪ Or, think perhaps about a head of lettuce. You discard its outer leaves. But before you bought it, other lettuce waste was produced by the farmer and supplied to the grocery store. A food waste can be composted. But often this does not happen. ▪ For a sense of the amount of waste that producing a product generates, look at chemical products (Table 11.1). Oil refining produces a great deal of waste, but – especially as compared to the mining mentioned above – it produces little waste because almost all petroleum is refined into burnable products. Only a few percent of the oil is used to manufacture chemicals. However, *bulk chemicals*, those produced in large quantities such as benzene typically require only a few steps to make, so (although the tons of waste produced per ton of product is much higher than in oil refining) the total amount produced is relatively low. Notice that fine chemicals and pharmaceuticals have a higher waste/product ratio. This is because it takes more steps to make them, and each step produces waste.

And what happens to a product such as a book or television set, at the end of its useful life? Very often it becomes waste. Recycling the product is preferred, but that produces waste too. ▪ Wealthy societies produce much more waste per person, but less-developed countries produce staggering amounts too: even though less waste per person is produced, populations in many of these cities are huge and waste management practices are poor. Thus, discarded wastes are often a major problem. See Figures 1.4 Poverty and pollution and 12.3. ▪ China's state media reported that, by 2020 – with 860 million people living in cities – it would produce 400 million tons (3.63 million tonnes) a year of garbage – as much as the whole world produced in 1997.³ And most now goes to landfills contributing to air and water pollution. China is calling for better waste management and public education.

³ China faces ticking rubbish time bomb. *Reuters*, January 10, 2007, <http://www.planetark.org/dailynewsstory.cfm/newsid/39748/story.htm>.

Municipal solid waste^{4,5}

You may not notice how you contribute to air pollution. You may likewise casually send the contaminated water you produce down drains and toilets. It's more difficult to ignore the solid waste that you produce. At a minimum you must take it to a curbside or to your garbage can. Historically, trash was the bane of many cities, as people dumped anything including bodily wastes onto streets. Solid waste still poses many problems.⁶

What is in MSW and who produces it?⁷

Household waste contains anything that we choose to discard, including still-usable and recyclable items: waste food, papers and newspapers, packaging, bottles, metal cans, batteries, grass clippings and other yard waste, clothing, furniture and appliances, paint and other discarded household chemicals (Figure 11.1); the "other" category includes appliances (white goods), furniture, batteries, and household hazardous waste (HHW). HHW includes residual paints, oily products such as automotive maintenance products, and pesticides. For many years paper has been the largest proportion of MSW in the United States, about 34% by weight in 2006. This figure shows only what the US federal government views as MSW. Some states also consider construction and demolition debris to be MSW, where it equals about 12% by weight. And some communities consider other wastes as MSW, which may include sludge from drinking-water treatment and wastewater treatment plants, septic tank sludge, medical and slaughterhouse waste, and fast-food grease.

Households are only one contributor to MSW. Others are institutions such as hospitals, government offices, schools, and prisons; and commercial businesses including restaurants, grocery stores, and offices. Industries too generate MSW, but industrial process wastes are considered and handled separately (Chapter 12).

Why does MSW concern us?

Almost any garbage is unpleasant. It has unpleasant odors. Diapers and other sanitary items have microorganisms, sometimes pathogens. So do rotting food and yard wastes. ■ Although HHW is only a small part of MSW, it can pose problems such as catching on fire, or injuring the skin or eyes of workers coming in contact with it, or breathing its fumes. However, a material need not be hazardous to present problems.

⁴ Municipal solid waste. *US EPA*, November 13, 2008, <http://www.epa.gov/epawaste/nonhaz/municipal/index.htm>.

⁵ (1) Zawadzinski, J. New York Author trails her trash in "Garbage Land." *Reuters*, July 13, 2005, <http://www.planetark.com.au/dailynewsstory.cfm/newsid/31629/newsDate/13-Jul-2005/story.htm>. (2) Hazen, D. The hidden life of garbage. *AlterNet*, October 31, 2005, <http://www.alternet.org/story/27456/>.

⁶ Miller, C. Profiles in garbage for 2007. *WasteAge*, December, 2008, http://wasteage.com/Landfill_Management/profiles_in_garbage_msw_2007_1208/.

⁷ Municipal solid waste generation, recycling, and disposal in the United States: facts and figures for 2006. *US EPA*, November 2007, <http://www.postcom.org/eco/sls/docs/USEPA-2006%20MSW%20Facts%20&%20Figures.pdf>.

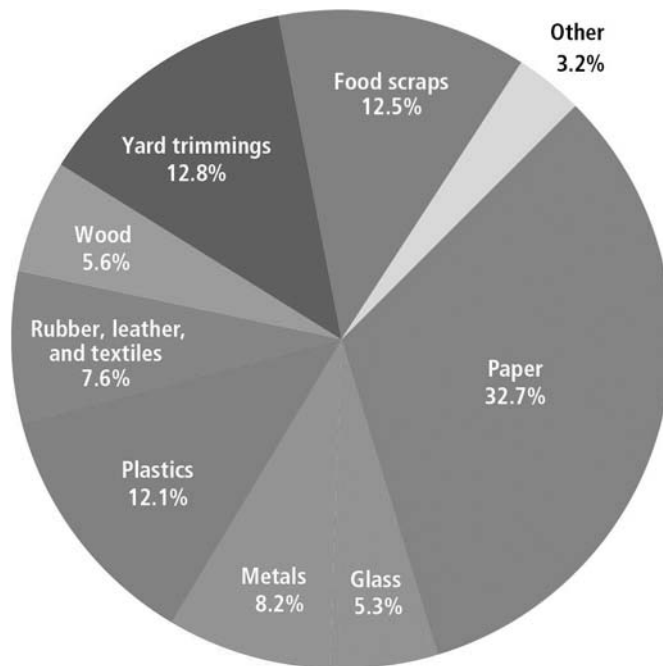


Figure 11.1 Materials in US MSW (2007) (254 million tons or 230 million tonnes before recycling). Credit: US EPA

- Large quantities of packaging are generated: its composition may make it difficult to recycle, or prevent it from biodegrading. And if it contains even trace amounts of hazardous metals, expensive controls are necessary to prevent metal emissions if it is incinerated.
- Some MSW, once disposed of in a landfill may last indefinitely. Even dumped in the open environment where there is sunlight, heat, and water, many items – especially plastics – are long lived.
- Even if MSW had no other characteristic of concern, the quantity generated creates difficulties. The United States alone with its 100-million households generated 251 million tons (228 million tonnes) of MSW in 2006; of this, Americans recycled only 61 million tons (55.3 million tonnes) (excluding composting). Compare this to 1960, when America produced only 88 million tons (79.8 million tonnes) a year of MSW, about 35% of the 2006 amount.⁸ See Figure 11.2. Population increase is one part of the problem: in 1960, the average person generated only 2.7 pounds (1.2 kg) MSW a day as compared to 4.6 pounds (2.1 kg) in 2006. In earlier times most families lived in rural locations, and household waste was not a major problem. If every household today had to manage its own garbage, a crisis would quickly develop: a household of four creates 18.4 pounds per day (8.3 kg) or 6716 pounds (3046 kg) a year. And waste management – whether by incineration, landfilling, or recycling – is expensive. The amount American communities pay for waste management is second or third only to spending on education and police protection.

⁸ Municipal solid waste, generation, recycling and disposal in the US: facts and figures for 2007. *US EPA*, November, 2008. <http://www.epa.gov/osw/nonhaz/municipal/pubs/msw07-fs.pdf>.

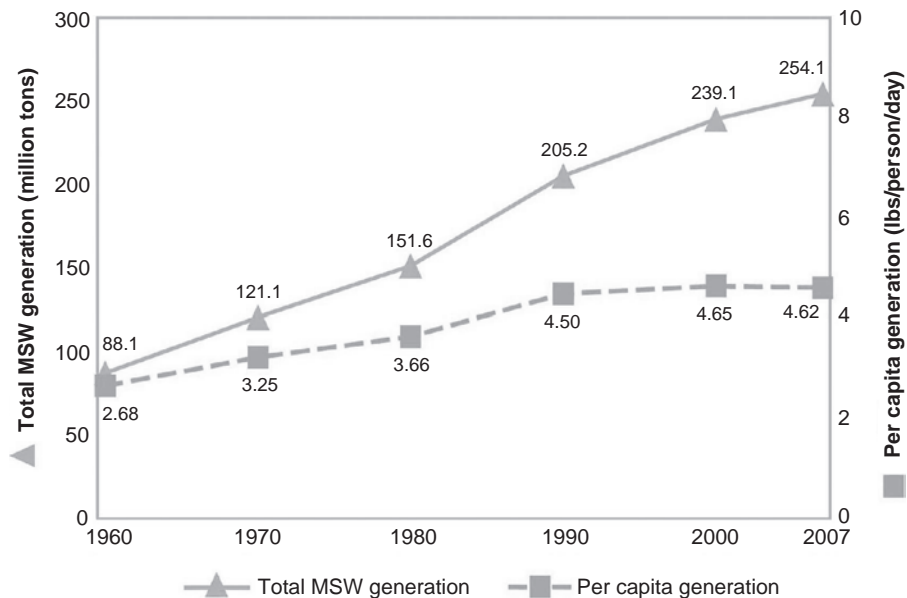


Figure 11.2

MSW generation in the US, total and per capita (1960–2007). Credit: US EPA

SECTION II

MSW and the waste management hierarchy⁹

In 1976 the United States passed the Resource Conservation and Recovery Act (RCRA), a mammoth complicated law, which has been extensively updated over the years. RCRA regulates all the wastes noted above including MSW. As its name implies, RCRA's purpose was to stimulate communities to manage waste in an environmentally sound way and to recover materials and energy. Recall the waste management hierarchy (Figure 2.2). The hierarchy is sometimes represented differently for solid waste management, see Figure 11.3. The top of the hierarchy is waste prevention – source reduction and reuse (most preferred). Source reduction is pollution prevention. Composting and recycling is the next step down – composting organic materials is considered recycling. Treatment (not shown here) is often considered the next step down. Combustion of MSW is often considered treatment. Treatment serves two purposes, either reducing waste volume or reducing its toxicity. The bottom of the MSW pyramid shown here is landfilling or combustion.

⁹ Reduce, reuse, and recycle. *US EPA*, February 18, 2009. <http://www.epa.gov/epawaste/conserve/tmr/index.htm>.



Figure 11.3

Solid waste management hierarchy. Credit: US EPA

Reducing MSW by¹⁰ waste prevention (P^2 or source reduction)

P^2 is source reduction, and conserves resources. For MSW, source reduction means that a lowered volume of waste is generated. Illustrations:

- Concentrated detergent When manufacturers began to design laundry detergents that were more-concentrated than earlier detergents, this led to a cascade of results. The concentrated product weighs less, its volume is less, and fewer resources go into manufacturing it. Resources are conserved. Resources are further conserved because less packaging is needed and less packaging waste is produced. And less energy is needed to transport a given amount of cleaning power, so energy is conserved with fewer pollutants emitted. Moreover, because the consumer needs less of the concentrated detergent, less polluted water goes to the sewer.
- Light-weight containers While maintaining container strength, manufacturers from the late 1970s to 1993 reduced the weight of plastic soda bottles by 25%, the weight of glass bottles 31%, and of aluminum containers even more. This *light-weighting* has all the advantages just noted for concentrated detergents. There are resource and energy savings, less pollution produced, and less MSW generated.
- Photocopying both sides of paper This cuts the amount of paper used in half, thus halving paper waste, and has other of the advantages just noted. And it raises another important point: we could not photocopy both sides of the paper if photocopiers were not designed to make such copying possible.

These P^2 examples all involved a change in product design: *design for the environment* (DfE). DfE is a major means to conserve natural resources, and promote reuse and recycling. DfE will come up frequently below.

¹⁰ Pollution prevention and recycling links. *California Department of Environmental Control*, 2007, <http://www.dtsc.ca.gov/InformationResources/resources.cfm#PPR> (look under pollution prevention and recycling).

Reducing hazardous metal levels in products

Waste prevention and DfE examples were given above that can reduce the volume of MSW. How can we reduce its toxicity? Here we will consider hazardous metals. Many hazardous metals such as lead or chromium are found, albeit in low amounts in a number of products. Because metals don't degrade, even small amounts can build up over time.

- Printing Newspaper and magazine printers traditionally used lead ink, and for colored sections hazardous metal pigments. As soy bean and organic inks were developed, the use of metals has diminished.
- Packaging and plastics Metals served useful functions in packaging and plastics, and could not arbitrarily be eliminated. But, when a search for alternatives was undertaken, it was possible to find relatively benign organic molecules to serve equivalent functions, and reduce hazardous metal content in these products.
- Lead and mercury in products Major reductions have been made in the content of the hazardous metals, lead and mercury in many products (Chapter 15).

Reducing food waste

Remember that food waste is also part of MSW. Figure 11.1 shows food scraps as 12.5% of MSW. Food is thrown away in homes, grocery stores, and restaurants, often edible food, not food waste.¹¹ In New York City and other municipalities, organizations have begun to pick up leftover food from restaurants including whole untouched pans of food. These are taken directly to places serving the needy or are frozen. For food that cannot be consumed by humans, some is offered to farmers for livestock consumption. Another means to reduce food wastage is to eliminate trays in school and college cafeterias: this leads to students taking less food. At the very least, waste food can be composted; see Composting and biotreatment below.

Box 11.1

Reducing waste through environmentally preferable purchasing¹²

*Environmentally preferable products*¹³ are those that have been analyzed and selected on the basis of having lesser impacts on human health and the environment as compared to others that serve the same purpose. Buying them represents P². The title of one article expresses the enthusiasm of those espousing this approach: "Buying Green, Harnessing the Incredible

¹¹ Martin, S. One country's scraps, another country's meal. *New York Times*, May 18, 2008, <http://www.nytimes.com/2008/05/18/weekinreview/18martin.html>.

¹² Good stuff: a behind-the-scenes guide to the things we buy. *Worldwatch Institute*, 2008, <http://www.worldwatch.org/taxonomy/term/44>.

¹³ (1) Environmentally preferable purchasing. *US EPA*, November 7, 2007, <http://www.epa.gov/opptintr/epp/>. (2) The environmentally preferable purchasing guide. *Rethink Recycling.com*, April 25, 2008, <http://www.greenguardian.com/government/eppg> (guidelines for goods and services, paper products, printing services, office machines, motor-vehicle products, cleaning products, carpets, grounds and building maintenance, including integrated pest management, and many others).

Procurement Power of Governments, Hospitals, Colleges and America's Biggest Corporations to Protect the Environment." In the United States, EPA has developed guidelines to identify environmentally preferable products, and federal agencies are asked to give buying preference to these. The expectation is that government buying power will drive change: businesses wanting to sell to government agencies will modify their products to fulfill the guidelines. State and municipal agencies, universities and colleges can also use the guidelines. The EPA developed the following symbols to assist product identification.

Less hazardous Buy a product with the lowest level of hazard able to do the job. This is indicated on the label. *Caution* refers to mild to moderate hazard. *Warning* refers to moderate hazard. *Danger* is the highest hazard (corrosive, extremely flammable, or highly toxic). *Poison* is also at the highest level, but refers specifically to a toxicity hazard. If low-hazard products are not available, or one must buy the more hazardous product, follow all precautions on the label and use the least amount possible for the job. Use the product up entirely to avoid creating HHW.

Conserves energy¹⁴ Buy energy efficient products. In the United States the *Energy Star* label identifies these products, which also save money on energy bills.

Recycled content If the label says *pre-consumer* content, this indicates that manufacturer scrap was recycled. *Post-consumer* is materials actually used by consumers, such as paper, cans, glass, or plastic, and then collected after use and recycled.

Prevents waste(P²) Buy the least amount of material possible to accomplish a task. When possible buy a product that is repairable, durable, refillable, or able to be reused.

Low volatile organic compounds Examine labels to find low-VOC products. VOCs evaporate from many consumer products including office equipment, adhesives, carpeting, upholstery, manufactured wood products, paints, solvents, pesticides, and cleaning products. Because they can concentrate in indoor air, they are of special concern in offices and homes.

Conserve Water Choose water-conserving products and services such as automatic flushers and low-flow faucets and toilets. These also save money on water and sewer bills.

End of life management

What happens to a product after we use it? Some materials cannot go in the trash because they are hazardous in some way and therefore need separate – and sometimes expensive – special management. Some products are more easily recycled than others that do the same job. Making wiser buying choices can prevent a disposal concern at the end of a product's useful life, keep hazardous materials out of the environment, and expand options for recycling and reuse.

End of life

What happens to this product at the end of its useful life? Is it recyclable? If so, is it likely to be recycled? Does the manufacturer have a *take back* policy, i.e., will it take it back after its useful life is over? Might it be a hazardous waste that needs special handling?

¹⁴ States and cities follow federal lead in energy-efficient purchasing. *EETD Newsletter*, Winter 2004, 7, <http://eetdnews.lbl.gov/nl16/eetd-nl16-4-estar.html>.

Some states and cities are more ambitious than the federal government. Massachusetts and the city of Santa Monica, California have vigorously pursued environmentally-preferable products; so have Minnesota's Twin Cities. Such products can save money if they conserve energy or water. In the workplace, using less-hazardous products can reduce liability, improve worker safety, and lower disposal costs. Products that are reusable, refillable, more durable, or can be repaired are more cost-effective in the long run.

Other "green procurement" efforts¹⁵

Some European countries and Canada place green labels on products to denote those judged environmentally preferable. China's government started a "green procurement" program in 2007 applicable to both central and provincial governments. It specifies the recommended products, which carry the China Environmental Label (Figure 11.4). Government purchasers must buy products from the list when available; otherwise they may not get reimbursement. China's environmental agency, SEPA hopes that the government "could become the real driving force for industry to develop green technology."

Individual action

Buying environmentally preferable products: as an individual you can choose to buy durable goods, or to buy a television set or appliance that can be repaired. Consider EPA guidelines when purchasing a car. Choose one with good gas mileage and maintain it well to reduce gasoline consumption, and reduce pollutant emissions from the vehicle. A clothing drier is a major energy user in the home, so purchase an energy-efficient model. Small steps are important. If you can use it up, buy a product in bulk because that has less packaging per unit of product. Take fabric bags to go shopping rather than accepting new bags. Paper bags too can often be reused many times. This saves resources and prevents the pollution used to manufacture new products. There are hundreds of ways to reduce energy and water use, and to produce less household waste. Multiplied by hundreds of millions, the net impact is indeed significant. But be aware that guidelines are not absolute. There are always instances where a product preferable in one or more respects is less desirable in others. The individual buyer must still make judgments. Recycled-content products save energy and resources, while also keeping waste out of landfills and incinerators. Recycled-content products can be made with post-consumer content, pre-consumer content, or a mix of both. Products made with post-consumer recycled content support our recycling programs at home and at work. If people do not buy products with post-consumer recycled content, manufacturers will no longer want the paper, cans, glass, or plastic we separate from trash. Pre-consumer content comes primarily from manufacturer scrap, and as such does not directly support such recycling efforts.

¹⁵ ¹ Li, L. Chinese government to start "Buying Green." *Worldwatch Institute*, November 30, 2006, <http://www.worldwatch.org/node/4760>.



Figure 11.4

China's environmentally preferable label. Source: Worldwatch

Reuse of component parts of products – remanufacturing

Design for disassembly (DfD) is similar to DfE except designers focus on designing efficient disassembly into a product so that its reusable components can be quickly obtained. At the end of one of its lives, a machine, such as a photocopier, can be disassembled into reusable and recyclable parts. These are examined, refurbished, and become parts of newly assembled products that meet the same standards as a new product – it has been *remanufactured*.

- Caterpillar, Inc. refers to its remanufactured products as Cat Reman. Whereas previously 70% of Caterpillar's costs when making new machines were for raw materials, those costs are largely eliminated by refurbishing and reusing old machine parts.¹⁶ The savings for companies that use remanufacturing is as much as 70%. This makes remanufacturing beneficial environmentally and economically.
- Seventy to 90% of auto parts are remanufactured. When you replace an alternator, clutch, or brake-caliper in your car, the new part was probably remanufactured from a previously-discarded one. The part is inspected, cleaned, and rebuilt to specifications. While reducing pollution, this also reduces the need for energy and labor to half that required for a new part.
- Cell phones are very conducive to remanufacture: a Nokia cell phone can be disassembled in two minutes, and Nokia has a prototype, which can "pop" apart in seconds. Most of its parts, including a titanium-coated capacitor, can be used multiple times. Nokia phones also have enough gold that it would take the gold from only 200 phones to make a gold ring.

As these examples show, remanufacturing is especially feasible for metal products. This is fortunate because a number of metals are becoming harder to recover. The US Geological Survey (USGS) reports that, at the rates of current use, there is only enough economically recoverable lead left for 18 more years. This figure is 20 years for tin, 25 years for copper, 69 for bauxite (from which aluminum is extracted), and 64 years for iron (from which to manufacture steel). About 71% of steel is now recycled from scrap, and is found in almost all cars, 90% of household appliances, and 60% of cans.¹⁷ ■ Unfortunately, the US industries

¹⁶ Remanufacturing. *Caterpillar*, 2009, <http://www.cat.com/parts/remanufactured-products>

¹⁷ Rhodes, C. Metals shortages, September 16, 2008, <http://www.scitizen.com/stories/Future-Energies/2008/09/METALS-SHORTAGES-/>.

that make computers and other electronics have been much slower to act without a law requiring them to do so.¹⁸

Questions 11.1

Because of lack of education or of environmental awareness, we may overlook many opportunities to buy environmentally preferable products.

- (1) The United States with 4.5% of the world's population uses about half the world's detergent. Most people buy top-loading washers although front-loading machines require less detergent and less water; they then run the machines with less than full loads of clothes. (a) In addition to these examples, how else can clothing be kept clean with less detergent? (b) In addition to saving detergent, what are the other environmental advantages of front-loading machine?
- (2) How can we motivate individuals who can afford to buy larger models to buy smaller more energy-efficient refrigerators and cars?
- (3) The United States uses 30% of the world's paper production. Each year, a person consumes the equivalent of 670 copies of the daily New York Times. How can we use less paper without detracting from quality of life?
- (4) Box 11.1 provides instances of how individuals can lessen their environmental impacts by the purchasing decisions that they make. Provide examples of purchases that you think you yourself may begin to adopt. Which purchasing decisions seem too confusing or too much trouble to you?

Recycling¹⁹

Recycling may be lower on the WMH than P² or reuse (and remanufacturing), but it is vital. Its environmental benefits include saving resources, using less energy, and producing less pollution than making a product from virgin resources.²⁰ Recycling also provides jobs. About 8500 US curbside recycling programs existed in 2005. These serve over half the population, and 84% of US cities. Recyclables could be dropped off at 12 000 other sites. Materials collected include paper, steel (tin) and aluminum cans, glass containers, plastic containers (especially #1 and #2) and waste oil (Figure 11.5). Although the US recycling rate increased sharply in the years before 2000, it has since almost leveled off and in 2007 was only 32.5%. However, some cities, San Francisco is one, has a 69% recycling rate; this city does not ask citizens to separate recyclables, but collects them in a single stream which are later sorted in a facility that combines machine and human separators. One way the city

¹⁸ Slade, G. E-waste watch: why not a national law? *E The Environmental Magazine*, September, 2008, <http://www.emagazine.com/view/?3568>.

¹⁹ Granger, T. Eight ways to green your recycling. *Earth911.com*, February 18, 2008. This story is one of a series showcasing ways to increase ways of living with greater environmental awareness, <http://earth911.com/blog/2008/02/18/eight-ways-to-green-your-recycling/#panel-recycling-search>.

²⁰ The truth about recycling. *The Economist*, June 7, 2007

keeps the amount of trash down is through a pay-as-you throw system where the fees residents pay depend on the number of trash bins that they use.²¹ However, a German commenting on San Francisco's system pointed out that Germans are much more thorough.²² A number of other West Coast cities also have high recycling rates. ■ Incinerating or landfilling is costly to a community. However, recycling – excepting high-value materials like aluminum – is sometimes accused of being more costly still. New York City cancelled plastic and glass recycling programs because of cost, but as landfill costs went up, recycling of these was reinstituted and the city worked vigorously to cut costs. Many cities have saved on costs after buying, as did New York City, automatic sorting and processing machinery. Some coastal cities, New York is one, found that it pays to export recyclables to less-developed countries where their value is greater. Some cities pick up recyclables less often, but have found that residents, angered by the accumulating recyclables, recycled less. See Box 11.2 for the recycling of specific materials.

Box 11.2

Recycling of common materials

Also see Figure 11.5 and see Wastes quick finder, A-Z topics. *US EPA*. <http://www.epa.gov/epawaste/index.htm>

- Aluminum²³ In 2008, barely half of the aluminum cans used in the United States were recycled, this despite the fact that aluminum is a valuable metal, and recycling aluminum pays for itself. Moreover, the United States has only about 1% of the bauxite ore from which aluminum is recovered, so thrown-away cans could become an ongoing aluminum mine. Aluminum cans are also relatively easy to collect. Collecting aluminum foil, pie pans, lawn furniture, or aluminum used in siding, gutters, and window and door frames is more difficult, but can be done. Aluminum recycling has major environmental advantages – it uses up to 95% less energy than mining it from bauxite, and reduces air and water pollution about the same amount. Meanwhile, 3% of the world's electricity goes into making new aluminum cans and about a third of that electricity is generated from coal-burning power plants
- Steel cans Recycling steel cans reduces energy consumption about 60% compared to starting with raw materials. Both bauxite mining for aluminum and iron mining for steel can be highly polluting and also result in major land degradation in the area where mining occurs. These are also called tin cans because some are still tin coated.
- Paper Recycling paper can reduce energy use 40% as compared to making paper from new trees. In 1999, the paper industry recovered 45% of the paper and paperboard used in the United States. By 2001 paper recycling increased to 48%, close to the 50% goal the industry

²¹ Barringer, F. A city committed to recycling is ready for more. *The New York Times*, May 7, 2008, <http://www.nytimes.com/2008/05/07/us/07garbage.html>.

²² Amann, S. How one German views recycling in San Francisco: you have only just begun. *San Francisco Chronicle*, August 12, 2008, <http://www.sfgate.com/cgi-bin/article.cgi?f=c/a/2008/08/12/ED9Q1283C5.DTL>.

²³ The Good Earth Correlation Guide, 2001. Physical geology, Updated Internet Edition, 2001, <http://www.mhhe.com/earthsci/geology/plummer/information/olc/plummercorrelation.mhtml>.

had set for itself. Most recovered paper is post-consumer waste, not mill scraps. About half is old corrugated cardboard containers. By 2007 it recycled 56% and now has a goal of 60% by 2012. The 54.3 million tons (49.3 million tonnes) of paper recovered in 2007 amounts to more than 360 pounds (163 kg) for every American. Each percentage point gained represents enough paper to fill more than 14 000 railroad cars.²⁴ However, the higher the recycling rate, the greater the difficulty there is as most good-quality paper is already recovered. However, poorer-quality paper can be composted or incinerated for its energy.

- **Plastics**²⁵ The world produces 250 billion pounds (~113 billion kg) of plastic pellets a year. It is from these that all plastic products or plastic composite products are made from soft-drink bottles to medical equipment or cars. Plastic discards in US MSW were less than 1% by weight in 1960, but by 2006 they were 11.7%. See Box 11.3. Types of plastics included 14 million tons (12.7 million tonnes) as containers and packaging, over 6 million tons (5.4 million tonnes) as nondurable goods, and about 9 million tons (8.2 million tonnes) as durable goods. In the 11 US states in 2008 that charged deposits on beverage containers – plastic bottles and aluminum cans – recycling rates are higher than in states without deposits. Deposits are returned when the bottles are returned.²⁶ In states with deposits, more people save containers to get their money back; others add to their incomes by collecting plastic bottles and aluminum cans discarded by others. Some of the 11 states are working to increase the deposit charged; yet other states are introducing bills to start charging deposits. The average rate of recycling plastic bottles remains low (Figure 11.5). Only about 4% of plastics in the MSW stream are recycled; however, the figure for two specific plastics is higher. The rate for polyethylene terephthalate (PET) soft drink bottles was 31% in 2007, and recovery of HDPE milk and water bottles about 31%. Recycling the PET used to make soft drink bottles uses 47% less energy than making it from raw materials.
 - Recycling plastics poses challenges. One is collecting and separating multiple types of plastics. Another is recovering plastics from products more complicated than plastic bottles or other simple plastic products. An instance is the tens of millions of plastic casings on computers that are discarded in increasing quantities. It's even more difficult to recover plastic from composite products where plastic is only part of the composition. ▪ However, once discarded plastic has been collected and sorted, it is valuable and goes into products such as TyvekTM (disposable medical suits and insulation), fleece garments, plastic lumber, and water-repellent coatings for shipping boxes, and asphalt too. Compared to other products, plastics are often more durable, perform better, or weigh less than counterparts made from other materials. For example, plastic lumber can last much longer than real wood. Although valuable, businesses often cannot be assured of a dependable supply of used plastics. Moreover, the price that plastic recyclers pay varies with the price of oil. Most common plastics are thermoplastics; that is, they can be melted down and reshaped into new plastic products.

²⁴ US Paper recycling hits record high. *International Council of Forest and Paper Associations*, April, 2008, http://www.icfpa.org/media_center/press_releases/uSPaperRecyclingRecord.php.

²⁵ Wastes. Resource conservation: plastics. *US EPA*, <http://www.epa.gov/epawaste/conservation/materials/plastics.htm>.

²⁶ Miller, C. The bottle battle. *Waste Age*, June 1, 2007, http://wasteage.com/mag/waste_bottle_battle/index.html.

- Used oil²⁷ Of the 1.3 billion gallons (4.9 billion liters) of used oil generated each year in the United States, only 3.4% is refined into new automotive oil, whereas about 15% is illegally dumped into backyards, drains, or streams. In addition to the environmental impacts of this oil is the lost possibility of re-refining it into motor oil: 1 gallon (3.8 liters) of used motor oil provides 2.5 quarts (2.4 liters) of lubricating oil, the same amount as obtained from 42 gallons (159 liters) of crude oil. Most of the rest of used oil generated is collected with most used for industrial fuel or space heating.²⁸
- Glass Recycling glass saves energy, about 30%. About a quarter of glass containers are recycled.
- Electronics Although electronics are an increasing part of our waste stream, only a small portion is responsibly recycled. Beginning in 2007, European Union (EU) citizens began taking their used computers, iPods, radios, and other electronic waste to collection points. This was in response to the EU Waste Electrical and Electronic Equipment (WEEE) Directive, which requires producers in member states to finance electronic waste take-back programs; they must also treat the waste. Electronic waste has been increasing three times faster than MSW as a whole. It is expected that WEEE will encourage producers to practice DfE: design changes in their electronic products that make for easier disassembly, recycling, or reuse.
 - Another EU directive is also pushing DfE, the restriction of hazardous substances (RoHS) in electrical and electronic equipment. RoHS largely bans products containing lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and polybrominated diphenyl ethers.²⁹ Because these are found in electronic equipment, this directive will be another stimulus to DfE. In the United States, the EPA has formed partnerships with industry to promote safer electronics; this includes using safer chemicals.³⁰ Also in the United States, an increasing number of communities and states ban computers and TV monitors from landfills, which also exerts pressure on manufacturers. Electronics are not intrinsically hazardous. Yet the quantity of electronic waste and the way it is often dealt with can make it hazardous (See Chapter 12).
- Appliances Many millions of used appliances are discarded each year – air conditioners, dishwashers, dryers, washing machines, refrigerators, freezers, stoves, microwave ovens, water heaters, etc. Some states ban appliances from landfills. Although they contain recyclable metals, these can be difficult to recover.
- Packaging This is the largest component of US MSW, almost 32% by weight; about half is paper. Over the years, the use of glass and steel in packaging has decreased; aluminum is staying about the same. Meanwhile, plastics use, has increased dramatically. See Figure 11.6• If you examine products in US stores, you see many with unnecessary packaging. However, proper packaging performs valuable functions: on food, it reduces spoilage and the amount thrown away. In the United States, 15% to 20% of food is disposed of as

²⁷ Wastes: Resource conservation, used oil management program. *US EPA*, August 29, 2008, <http://www.epa.gov/epawaste/conservation/materials/usedoil/index.htm>.

²⁸ Used oil collection. *RS Used Oil, Inc.*, 2009, <http://www.rsusedoil.com/usedoil.cfm>.

²⁹ Burke, M. E-waste campaign begins in the U.K. *Environmental Science & Technology*, **41**(13), July 1, 2007, 4492.

³⁰ Design for the environment. *US EPA*, February 19, 2009, <http://www.epa.gov/dfe/pubs/about/index.htm>.

waste between leaving the farm until it reaches the consumer's table. In contrast, in very poor countries, foods lack protective packaging, and 40% to 70% is thrown away because it spoils during shipping and storage.³¹ For non-food items, appropriate packaging also serves protective functions. Recycling • About 40% of packaging materials in the United States was recovered for recycling in 2006.³² • The EU started an EPR program for packaging in 1994 called "The Producer Pays." Producers must accept back their packaging, which can be left at the place of purchase, or sent to producers at their expense; or a fee is paid to the Green Dot organization to handle it. The Green Dot take-back program is used in dozens of EU countries, but not in the United States. Nonetheless, many United States businesses are undertaking major efforts to reduce packaging.³³ Wal-Mart is pushing its 660 000 vendors to get rid of excess packaging. It also pledges to recover as much packaging material as possible through recycling, reuse and, possibly composting.³⁴ A group of other companies have formed a Sustainable Packaging Coalition, which has produced a guide for designers to move toward sustainable packaging.

Recycling can go far beyond the examples shown here. With a little readjustment in our perspective, recycling could become one of life's routines. Recycling is not without problems. Consider paper. It contains coaters, fillers, and pigments, which must be removed before the paper fiber can be recycled. These extraneous components, not currently reusable, are land-filled. And working in recycling facilities is not easy. Workers are injured, occasionally killed in accidents involving equipment used to recycle cans, bottles, and paper. Injuries occur even in industrialized countries. Imagine then recycling done from dumps such as one described below in the Philippines. And recycling facilities suffer the same resistance to having them in the neighborhood as do landfills and incinerators, the not-in-my-backyard, or NIMBY, phenomenon.

Box 11.3

The Great Pacific Garbage Patch and beyond

"In a high-tech era of radiation, carcinogenic chemicals, and human-induced climate change, the problem of the trash produced by ocean-going vessels or litter swept out to sea must seem old-fashioned by comparison. Regrettably, that perception is wrong."
(US Senator, Daniel Inouye, Hawaii)

³¹ In addition to a lack of packaging, there is also a lack of infrastructure to transport food quickly (especially in sub-Saharan African countries). Insect and microbe damage, and high humidity also play a role in lost food according to the UN Commission on Sustainable Development.

³² Hartwell, S. Recyclability of packaging in the United States. *US EPA*, April 30, 2008, <http://www.ftc.gov/bcp/workshops/packaging/presentations/hartwell.pdf>.

³³ Deutsch, C. H. Incredible shrinking packages (companies reducing packaging, and barriers to doing so). *New York Times*, May 12, 2007, <http://www.nytimes.com/2007/05/12/business/12package.html?ei=5088&en=007ee5ef59b64410&ex=1336622400&partner=rssnyt&emc=rss&pagewanted=print>.

³⁴ Maestri, N. Wal-Mart's new packaging credo: let's get small. *Reuters*, April 19, 2007, http://www.boston.com/business/articles/2007/04/19/wal_marts_new_packaging_credo_lets_get_small/.

To get a sense of our problem with irresponsible disposal of plastics³⁵, examine Figure 11.7. This shows only one creek flowing into the ocean in the city of Baltimore, one creek in one city among a multitude of coastal cities. The debris shown is not all plastic, but much is, especially plastic bottles. Under this bridge a trash interceptor catches the debris, preventing it from entering Baltimore Harbor. This one interceptor collects about 5 tons (4.5 tonnes) of trash a month,³⁶ a “drop in the bucket” compared to the massive quantities of trash washing into our oceans. The interceptor is used for public education, letting people know what happens when we litter. Consider the countless streams and rivers flowing into our Earth’s oceans where human detritus is not intercepted, and you may begin to understand why any coastal place you visit in the world including isolated places have junk, especially plastics on the beaches.

The Great Pacific Garbage Patch^{37,38}

More striking than trash on beaches is a phenomenon that most people will never see (Figure 11.8). A great swirling field of trash – held in place by underwater currents – is found in the Pacific Ocean stretching “from about 500 nautical miles off the California coast, across the northern Pacific, past Hawaii and almost as far as Japan.” Swirling within this vortex (actually two vortices, “the Western and Eastern Pacific Garbage Patches”) are an estimated 100 million tons (91 million tonnes) of refuse. Trash escapes when a vortex comes close to land, throwing large quantities of debris onto beaches. Tony Andrady of the US Research Triangle Institute, says: “Every little piece of plastic manufactured in the past 50 years that made it into the ocean is still out there somewhere.” These materials cannot be seen from space as they swirl below the water’s surface, but they are observed from ships, and investigators at the sea’s surface level can pull up samples – see Figure 11.9 for some smaller pieces found. About 80% of ocean debris originates on land, the other 20% from ships or oil platforms. Flotsam has always been pulled into these vortices but, before plastics existed, most flotsam biodegraded. However, now the UNEP estimates that plastics are about 90% of the mass. Through the action of salt water, sun, and wind, plastic pieces very slowly erode

³⁵ Six resins are used to make most plastic containers and packaging. Each has a code number often found on the container. Code #1: Polyethylene terephthalate (PET), a strong, clear polymer used to make soft drink bottles and medicine containers. Code #2: High-density polyethylene (HDPE), often found in milk, juice and water bottles and in containers for household cleaners such as detergent. Code #3: Polyvinyl chloride (PVC) or vinyl (V) is found in clear films used, e.g., to protect meats. It allows air to pass through it, clings, and is puncture resistant. Vinyl is also found in pipes and sporting goods. Code #4: Low-density polyethylene (LDPE) is flexible and strong. It is commonly used in grocery and garbage bags, and in shrink and stretch film. Code #5: Polypropylene (PP) has a high melting point, so it can be filled with hot products, which can then cool within the bottles. It is also used for caps and yogurt containers. #6: Polystyrene (PS) is a hard, often colorless plastic. In its expanded form, *foam*, PS provides shipping protection for products such as electronics.

³⁶ It’s a trash interceptor. *The Container Recycling Institute*, <http://www.container-recycling.org/general/interceptor.htm>.

³⁷ Marks, K. and Howden, D. The world’s rubbish dump: a garbage tip that stretches from Hawaii to Japan. *The Independent*, February 5, 2008, <http://www.independent.co.uk/environment/the-worlds-rubbish-dump-a-garbage-tip-that-stretches-from-hawaii-to-japan-778016.html>.

³⁸ Allsopp, M., Walters, A., Santillo, D. and Johnston, P. Plastic debris in the world’s oceans. *Greenpeace*, 2006, http://oceans.greenpeace.org/raw/content/en/documents-reports/plastic_ocean_report.pdf.

away – they do not biodegrade – into smaller pieces and finally into microscopic granular or fiberlike fragments, which continue to steadily accumulate in our oceans as well as in the sand of beaches.

Animal deaths

The UNEP estimates that plastic debris causes the deaths of a million seabirds a year and at least 100 000 marine mammals.³⁹ As one instance, the most endangered mammal species in the United States, the monk seal, gets entangled in cheap plastic nets lost or discarded. Another is the Hawaiian green sea turtle, which eats the debris, mistaking it for food as when a plastic bag may be mistaken for a jellyfish. Large plastic items including plastic six-pack rings and discarded fishing lines and nets can entangle, suffocate, or disrupt digestion in birds, fish, and mammals. “Syringes, cigarette lighters, and toothbrushes have been found inside the stomachs of dead seabirds.” The seabirds skim the ocean’s surface and scoop up debris as they would small fish, crustaceans, and other food; the debris with its jagged edges becomes trapped in their GI tracts, leading to their deaths. Such items, fed by a parent to its chick can kill it too: one dead Laysan albatross chick had “cigarette lighters, bottle caps, and hundreds of other pieces of plastic” in its gut. Ellen Anderson, walking along a beach in Washington State had something bright and red catch her eye. Investigating, she found a dead bird with “its exposed belly filled with shiny bits of plastic. Chunks yellowed like old teeth, a perforated pink rectangle, hairy tan slivers,” and the red shard that had first caught her attention. This bird, a Northern fulmer was subsequently found to contain 59 pieces of plastic within its gut. Anderson discovered this was not a rare find.⁴⁰

Microscopic impacts

Other researchers are examining what happens to the microscopic fragments and fibers into which larger pieces of plastics eventually break down.⁴¹ These fragments have been found to be widespread in the open sea, in sediments of estuaries and in the sand of beaches. They are ingested by marine organisms: one group of investigators kept amphipods, lugworms, and barnacles in aquaria containing small quantities of microscopic plastics. All three species ingested the plastics within days. The researchers note that the environmental consequences are not known. The Algalita Marine Research Foundation expresses greater concern. Its researchers have extensively sampled surface waters in one of the vortices noted above, and collected a “rich broth of minute sea creatures mixed with hundreds of colored plastic fragments – a plastic-plankton soup” with six times more plastic particles by weight than zooplankton. Moreover, these particles absorb oily and persistent pollutants that may

³⁹ Effects of marine litter. *UNEP*, <http://www.unep.org/regionalseas/marinelitter/about/effects/default.asp>.

⁴⁰ Block, P. Oceans of waste, waves of junk are flowing into the food chain. *Seattle Times*, April 23, 2006, http://www.k-state.edu/environment/ArticlesoftheWeek/Article04-30-06_05-06-06.htm. The article notes: “Dutch researchers [use] fulmars to monitor litter in the North Sea, and have analyzed stomach contents of hundreds of birds over two decades.” In the early 1980s, 92 percent of the fulmars had ingested an average of 12 pieces of plastic. By the late 1990s, 98 percent of bird stomachs contained an average 31 pieces of plastic.

⁴¹ Thompson, R. C. *et al.* Lost at sea: where is all the plastic? *Science*, **304** (5672), May 7, 2004, 838, <http://www.sciencemag.org/cgi/content/full/304/5672/838>.

concentrate several thousand times over levels found in surrounding water. These ingested bits could be impacting these creatures near the bottom of the ocean food chain.

Solutions?⁴²

An international treaty, MARPOL (International Convention for the Prevention of Pollution from Ships) prohibits dumping plastics in the ocean. However, recall that 80% of the debris originates on land. Thus, MARPOL is at best only a partial solution. The UN and several concerned nations are aware of the problem, but there is as yet no coordinated international effort that might lead to a treaty. It is impossible to clean up the ocean: thus we must emphasize prevention and waste management. The international environmental organization Greenpeace calls for a global network of marine reserves covering 40% of the world's oceans; it also calls on coastal countries to help prevent this great input of plastic and other debris to our oceans.

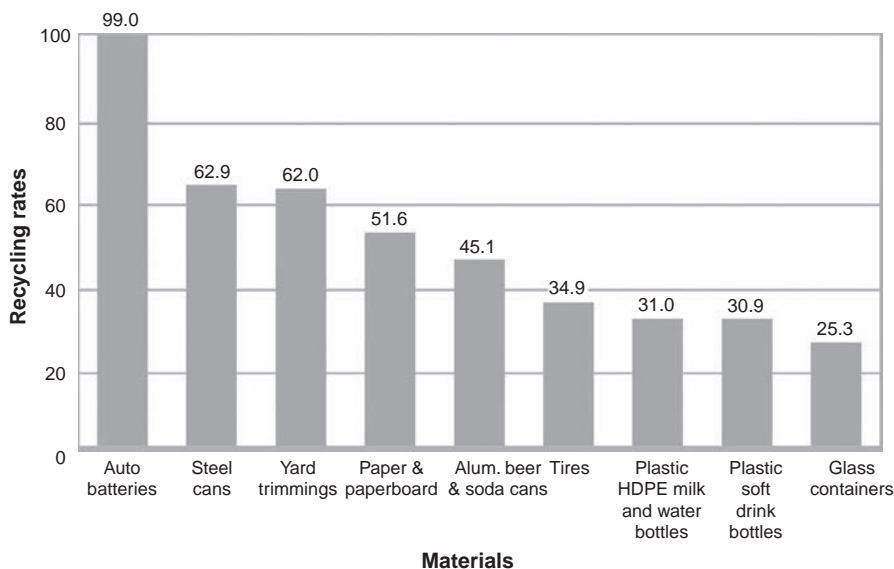


Figure 11.5

Recycling rates of common materials (in 2007). Credit: US EPA

⁴² (1) Jeavans, C. Top tips from plastic-free bloggers. *BBC News*, August 30, 2008, http://www.bbc.co.uk/blogs/monthwithoutplastic/2008/08/top_tips_from_plasticfree_blog.html. (2) Waste reduction fast facts: plastics. *Metro*, <http://www.oregonmetro.gov/index.cfm/go/by.web/id=25410>.

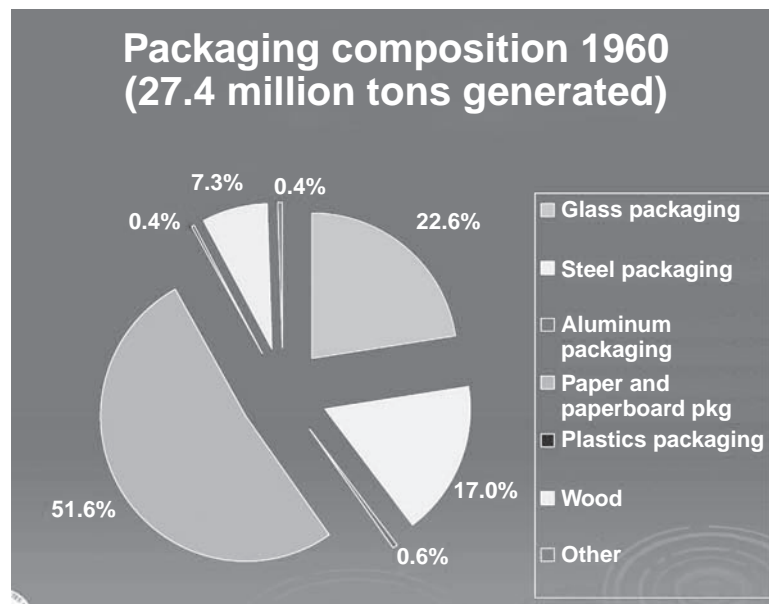


Figure 11.6

Type of packaging found in US MSW. Credit: US EPA



Figure 11.7

Trash intercepted at one creek flowing into Baltimore Harbor. Credit: Baltimore Harbor Watershed Association

Composting and “bio-treatment”

Organic wastes (grass, leaves, and other yard wastes) and most kitchen wastes can be composted. Composting is considered recycling. The number of US communities collecting and composting yard wastes increased from 3227 in 2002 to 3470 in 2005. Compost can be sold to improve soil quality. Some homeowners compost their own wastes. Composting is a

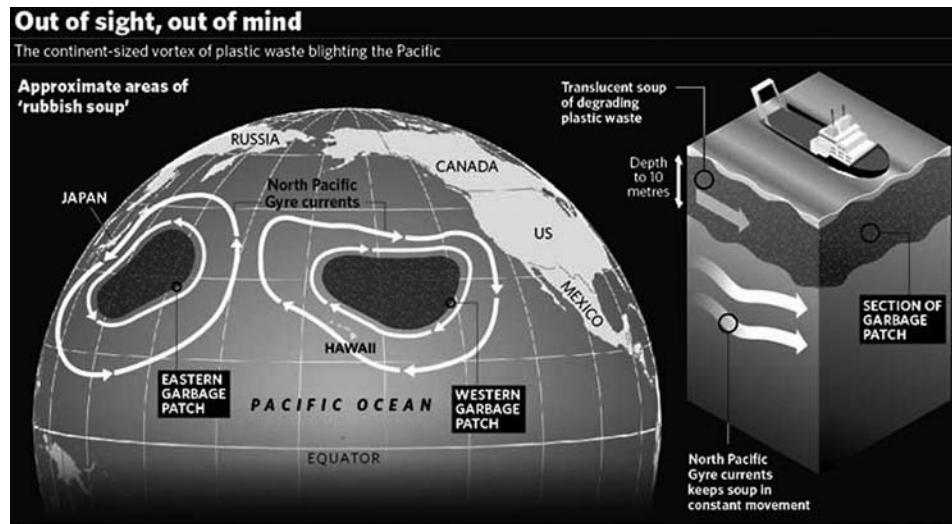


Figure 11.8

The great Pacific garbage patch. Credit: Greenpeace

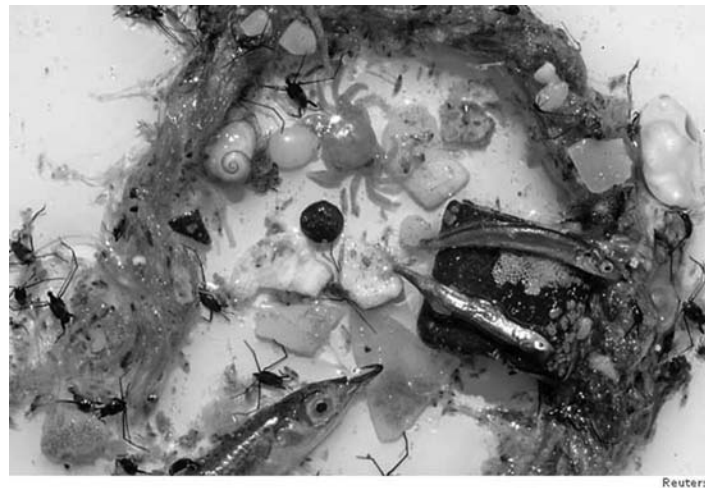


Figure 11.9

Material brought up in a net lowered into swirling vortex in the Pacific. Credit: Alex Hofford, Greenpeace

form of *bio-treatment* because microorganisms degrade the materials to yield a soil-like product. Composting food wastes with worms is another form of bio-treatment. Other examples of beneficially using bio-treatment are seen in this text: microorganisms degrade organic matter in landfills, in secondary wastewater treatment, and can treat some hazardous wastes (Chapter 12). More broadly, the degradation of wastes by microorganisms, worms, and other creatures is a major natural service.

Box 11.4**Junked cars**

The United States has 210 million vehicles on the road with more added all the time. Fifteen million are junked each year. Fortunately, 95% are mostly recycled. About 75%, by weight, mostly metal, of discarded automobiles are reused or recycled. Much of the iron is recycled. Lead-acid batteries, starters, tires, generators, and other engine parts are also typically reused or recycled. The rest of the car, “fluff” (plastics, liquids, and glass) has, in the past, gone to a landfill. ■ Legislation in the EU dictates EPR for automobiles: auto manufacturers must take responsibility for their vehicles over their whole life cycle, including the end of their useful lives; the legislation mandates that 95% of a discarded vehicle must be recycled by 2015 (at no cost to the auto owner).⁴³ To comply, European companies, BMW (Germany), Fiat (Italy), and Renault (France) have developed facilities to dismantle, shred, and recycle components of their discarded cars. They share information and technology, and each accepts used vehicles from the others.

No EPR laws exist in the United States. However, US manufacturers selling cars in EU countries must comply with their law. Thus, a US Vehicle Recycling Partnership has emerged, working with the US Department of Energy and the American Plastics Council to develop means to recycle a higher percentage of an auto. Although plastics are barely 5% of an auto’s weight they are 50% by volume. Plastic use has led to an auto being 400 pounds (181 kg) lighter than the average vehicle of the mid-1980s. However, plastic is a big reason that only 75% of a junked car has been recyclable: much of the remaining 25% is plastic. In Japan, to facilitate recycling as much as 95% of a vehicle, they use only one type of plastic.

Design for Disassembly

DfD is one form of DfE and its use led the Japanese to mark each material for easy identification. Nissan already has several car models that allow a recovery rate of 95% of junked autos.

Life-cycle assessment

To effectively utilize DfE for a product, one needs to know its current environmental impact. The Swedish car manufacturer, Volvo did a Life-cycle assessment (LCA) on a Volvo to evaluate its impact from the extraction of raw materials used to manufacture it, the manufacturing process, and its use, maintenance and disposal. LCA results are very helpful in designing more environmentally sound vehicles. DfE includes DfD, and reuse, and for recycling of component parts.

Promoting recycling

First, recognize used materials as products or commodities, not waste. Society can promote recycling in many ways. Following are some – by no means all – approaches that communities, states, and countries are using to promote recycling.

⁴³ Motavilli, J. Here today, gone tomorrow: the auto industry ratchets up recycling *Emagazine.com*, November, 2005, <http://www.emagazine.com/view/?2959COMMENTARY>.

- Promote technology development. Plastics contain a number of different resins, which, if mixed together, are useful in manufacturing only a few products. As technology develops to collect and sort plastics more efficiently and economically, each can be recycled to specific higher-value uses. New technologies may also find more uses for mixed plastics.
- Reward recycling A government can promote recycling by providing incentives to businesses using secondary (used) materials rather than virgin ones. Some American cities, Philadelphia, Pennsylvania, and Cherry Hill, New Jersey, reward householders: “RecycleBank,” a non-profit group provides coupons to households that separate recyclables from garbage. The worth of coupons depends on the weight of recyclables collected. Coupons can be used at hundreds of local businesses cooperating with the program. These cities’ recycling rates have greatly increased.^{44,45}
- Promote education, social and behavioral changes to improve recycling. Governments can support recycling and waste reduction education in schools; sponsor television, radio, or newspaper ads that promote recycling. Emphasize the important role that citizens have in sorting trash from recyclables or in buying products with recycled content.
- Governmental mandates may help to enhance recycling. Some governments give preference to environmentally preferable products when making purchases (Box 11.1). Require citizens to pay deposits on beverage containers, tires, car batteries, furniture, or appliances at the time of purchase. A bottle bill to promote container return is an example. So is a law charging a tax on each new tire sold, and using the revenue to subsidize recycling. ■ The EU requires member states to recycle 60% of glass and paper, 50% of metals and 22.5% of plastic packaging. It recently set new goals: by 2020, increase recycling rates to 50% of MSW and 70% of industrial waste. Consider Germany’s experience: its tough recycling law includes a program to collect packaging materials. So much packaging was collected in the early 1990s that Germany could not recycle it all. The excess was shipped to other EU countries, which interfered with their recycling programs. The EU now forbids member states from setting recycling targets far in excess of what they can handle within their own borders. But the German law had the desired effect – the amount of packaging used went down, 4% in 1993 alone. German manufacturers now tend to package products in more easily recycled glass and paper than in harder to recycle plastic. Other European countries began to follow Germany’s example.
- Use deposits, fines, and other incentives Recycling rates are enhanced when citizens must pay deposits on beverage containers, tires, car batteries, furniture, or appliances at the time of purchase; the revenue can subsidize recycling. Require households and businesses that produce more trash to pay a higher price. Or, increase the frequency of

⁴⁴ New Jersey town doubles recycling rates in one week with the RecycleBank program. *Environmental News Network*, December 3, 2007, <http://www.enn.com/pollution/article/26368>.

⁴⁵ DiSimone, B. Rewarding recyclers and finding gold in the garbage. *The New York Times*, February 21, 2006, <http://www.nytimes.com/2006/02/21/business/businessspecial2/21recycle.html?partner=rssnyt&emc=rss>.

recyclables pick ups while decreasing trash collections. Require government offices, when purchasing products to give preference to environmentally preferable products.

- Tax throw-aways Taxing throw-away and hard-to-recycle products such as throwaway cameras and disposable razors⁴⁶ can stimulate business to look at the life cycle of their products and either redesign them for recycling or stop making them. One case is Tetra Pak drink cartons; their layers of different materials make recycling difficult. In the UK, less than 10% are recycled; however, Germany places a charge on the cartons to pay for their collection – this has led to 65% of drink cartons being recycled. At the same time, consumers think about switching to durable alternatives that are not thrown away.
- Make recycling mandatory. Some communities such as Pittsburgh, Pennsylvania, and the state of Connecticut require households and businesses to recycle all paper, cardboard, aluminum, glass, and plastic. Trash haulers may not collect trash until the recyclables are removed to the recycling bin. Other cities fine those found to have greater than the allowed amounts of recyclables in their trash; a second fine is much bigger than the first.
- Encourage businesses to make voluntary changes In cooperation with the US EPA's WasteWi\$e program, L. L. Bean of Maine formed teams to reduce waste. Bean set waste-reduction goals and an action schedule to meet them. As the name WasteWi\$e implies, waste reduction can provide financial rewards.
 - The EPA urges businesses to preferentially buy recycled products when making purchasing decisions, and manufacturers to include recycled content in their products.
 - To make greater use of DfE, encourage designers to develop products that are easily disassembled into reusable or recyclable parts. The result can be fewer types of plastics in products, plastics labeled for easy identification, and use of plastic in ways that allows easy separation from other components at the end of product life. A few companies have zero-waste targets. Even when unrealistic, it stimulates thinking on materials management and promotes thinking about the entire life cycle of a product. This brings us back again to DfE, designing excess material out of the product, designing it for easier recycling?

Box 11.5

Reducing waste by Extended Producer Responsibility: take-back programs

Take-back – also referred to as *Extended Producer Responsibility (EPR)* – programs promise to enhance the use of DfE. When producers must, by law take back discarded products, such as TVs or computers, they have an incentive to design easy to disassemble products so components can be reused or recycled. Several US corporations have pilot take-back programs for consumer electronics including TVs and computer monitors. ▪ Japan has very active take-back laws and programs for many products including electronics, home appliances, and cars.⁴⁷ The intent is to shift responsibility for discarded products away from municipalities to producers. But responsibility in Japan goes beyond producers to include consumers and retailers.

⁴⁶ Tax throw-away culture. *Reuters*. November 20, 2006, <http://www.theage.com.au/news/world/british-call-for-tax-on-throwaway-goods/2006/11/19/1163871272286.html>.

⁴⁷ Ogushi, Y. Assessing extended producer responsibility laws in Japan. *Environmental Science & Technology*, 41(13), July 1, 2007, 4502–4508.

Consumers, when purchasing a car or computer must pay a fee to cover its end-of-life expenses. Retailers must collect discarded products. Only then do producers see to the reuse or recycling of the collected products. Home appliances for instance are disassembled, and the separated parts treated as raw materials. Japan's laws also cover rechargeable batteries and construction waste. The laws don't always work. The fee for home appliances is paid not at the time of purchase, but at disposal, and only an estimated 50% of old appliances come back to producers. This happens because some retailers find it profitable to charge consumers less than the full fee when collecting appliances; they then sell the appliances for export and reprocessing abroad. Other consumers avoid the fee entirely by placing appliances at the curbside for pickup by municipalities that don't strictly enforce the take-back law. In the case of cars, a manifest system tracks cars end-of-life. The Japanese continue working on making their EPR laws more effective. Meanwhile, Japanese manufacturers are developing new technologies, some very sophisticated, to separate product components; they are obtaining many patents for their efforts. • EU countries have mandatory take-back programs also and they too encounter problems. So the EU has created incentives including a product certification label to stimulate manufacturers to take DfE more seriously. Electronics take-back will be discussed in Chapter 12. Examine Figure 11.10, and you'll see one reason for Japan's special interest in EPR. They have a scarcity of usable land and landfills take space. The country makes a major effort to reuse or recycle as much as they can.⁴⁸ For the wastes that are generated, they prefer incineration. Up to 80% of MSW is incinerated; in the United States about 80% is landfilled.

Questions 11.2

1. Instead of a flat fee to haul a household's waste away, regardless of the quantity, some communities charge per bag. (a) What are possible disadvantages to this? (b) If your community charged you per bag, what steps if any would you take to reduce waste?
2. Ponder this quotation from Agenda 21, a document resulting from the 1992 World Summit: "the major cause of the continued deterioration of the global environment is the unsustainable pattern of consumption and production, particularly in industrialized countries." (a) Do you agree with this assessment? Explain.
3. The Union of Concerned Scientists carried out risk assessments of common activities. (a) They found that an individual's major environmental impact comes from the use of transportation. How do our transportation decisions affect the environment? (b) Eating meat is another activity with a major environmental impact. Why does eating meat have more adverse environmental impact than eating grains, fruits, and vegetables?
4. How could coastal countries keep plastic debris out of the oceans? What control can be used to lower the amount of debris entering the oceans? What pollution prevention methods might be used?

⁴⁸ Onishi, N. How do Japanese dump trash? Let us count the myriad ways. *New York Times*, May 12, 2005, <http://www.nytimes.com/2005/05/12/international/asia/12garbage.html>.

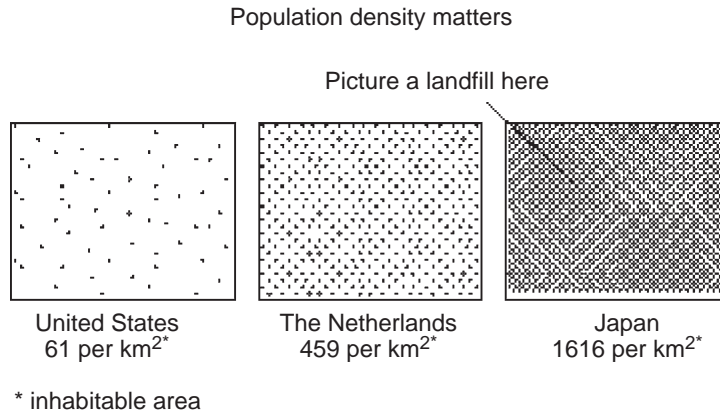


Figure 11.10 Siting a landfill in a densely populated locale is difficult. Credit: Dr. Cynthia F. Murphy, University of Texas, Austin⁴⁹

5. Banning plastic bags: (a) What is the environmental advantage of banning plastic? (b) What is the environmental disadvantage of using more paper rather than plastic? (c) What might happen if, after banning plastic bags, nothing more is done? (d) Should plastics' producers share the responsibility for what is done with waste plastics? If so what should they do?

Disposal

The fate of disposed MSW

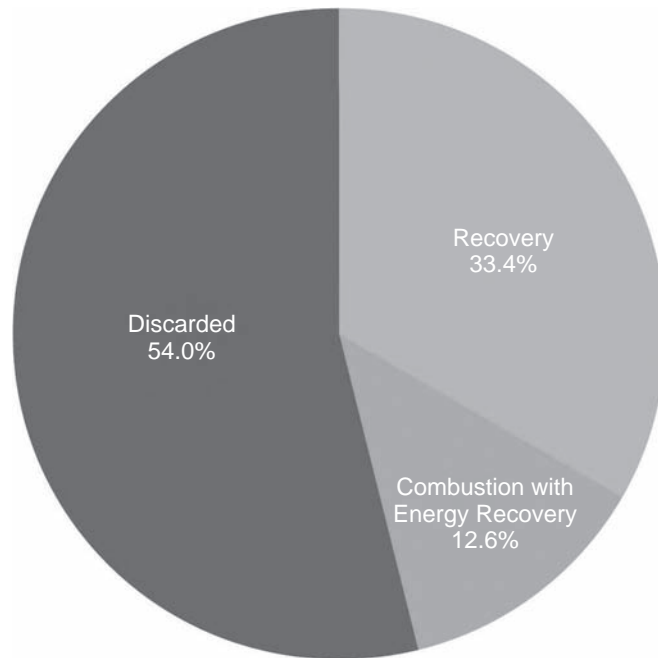
At the bottom of the WMH is disposal. In practice that typically means landfilling or incineration (combustion) (Figure 11.11). In modern facilities, both these options are carefully regulated.

Incineration⁵⁰

The purpose of treating waste is to reduce its quantity or its toxicity, or both. Combusting MSW reduces volume by up to 90% and 75% by weight. Ash uses only about a third as much landfill space as does MSW.

⁴⁹ Gutowski, T., Murphy, C., Allen, D. *et al.* Environmentally benign manufacturing. WTEC Panel Report, April, 2001, <http://www.wtec.org/loyola/pdf/ebm.pdf>.

⁵⁰ Wastes. Non-hazardous waste: municipal solid waste: combustion. *US EPA*, <http://www.epa.gov/epawaste/nonhaz/municipal/combustion.htm>.

**Figure 11.11****Management of MSW in the US (2007). Credit: US EPA**

Combustion, pros and cons

Proponents believe combustion is important to MSW management, especially in large-population centers with limited landfill space; recall how Japan uses combustion. Others argue that combustion does not reduce toxicity because, once the organic materials of MSW are burned away the metals in ash are more concentrated than in MSW. About 90% of the ash from incineration is landfilled, and metals may leach from the ash. Landfill leachate⁵¹ is ordinarily captured and treated, but cases exist of leachate escaping and contaminating groundwater. To allay this concern some communities remove metals as much as possible from MSW before combustion. Ferrous (iron-containing) materials are often valuable and recovered before burning, and the ferrous fraction in combustor ash is also recovered. Burning lead-acid batteries from motor vehicles is prohibited in many states. Instead, almost all batteries are recovered and recycled. It is harder to remove small button batteries, which have become a major source of mercury in MSW. Although expensive, it is possible to vitrify (convert into a glasslike material) the metals in the ash; this greatly reduces leaching.

- Some consider ash less toxic than garbage. Consider: metals are more concentrated in ash leachate from an ash landfill. However, the solids content is lower than in the leachate from raw MSW. Ash is also free of the microbes and organic materials that make garbage

⁵¹ Water percolating through a landfill dissolves contaminants as it goes: the product is leachate.

Table 11.2 Recycling is not just about paper and cans¹

Using incinerator ash to make an island and to make roads	<p>An island: land-poor Singapore has constructed a 865-acre (350 hectare) island a 20 minute ferry ride from the mainland made entirely of the ash produced by its four incinerators.² Incoming ash, after being carefully protected, is covered with sand and planted with mangrove trees. The island itself, and its adjoining marine waters, have rich ecosystems. It has enough space to continue serving Singapore until 2045.</p> <p>Roads: some European countries, after stabilizing incinerator ash to prevent leaching, incorporate it into aggregate for use in road paving.</p> <p>Building: incorporating ash into cement and other building materials</p>
A park made from asphalt and a garden made from a garbage dump	<p>San Francisco converted a former Air Force base, the Presidio, into a park; 70 acres (28.3 hectare) of asphalt and concrete from its air field were crushed and reused beneath pathways and parking lots.³</p> <p>Curitiba Brazil converted an 11-acre (4.5-hectare) garbage dump into a botanical garden.</p> <p>Curitiba converted a derelict quarry into a Free University of the Environment, which holds free courses on land-use and environmental issues</p>
Old clothing and textiles	<p>Paper, in the nineteenth century, was made from cotton rags, and clothing made from discarded woollens. Today, clothes are recycled by selling at yard sales or donating them. Old clothing is often exported to poor countries. Clothing that cannot be reused is processed into rags or mixed into asphalt to make roof shingles.</p>
Disposable diapers	<p>By age 30 months, a child may have used 5000 diapers. A number of cities worldwide, including Toronto recycle them. Wood pulp is extracted from the used diapers as are the super-absorbent polymer and plastic.</p>
Grease	<p>Fast-food restaurants discard billions of pounds per year of used cooking grease. This can be processed into ingredients of poultry and cattle feed, or used as lubricating oil. Another growing use is as a bio-diesel fuel for motor vehicles.</p>
TV sets and telephones	<p>European TV and glass manufacturers formed a consortium to recycle picture tubes from discarded TV sets. Germany's largest telephone company has formed a consortium to recycle telephones.</p>
Building materials	<p>Wood and other materials from old buildings can be recovered, often reused. Builders can incorporate materials into new construction – discarded tires, plastic bottles, or metal cans, but it may be difficult to obtain building permits. Incinerator ash can go into concrete, and old newspapers into insulation</p>
Discarded sinks, tubs, and toilets	<p>EnviroGLAS uses these to make colorful durable countertops and flooring tiles⁴</p> <p>California crushed discarded toilets into aggregate to add to concrete for road building projects.</p>
Telephone poles	<p>Old telephone poles contain creosote and pentachlorophenol, wood preservatives that are now banned. However, using a <i>bioremediation</i> process, poles are chipped into small pieces and composted with microorganisms that can degrade creosote and pentachlorophenol. Clean wood fiber is then sold to paper mills.</p>
Fluorescent lamps	<p>The United States uses more than a half billion fluorescent lamps yearly. They contain a glass tube, aluminum end caps, inert gases, phosphor powders. Because they also contain 20-50 mg of mercury, many states ban them from MSW landfills.</p> <p>Techniques are available to recover and recycle the mercury, aluminum, and other components. Newer lamps such as CFLs contain much less mercury.</p>

Table 11.2 (cont.)

Radioactive materials	Without a long-term storage site – the nuclear power industry recycles metal from used radioactive pumps into new pumps used within the industry.
Old subway cars	Remanufacture them into new cars. Submerge unusable cars along coastal areas for use as artificial reefs

¹ For more illustrations, see: Deneen, S. Emptying the Landfills, One Product at a Time. *E//Magazine*, June 23, 2006. <http://www.alternet.org/envirohealth/37959/>

² Lin, K. Singapore's Eco-landfill. *The Globe and Mail*, August 31, 2005 <http://www.theglobeandmail.com/servlet/story/LAC.20050831.SINGAPORE31/TPStory/Travel>

³ The rest of the project involved planting 100 000 plants on recovered land. These represented 73 native species. Twenty acres (8 hectares) of tidal marsh were constructed, attracting birds and animals not seen in the area for many years. Twenty-eight acres (11 hectares) of grassy fields and sandy beaches are also a part of the park. The US Park Service sponsored the work, with thousands of volunteer assistants, and more than 2400 donations (\$34 million).

⁴ Bates-Ballard, P. Recycled Toilets Find a Home. EnviroGLAS Products Inc., October 19, 2006

objectionable.⁵² And, without organic material, ash does not generate methane gas as garbage does. MSW incinerators are highly regulated in developed countries including strict regulations on emissions of dioxin and hazardous metals, including mercury. The United States burns about 17% of its MSW. ▪ But concentrated metals are not ash's only problem. It is rich in mineral salts. In small amounts, salts may pose no problem. However, in the quantities generated by burning large amounts of MSW, they pose the same problem posed by piles of salt used to control road ice in winter. Salts dissolve in water and run off into surface water or percolate into groundwater. Thus, even ash without hazardous metals contains salts such as those of calcium, magnesium, and potassium. So proper landfilling is very important for ash as well as trash to prevent leaching into the environment. ▪ In the United States, most ash is landfilled. However, as traditional resources become more expensive or technologies develop more may be put to use. Innovative uses of incinerator ash are seen in Table 11.2.

Energy value of MSW⁵³

Combustion can recover some of the fuel value of plastics, paper, and other carbon-containing wastes in MSW, producing steam and electricity. Certain materials have especially good fuel value. Polystyrene a plastic used in foam has an energy value of 17 800 Btu/lb (4487 kcal/kg), and waste tires have 15 000 Btu/lb (3781 kcal/kg). Both values are much

⁵² Tiny amounts of organic chemicals are formed during incineration and are found in *fly ash*. Fly ash is fine ash, which could "fly" into the atmosphere if not captured. The organic chemicals formed include dioxins and furans, which make it especially important to capture fly ash. Dioxins formed can be much minimized in a well-operating incinerator.

⁵³ (1) Municipal solid waste, electricity from MSW. *US EPA*, February 5, 2009, <http://www.epa.gov/cleanrgy/energy-and-you/affect/municipal-sw.html>. (2) Clean energy, air emissions (from various energy sources: natural gas, coal, oil, MSW, etc.). *US EPA*, December 28, 2007, <http://www.epa.gov/cleanrgy/energy-and-you/affect/air-emissions.html>.

higher than wood; its Btu/lb value is 6700 Btu/lb (1689 kcal/kg). However, the fuel value of trash with its many components is much less. Wet garbage must be heated before it even burns. To generate electric power from MSW, a combustor must be well supplied with fuel-rich materials such as paper and plastics. This may hinder recycling by taking away recyclable materials. The value of recyclables must be high to promote recycling over incineration. ▪ Only a few percent of plastics are recycled (with the exception of PET and HDPE). But, plastics are made from petroleum – and most petroleum is burned as fuel anyway (only about 4% goes to chemical manufacture). Some argue that, we already burn more than 90% so why object to burning somewhat more?

Mass burn and RDF incinerators Mass-burn incinerators burn everything in MSW although some recyclables may be removed first. In RDF (*refuse-derived fuel*) incinerators, non-combustible wastes such as ferrous materials, glass, and grit are first removed and the residual trash is shredded into fluff before burning. ▪ Recent technologies⁵⁴ One recent technology pyrolyzes MSW (decomposes it at high temperatures in the absence of oxygen); this converts MSW into gases (methane, hydrocarbons, hydrogen, and carbon monoxide), which can be burned for fuel. A variation on pyrolysis is thermal gasification in which a limited amount of oxygen is present. This also produces combustible gases. ▪ Even more recent is a technology introducing MSW into a very high temperature, up to 5000°C (9032°F) plasma arc furnace. This creates combustible gases, which can fuel the plant, but other gases produced are potential pollutants, which must be captured. In the plasma arc process, molten metals are tapped off and cast into ingots for recycling. Almost everything else in the plasma furnace process is converted into glasslike substances, which can be processed into bricks, tiles and other useful materials.

Sanitary landfills⁵⁵

In the United States, 54% of MSW was discarded to landfills in 2007 (Figure 11.11). ▪ In addition to MSW, landfills often hold construction and demolition debris, municipal sludge, agricultural wastes, combustion ash (unless it has been determined to be hazardous), non-hazardous mining and drilling debris, and non-hazardous industrial process wastes. ▪ Hazardous wastes, excepting those from households cannot be landfilled. Leachate A sanitary landfill is engineered to minimize water infiltration. Nonetheless leachate is produced, and must be collected and treated. Large facilities (such as New York City's Fresh Kills Landfill closed in 2001) produce enormous amounts of leachate. In the early years after a waste has been landfilled, its leachate contains foul-smelling organic compounds. This is collected and treated to meet EPA standards before discharge. Methane gas Because most landfills have little oxygen, anaerobic microorganisms degrade the organic materials and produce methane gas. This must be managed to prevent explosions. However, methane is a valuable fuel and many landfills collect and use it as a fuel.

⁵⁴ Geary, P. Company touts plasma technology to reduce waste, create alternative fuel. *ENN*, March 22, 2005, http://www.enn.com/top_stories/article/12909.

⁵⁵ Landfills. *US EPA*, September 11, 2008, <http://www.epa.gov/epawaste/nonhaz/municipal/landfill.htm>.

Bioreactor landfills⁵⁶

Organic materials can biodegrade. However, this happens very slowly in most landfills because landfill microorganisms, which degrade organic materials, lack the water and nutrients needed to do so. Indeed, landfills are often criticized as places to store mummified trash, “dry tombs,” mummified foods and newspapers can be found intact many years after being disposed. The US EPA in cooperation with a number of landfill operators has been studying *bioreactors*. Instead of treating and releasing landfill leachate, which is rich in organic chemicals, leachate is circulated in the landfill. Kept within the landfill, the leachate provides energy and nutrients to the microorganisms that degrade organic wastes. Re-circulating leachate greatly hastens *landfill stabilization* too. A landfill is considered stabilized after most organic material has biodegraded. At that point, it releases much lower amounts of organic contaminants into the leachate and generates much less methane gas. In an ordinary landfill, stabilization can take many years. However, if leachate is re-circulated, this can happen in 5 to 10 years. Furthermore, in the years before stabilization, bioreactors produce much more methane gas than typical landfills making them a richer source of this valuable fuel. A traditional landfill, once full, is capped with an impermeable layer and its discharges are monitored for 30 years. However, if waste is quickly stabilized in a bioreactor landfill, it may be possible to reduce monitoring to as little as 10 years. Moreover, once organic materials degrade, landfills could be more easily mined for recyclables. One obstacle to bioreactor landfills is that they are initially more expensive because they need machinery and pipes to re-circulate leachate.

Landfill siting

Dumps Historically, trash was dumped in the open, often close to rivers or over groundwater. In fact, dumps were sometimes deliberately placed on river banks so spring floods would wash the trash away. Open burning of trash in dumps continued into the 1970s. Landfills Starting in the 1980s, strict regulations came into force in the United States as to where landfills could be sited, and how they needed to be built, maintained, and monitored. When possible, landfills are sited over near-impermeable clay to provide natural containment for the waste. To further trap water percolating through them, landfills have synthetic liners, and a collection system to recover and treat the leachate. Monitoring wells are built around the landfill and regularly sampled to detect leaks. Such landfills, built according to strict regulations and carefully engineered standards, are clearly safer than “dumps.” Even so, there is concern that leachate may escape into the environment before wastes have degraded to the point where leakage is of much less concern. However, a carefully constructed facility may remain leak-free past the point where leakage poses a problem. Such sophisticated landfills are very expensive to build. From that perspective, they provide a waste-reduction incentive – the more expensive it is to landfill materials, the more attractive are recycling options.

NIMBY Not in my backyard (*NIMBY*) is a potent force making it extremely difficult to site landfills or incinerators. This is true although the United States has a much lower population

⁵⁶ Wastes, Bioreactors. *US EPA*, <http://www.epa.gov/epawaste/nonhaz/municipal/landfill/bioreactors.htm>.

Box 11.6

We can reduce but not ordinarily eliminate waste

Ideally we reuse or recycle materials but, except for metals and glass, which can be recycled indefinitely, recycled materials become trash too. Some materials, we cannot recycle at all. Combustion lowers waste volume, but leaves ash. Waste will thus remain with us into the foreseeable future – “I am, therefore I pollute.” *But* we can redefine wastes as by-products, and find uses for these by-products.

density than many other countries (Figure 11.10). There are several reasons for NIMBY. A modern landfill must be large to be cost-effective. But a small community doesn't need a large landfill, nor can it afford to build one. Instead, a regional landfill serving many communities is built. People have no sense of ownership in a landfill many miles distant; and communities hosting landfills feel resentful at taking others' trash. Moreover, truck traffic with its pollution, noise, and road degradation comes with the landfill. Property values often go down. Landfills and other waste facilities are disproportionately built in poor and minority communities, and as these became more socially aware, they increasingly object.

Landfill mining

Sometimes *landfill mining*⁵⁷ is useful. Materials such as metals are excavated from a landfill because they have value or because space is required for more waste. Mining is done after the organic materials have mostly decomposed to avoid unacceptable health and safety concerns.

So, instead of closing landfills, it is sometimes possible to extend their lives. Many older landfills contain up to 70% dirt and only 30% trash. Even if recovered materials have little value, removing the dirt creates space for more trash. And, the dirt recovered can serve as a landfill cover. Recovered materials go to a sorting plant, where wood, rubble, and metals are removed. Materials not worth recovering are incinerated or returned to the landfill. In the future as some raw materials become more expensive or scarce, landfill mining may become more common. When landfills are full, they are either covered with grass or developed into a park or golf course.

Box 11.7

Batteries and the WMH⁵⁸

Manufacturing a disposable battery takes about 50 times more energy than the battery provides when used. US residents purchase and throw away about 3 billion dry cell⁵⁹ batteries

⁵⁷ Landfill mining, preserving resources through integrated sustainable management of waste, technical brief. *World Resource Foundation*, <http://www.enviroalternatives.com/landfill.html>.

⁵⁸ (1) Batteries. *European Commission*, March 11, 2009, <http://ec.europa.eu/environment/waste/batteries/index.htm>. (2) Batteries. *US EPA*, August 28, 2008, <http://www.epa.gov/epawaste/conservation/materials/battery.htm>. (3) Wastes. Partnerships—product stewardship: batteries. *USEPA*, September 25, 2008, <http://www.epa.gov/epawaste/partnerships/stewardship/products/batteries.htm>.

⁵⁹ Wet cell batteries are most commonly the lead-acid batteries used in motor vehicles. Included among dry-cell batteries are common household batteries that we use for so many purposes such as powering toys, the button batteries that run our watches and hearing aids, and rechargeable batteries.

a year. This uses resources inefficiently and contributes hazardous metals to MSW. This complicates both combustion and landfilling. How can we manage batteries more efficiently?

- P²: avoid unnecessary batteries. Buy toys and appliances that don't need batteries.
- P²: in another form of P², manufacturers eliminated mercury and cadmium from some batteries although button batteries still contain mercury or silver. These were a source of mercury emissions if MSW is incinerated. Buy mercury-free zinc-air button batteries.
- Reuse: purchase rechargeable batteries. They require energy to recharge, but much less than manufacturing them from virgin materials. Solar rechargeable batteries are available in regions with plentiful sunlight.
- Recycling: when household batteries (A,C,D and 9V) are collected for "recycling," it is the metals within them that are reclaimed. Batteries are collected, sorted, and smelted as part of the reclamation process. Unfortunately, this does not pay for itself. Button batteries (used in watches, hearing aids, calculators, etc.) with their high percentage of mercury, silver or other high-value metals are valuable. The rechargeable batteries found in many appliances and lap-top computers, nickel-cadmium (Ni-cad) batteries can be removed and reprocessed for metal reclamation.
- Disposal: most disposable household batteries are indeed disposed of, but some communities collect them to divert the metals away from MSW incinerators and landfills. Rechargeable batteries too, eventually wear out, and in the United States Nicad batteries have been a major source of nickel and cadmium in MSW.

European Union countries have a directive covering all batteries regardless of shape, volume, weight, material composition or use.⁶⁰ It also strictly regulates the mercury and cadmium content of batteries. And battery manufacturers must provide clear labeling with information to enable consumers to choose among batteries. The producer pays for collecting, treating and recycling all waste batteries as well as the cost of public information campaigns.

Questions 11.3

- 1 The above description of batteries and the WMH does not mention treatment. (a) Would you consider incineration of batteries a treatment? Why or why not?
- 2 Evaluate your battery use. (a) How many do you use? What kind? (b) What do you do with dead batteries? (c) Under what circumstances would you routinely have your batteries collected for metal reclamation? (c) Under what circumstances would you voluntarily use fewer batteries?

⁶⁰ Greek, D. Retailers will have to take back old batteries as EU directive comes into force. *Computer Active*, July 28, 2008, <http://www.computeractive.co.uk/computeractive/news/2222670/retailers-back-old-batteries>.

SECTION III

MSW Internationally

OECD countries

The average person in the 29 prosperous member nations of the OECD⁶¹ produces an average 3 pounds (1.4 kg) of MSW a day. Without preventive action this may increase to 3.8 pounds (1.7 kg) a day by 2020. Thus, the OECD believes that trash generation requires attention now. The situation is more serious than weight per person would indicate because the population is growing; although population in some western European countries is stagnant, the population of the United States is growing about 1% a year. About two-thirds of OECD garbage is landfilled, less than a fifth is incinerated, and only 18% is recycled. The OECD targets for 2020 are 33% recycling, 50% landfilling, and 17% incineration.

Waste in less-developed countries

Residents of poor countries produce less trash per person than those in wealthy countries. Still, waste is a major problem and it may double within 20 years. This is happening in countries with few resources to deal with the waste that contributes to clogged and filthy streets and canals, and to disease. In Kabul, Afghanistan, the planning director said the city is becoming “one big reservoir of solid waste.” In Asia, except for Japan and Singapore, litter is everywhere, especially plastic litter. And Hong Kong, despite its riches, is as author J. Tremblay notes “plagued by litterbugs,” where individuals don’t take responsibility for their own waste. In Africa, the UN estimates that only 10% of trash is collected and taken to dumps. Many governments believe they have more serious problems to deal with.

Garbage and slums The UN estimates that more than a billion people worldwide live in slums in cities such as Bombay, Bogata, Cairo, or Manila. Their numbers mount daily. In Asia more than half the urban population lives in slums, often in extreme poverty. City governments typically don’t pick up garbage so it piles up, litters neighborhoods, and fouls local waters, see Figure 1.4. Residents sometimes burn garbage to reduce its volume, which creates noxious fumes. Lack of passable roads can be a problem, making it impossible for pickup trucks to enter neighborhoods to collect garbage. The garbage plus, often, excrement are sources of pathogens and disease. Residents want better conditions, and often attempt to create them. However, they typically lack title to the plots holding their make-shift dwellings; in some places the government periodically bulldozes these homes or otherwise evicts their inhabitants. Some governments are working to give slum inhabitants legal title to their habitations. ■ Self-help organizations for slum dwellers have formed in many cities. In

⁶¹ The OECD (Organization for Economic Cooperation and Development) has 29 member states, mostly developed nations. These include the United States, UK, other western European countries, Australia, New Zealand, and Japan.

Bangladesh, *Waste Concern*, a nonprofit organization promotes waste composting. With assistance from outside organizations, it pays individuals in Dhaka to collect and sort trash, and compost its organic waste. This practice also produces useful compost, creates jobs, and curbs disease. The organization is working to spread the project throughout Bangladesh.

- The UN is testing a garbage-burning oven in a Nairobi (Kenya) slum.⁶² After being heated to a high temperature with waste “sump oil,” the temperature is maintained by garbage shoveled into it, about a half ton a day. It badly pollutes local air, but has benefits. While it burns garbage, people for a small fee can use an interior chamber to bake, or can heat water on its top. The oven has led to cleaner drainage ditches in its vicinity as rubbish is collected to feed the cooker. If the concept is workable, and the pollution can be partially corrected, it may receive wide usage. This would cut the enormous trash problem of huge slums, ameliorate the deforestation resulting from widespread use of wood and wood charcoal for fuel, and also the organic portion can be composted. A Kenyan supermarket chain has pledged funding for 20 more ovens, which can be operated by local people. Many such projects are needed.

Philippines In the city of Manila, people living in regular housing typically have their garbage picked up. However, the dumps to which garbage is taken – as is also the case in many other impoverished cities – are not the sanitary landfills of industrialized countries. Many thousands of Manila’s 10-million residents work – and live and eat – amidst this garbage. They scavenge recyclable paper, plastics, bottles, and metals, and often eat waste food. Many children and whole families are among the workers. An estimated 60 000 people are at one dump called Payatas, and another 100 000, whose livelihoods are based on “the recycling-waste chain” live around it. Scavengers are exposed to broken glass and cans, and to the microorganisms multiplying in the garbage. They work without masks, gloves, sometimes without shoes, and without first aid stations. They continued working even after a flashflood and fire destroyed many tents and shacks in 2000 killing about 100 people and “disappearing” another 150. Better-off Manilans, says environmentalist Alvin Sotero, regard them “as little better than the trash they handle.” He asks what Manila would do without the scavengers. He hails them as “the city’s environmental heroes.” Not all is bleak. “Shanties are hung with flowerpots and posters of athletes and movie idols. There are tiny barbershops and ice cream stands . . . births and weddings and school graduations.” These conditions are not unique to the Philippines. They are found in many impoverished places.

China Imagine a nation with 1.3 billion people, but poor waste practices. Waste is described as an “ever-growing ocean,” increasing about 10% a year. Lacking enough treatment and disposal facilities, waste is often dumped in the open causing soil, air, and water pollution, and posing risks to humans and wildlife.⁶³ Where there are dumps, it can be considered a waste of land in a country without land to spare. In 1995 China enacted the Prevention and Control of Solid Waste Pollution to the Environment Act mandating source reduction, recycling, treatment, and sound disposal. The law was poorly enforced: there was little money to build processing facilities and train workers, the public was not educated, and

⁶² Crilly, R. Kenyan slum cleans streets with trash oven: UN-sponsored program places garbage-burning ovens in an African shantytown. *Christian Science Monitor*, November 1, 2007, <http://www.csmonitor.com/2007/1101/p01s05-woaf.html>.

⁶³ China faces ticking rubbish time bomb. *Reuters*, January 10, 2007, <http://www.alertnet.org/thenews/newsdesk/PEK208804.htm>.

recyclables continued being mixed with garbage. Hongtao Wang and Yongfeng Nie, of Beijing's Tsinghua University urged that regulations be improved and *enforced*. They advocate a "polluter pays system" as an incentive for businesses and individuals to reduce waste generation, and separate out reusable and recyclable items. China now has new goals with a schedule to implement them, and is developing regulations and standards, training waste-management personnel, establishing college-level research and training in material recovery and reuse, composting, incineration, and landfilling. It has purchased some needed technologies, started demonstration projects, and established an information network. No one foresees quick changes especially with limited funding. Chinese waste experts believe that an urgent need exists for cooperative projects with developed countries to develop technologies and equipment suited to China's specific needs.

Plastic bags pose special problems

Around the world, perhaps 500 billion one-time-use plastic bags are used each year.⁶⁴ Thin ones, especially, are littered almost ubiquitously. Dudley Greeley of the University of Southern Maine speaks of a trip to Delaware Beach where he saw that "the snow geese and seagulls in the corn field stubble were outnumbered by white, windblown plastic bags. From a distance, they could be mistaken for hundreds of thousands of birds gleaning the stubble for food. Some of these "bird bags" flapped across the fields until snared by a bit of corn stalk." Greeley continued, "Plastic bags could be used as a symbol of waste and misuse." In poor countries they block water movement in narrow sewage channels, sometimes causing flooding. On land, after water collects in them they breed mosquitoes. They take a great many years to break down into ever tinier particles – they don't biodegrade. Banning bags More and more African and Asian countries are banning plastic bags. The industry making them in Taiwan warned, after Taiwan banned them, that it would move its plant and jobs to mainland China; however, China now bans them too.⁶⁵ So do some European countries. Ireland, after taxing the plastic bags used at retail stores saw their use fall by more than 90%. In the United States, San Francisco was the first major city to ban them although the states of New York and New Jersey require that retailers recycle them. In poor countries where the ban is strictly enforced, litter is much reduced. Often paper bags are used instead. However, sometimes creative changes are made as when Uganda started using – biodegradable – banana leaves instead.

A brighter picture: Curitiba Brazil⁶⁶

Curitiba provides a model of how successful recycling and waste management can exist even in a poor city, where the population tripled in less than 30 years as people came flooding in. It has a

⁶⁴ (1) Lohan, T. The great plastic plague. *AlterNet*, September 5, 2007, <http://www.alternet.org/environment/61607/>.

(2) Eco-friendly reusable bags plus facts and news on plastic bag issue. <http://www.reusablebags.com/>.

⁶⁵ Horovitz, B. Whole Foods sacks plastic bags. *USA TODAY*, January 22, 2008, http://www.usatoday.com/money/industries/food/2008-01-21-whole-foods-bags_N.htm.

⁶⁶ Orienting urban planning to sustainability in Curitiba, Brazil. *ICLEI*, 1995–2005, <http://www3.iclei.org/localstrategies/summary/curitiba2.html>.

“Garbage That Isn’t Garbage Initiative,” which led 70% of its households to sort recyclables, paper, metal, and glass in one bag, collected three times a week; organic waste goes into a separate bag. Two-thirds of the materials in recyclables bags are indeed recycled, furnishing half the cost of the collection system. In neighborhoods without paving where collection trucks cannot enter, a “Green Exchange” occurs: citizens bring their bags to trucks and, in exchange receive tickets to exchange for food or items such as school books. Much of the food used for the exchange is the excess produced by local farmers. Another project, “All Clean” clears litter from hard-to-reach areas especially those near the rivers, which the city works to avoid polluting. Children receive environmental education starting from an early age, and it is incorporated into the whole curriculum. People coming into the city, far from being evicted may receive small plots of land, and building materials with which to build dwellings. When possible, the city hires them for clean-up and recycling jobs. “In Curitiba, everything is recycled” including old buses and buildings. This approach to “waste” is part of a wider attitude to good governance that has also set up a model transportation system and non-polluting industries, and that uses land in ways that avoids polluting the land or the rivers and air around it. Curitiba decided to treat its citizens, “most of all its children – not as its burden but as its most precious resource.”

Delving deeper

Encouraging manufacturers to design for durability and to produce easy-to-repair products is difficult because they believe they would have fewer sales. Is there a way out of this conundrum?

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“I’ve worked with indigenous people on all continents but Antarctica, and one thing they all agree on is the Earth is sacred. We’re the only ones who look at it as a commodity.”

Dr. Paul Cox, ethnobiologist

A hazardous waste is one that is either ignitable, corrosive, reactive, toxic, or more than one of these. As with municipal solid waste, hazardous waste is a small percentage of the more than 12 *billion* tons (10.9 billion tonnes) of total waste that the United States generates each year. But hazardous waste has been abandoned at many thousands of sites in the United States, and around the world. At these sites, hazardous substances may contaminate soil, seep into groundwater, or run off into nearby water, and evaporate into the air. Section I of this chapter examines hazardous waste (HW) characteristics, locales of HW sites, and who generates HW. Section II returns to the Waste Management Hierarchy (WMH) as applied to hazardous waste. Section III deals with how human exposure occurs and how the risks of HW sites are evaluated. Section IV examines how to reduce the risk of HW sites, and examining cleanup methods including bioremediation. Section V moves on to HW dumping in impoverished nations and the international accord negotiated to combat this practice. One waste still moving into these countries is a stream of electronic discards. We look at how we can reduce that flow.

SECTION I

Introduction to hazardous waste^{1,2}

Characteristics

Hazardous waste is regulated by the US Resource Recovery and Conservation Act (RCRA). It has one or more of the following characteristics.³

- A *toxic* substance can adversely affect the health of living organisms exposed to it. Examples are arsenic, cyanide, pesticides, and many metals.

¹ Wastes, hazardous waste. *US EPA*, March 19, 2009, <http://www.epa.gov/osw/hazard/index.htm>.

² Hazardous waste data. *US EPA*, September 29, 2009, <http://www.epa.gov/osw/inforesources/data/index.htm#rcra-info>.

³ These same characteristics apply to the definition of a hazardous chemical. Indeed, hazardous chemicals often become hazardous wastes.

- A *corrosive* substance can cause grievous injury at the point of contact, skin, eyes, lungs, or mouth. Strong acids and alkalis are corrosive, as are chlorine and hydrogen peroxide. Although the concentrations of chlorine (as hypochlorite) and hydrogen peroxide found in household products is not corrosive, much higher concentrations are often used in industrial and laboratory settings.
- An *ignitable* or *flammable* substance can catch on fire, is a fire hazard. Petroleum distillates and many organic solvents are ignitable. Ethyl ether, once used as an anesthetic is highly flammable, and its volatility adds to its danger.
- A *reactive* substance reacts violently with water, air, or other substances. Ethers (used in industry and laboratories) can form explosive peroxides if left sitting in their containers for years. More familiar reactive substances are dynamite, gun ammunition, and firecrackers. In the household, chlorine bleach and ammonia, if mixed together react to form toxic fumes.

Hazardous waste is considered solid waste under RCRA, but includes containerized liquid or gaseous wastes. Some wastes that might be hazardous are exempted by law such as certain mining wastes and coal combustion ash. Household hazardous waste (about 1% of HW) is exempt even if it contains the same chemicals that are regulated when industry produces them. Types of HW that are generated are noted in Table 12.1. Separate laws address two other hazards, infectious agents and radioactive materials.

Box 12.1**Remember that a hazard differs from a risk**

For a HW to be a risk, a person, animal, or plant must be exposed to it, exposed in a way that can cause harm. Unless the waste has escaped into the environment, the greatest hazard is usually to the workers handling it. Corrosive, ignitable, or reactive wastes can also harm materials, as when a corrosive “eats” through a metal drum.

Table 12.1 Typical hazardous wastes generated by selected manufacturing industries

Industry	Hazardous wastes generated
Food and beverages	Animal waste, cleaning wastes, refrigerants
Chemical	Strong acids and bases, reactive wastes, ignitable wastes, discarded commercial chemical products
Metals	Paint wastes containing heavy metals, strong acids and bases, cyanide wastes, sludges containing heavy metals
Paper and printing	Ink wastes including solvents and metals, photography wastes with heavy metals, ignitable and corrosive wastes, heavy metal solutions
Construction	Ignitable wastes, paint wastes, spent solvents, strong acids and bases
Furniture and wood	Ignitable wastes, spent solvents, paint wastes
Vehicle maintenance	Paint wastes, ignitable wastes, spent solvents, acids and bases
Cleaning and cosmetics	Heavy metal dusts and sludges, ignitable wastes, solvents, strong acids and bases

Adapted from: UNEP http://www.grid.unep.ch/waste/images/22-23_table_hazarous.gif

Locations of hazardous-waste sites

In earlier years, generators of HW placed it in lagoons or trenches such as at the infamous Love Canal (Box 12.2). Other means of disposal included injecting it into underground wells, or disposing of it along with municipal solid waste (MSW). • Dumping metal drums containing HW onto land also occurred, usually at rural sites. It still occurs in some countries. There, corrosive wastes sometimes ate through the containers and escaped into

Box 12.2

Two complex and troubling Superfund sites

Love Canal⁴

The Love Canal, built in the 1890s, was never used as a canal. Then, starting in 1942, Hooker Chemical Co. disposed of 22 000 tons (20 000 tonnes) of HW there with more than 200 chemicals including halogenated organic chemicals and pesticides, some contaminated with dioxins. Hooker's disposal methods were standard practice for that time. The US Army was responsible for about 25% of the waste. In 1953, Hooker filled in the site, and capped it with a layer of protective clay. At the request of the city of Niagara Falls, Hooker sold the property to the Board of Education for one dollar. The deed warned that hazardous chemicals were buried at the site, but the city later said Hooker had not informed it of the hazards of the wastes. Occidental Chemical purchased Hooker in 1968 before Love Canal's problems became known, and Occidental was held responsible for paying a significant portion of the cleanup costs.

In 1954, the School Board built one school next to the landfill and a second directly over it. It sold a portion of the land to a developer, who put up hundreds of houses, some directly around the landfill. See Figure 12.1. The on-site school is seen in the photo as well as the houses around the site. In the 1960s, a highway bordering the development was built. During construction, roads and sewers were constructed over and also directly through the Hooker site, and its protective clay cap was partially excavated, allowing rainwater access to the waste. This highway created the greatest problem because it blocked the normal path of groundwater migration through the area. The result was that waste and an increasing amount of groundwater and rainwater became trapped in a clay "bathtub" (the canal). In the 1960s, this, along with its contaminants began overflowing into the basements and back yards of homeowners living nearby. People complained of odors. Complaints increased in the 1970s as the water table continued to rise. In 1980, the federal government in an emergency action, bought several hundred homes, and evacuated their occupants. Homes closest to the canal were destroyed, and the rest sealed off. By 1993, much contaminated soil had been removed from Love Canal. The 40-acre cap had been repaired and sealed with a thick layer of clay plus a high-density plastic membrane. Around the site, 8-foot-high (2.4-m) fencing had been built. Low-permeability clay was at the site's bottom; this greatly retards downward movement of leachate while a drainage system directs leachate to a treatment system. Occidental Chemical

⁴ Envirofacts Data Warehouse, Waste. *US EPA*, March 21, 2009, http://oaspub.epa.gov/enviro/ef_home2.waste.

assumed responsibility for maintaining the leachate system. These efforts cost about \$325 million dollars. However, this only stabilized, not remediated the site, which must be maintained for many years. After officials believed that it no longer threatened human health or the environment, they decided to redevelop the area and sell, at reduced prices, the homes that were still intact. New inhabitants, as well as those who never moved, are of two minds: some who had refused to leave, believe the risks were greatly overstated and blame the city and state for disrupting the canal. Others believe the site still poses unacceptable risks.

An ongoing study examines the health of local people. Children born at Love Canal were twice as likely as children in other parts of the county to be born with a birth defect. Those conceived there were more than twice as likely to be female compared with children conceived after the mother left the neighborhood. This is consistent with exposure to dioxins and with findings in Seveso, Italy, where more girls were born to fathers (in that case) who were exposed to dioxin released during a 1976 plant accident. However, there is no way to measure the psychological effects on those involved. One resident stated that "Niagara Falls is no longer the honeymoon capital but the toxic waste capital." It was Love Canal that, in 1980, led the US Congress to pass a law governing abandoned HW sites. This is called CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) or just "Superfund."⁵

Coeur d'Alene River Basin

This superfund site,⁶ located in the northern section of the state of Idaho is a *megasite*, one among many former mining sites in the western United States. Lead and silver were once mined in Coeur d'Alene. The site covers hundreds of miles and encompasses human communities. The site includes streams, rivers, wetlands, lakes and their sediments, and banks. About 62 million tons (56 million tonnes) of mine tailings ended up in local waters here. Lead concentrations are high enough in about 18 000 acres (7200 hectares) of wetland sediments to be acutely toxic to waterfowl. Children living near a former lead smelting complex at Coeur d'Alene – unlike the children in the Smuggler Mine community (Chapter 3) – once had greatly elevated blood levels of lead. Since the smelters were closed and the surroundings cleaned up, children living in the area have almost normal blood levels. Coeur d'Alene not only contains huge quantities of waste, but many different contaminants with many sources. Experts studying the site found that even removing limited amounts of wastes, as has been proposed would be costly, difficult, perhaps not even feasible. It would also take many years.

soil, air, or water. ■ Military bases are major locales of hazardous wastes sites. ■ Other early generators of HW legally released hazardous substance into waterways with little or no treatment leading to, in some places, water-based HW sites. In Chapter 14, you will read of a 40-mile section of the Hudson River, which is a HW site due to PCB contamination. ■ Sometimes a whole industrial production site becomes a HW site. ■ Many HW sites date from the nineteenth and early twentieth century, including locations where municipalities

⁵ Partnerships. *US EPA*, February 18, 2009, <http://www.epa.gov/wastes/partnerships/index.htm>.

⁶ Priority chemicals. *US EPA*, January 12, 2009, <http://www.epa.gov/epawaste/hazard/wastemin/priority.htm>.

produced *town gas* from coal or oil to use for lighting; many later became HW sites. Other old sites include early mines, contaminated with hazardous metals and acids.

Over time, the location and even the existence of many old sites were forgotten. ▪ Casual disposal was thoughtless rather than malicious; all kinds of waste were once disposed of casually. So long as the population was small and industrial and military operations relatively small, such disposal was largely disregarded. But operations producing HW grew in size and number. At the same time, human populations grew and urban areas spread into the countryside. It was inevitable that people and HW would make contact. Now it is possible to research what Superfunds are in your area and see who produces hazardous waste.⁷

Hazardous Waste Sources

Large petroleum refineries and chemical manufacturers generate up to 90% of the about 270 million tons (245 million tonnes) of HW that the United States produced in 1998. These facilities treat and dispose of about 90% of their waste on site. ▪ Manufacturers of metal products are another large generator producing wastewater with concentrations of metals high enough to be hazardous; most of this is treated. Also – as reported in the Toxics Release Inventory – more than a third of generators send their metal waste offsite for recycling, copper, zinc, lead, and others. ▪ Military operations often generate HW in large amounts as do government agencies especially the Department of Energy. ▪ Hospitals, universities, and commercial laboratories, generate small quantities. Other small-quantity generators include small businesses such as gas stations, photographic developers, dry cleaners, even beauty parlors. Although the definition of HW varies, the UN Environmental Program (UNEP) estimates that more than 300 million tons (272 million tonnes) are produced worldwide each year. See Table 12.1.

Household hazardous waste (HHW)

The HW produced in homes in the largest amounts is paint residue. Others are paint thinners and strippers; pesticides; cleaners and polishes that contain petroleum distillates; and alkaline drain and oven cleaners. Even some discarded cosmetics, such as acetone nail-polish remover are considered HW. Municipal solid waste incinerator ash, although derived from household trash, may be deemed HW if it does not pass an EPA-specified leaching test. ▪ A familiar HHW, which is both ignitable and toxic, is used oil. Many do-it-yourselfers change their own car's oil. Of this, the EPA estimates that much, at least 150 million gallons (568 million liters) a year ends up in landfills or sewer systems or poured on the ground. The EPA could regulate used oil as HW, but with millions of do-it-yourselfers this is impractical. Instead, the EPA developed standards for commercial handlers: If the oil is to be disposed, it may be treated as HW. It is treated less strictly if it is for recycling.

⁷ Hazardous waste recycling. *US EPA*, March 16, 2009, <http://www.epa.gov/osw/hazard/recycling/index.htm>.

SECTION II

Dealing with hazardous waste

Pollution prevention

Once waste is generated, it is too late for P². An exception is when the system is designed to treat the HW as a useful by-product to be fed into another process, i.e., industrial symbiosis (Chapter 2). However, HW can stimulate P² because companies want to avoid the costs of regulations, treatments, expensive disposal, and legal liabilities. Some partner with the US EPA in their efforts to reduce HW.⁸ There are many approaches to P² efforts including working to minimize the use of those chemicals that produce HW. EPA sponsors a National Waste Minimization Program to reduce 31 priority chemicals found in HW.⁹ See Chapter 18 (green chemistry and green engineering, using Design for the Environment to design more environmentally benign chemicals, etc.). Chapter 2 has examples of P², recycling, and reuse.

Recycling and reuse

Some industrial HW can be reused or recycled.^{10,11} Hazardous organic solvents used by industry can, after use, be purified and reused. The reuse-purification process may be repeated many times. However, some waste is necessarily produced including the contaminants removed during purification. A company sometimes produces a by-product useful to another company, and sells or gives it away, i.e., a limited form of industrial symbiosis (Chapter 2). ■ The EPA encourages metal recycling¹² and has different standards for metals. Industry already carefully manages many metals such as scrap metal from automobiles, and much more so for precious metals, e.g., silver. ■ Combusting organic HW can be used both to destroy the waste while also recovering its energy value. This is sometimes controversial because of concerns relating to air emissions during incineration.¹³

⁸ Safe hazardous waste recycling. *US EPA*, October 2000, <http://www.epa.gov/osw/wycd/manag-hw/e00-001d.pdf>.

⁹ Hogue, C. Recycling waste, EPA will allow companies to sell or reuse some manufacturing leftovers classified as hazardous. *Chemical & Engineering News*, **86**(41) October 13, 2008, 11.

¹⁰ Hogue, C. EPA Rebuked: Congress asks for more analysis of proposal for burning hazardous waste as fuel. *Chemical & Engineering News*, **85**(49), December 3, 2007, 13.

¹¹ Hazardous waste treatment and disposal. *US EPA*, September 5, 2008, <http://epa.gov/epawaste/hazard/tsd/td/index.htm>.

¹² Reynolds, K. A. Bioremediation: using microbes to clean up hazardous waste. *Water Conditioning & Purification*, **44**(9), September, 2002, <http://www.wcponline.com/column.cfm?T=T&ID=1725&AT=T>.

¹³ Genetically engineered poplar plants disarm toxic pollutants 100 times better than controls. *ScienceDaily*, October 16, 2007, <http://www.sciencedaily.com/releases/2007/10/071015193434.htm>.

Treatment

Recall that the two major purposes of treating waste are to reduce its volume or to reduce its toxicity. Four types of treatment are shown in Table 12.2, physical, chemical, thermal, and biological. Some reduce volume, some reduce toxicity, and some accomplish both. Treatment can lead to safer transport, storage or disposal of HW.¹⁴ ■ Reducing volume As with MSW, incineration is often used to reduce the volume of HW. However, in Table 12.2 notice that other methods can also decrease volume. ■ Reducing toxicity There are many variations of these methods that can lead to reduced waste toxicity.

Bioremediation

Bioremediation uses living creatures to treat waste, to reduce toxicity and sometimes to reduce volume too.¹⁵ Bioremediation is of great interest because it works with natural systems and sometimes has lower costs than other treatment methods. A precondition is that the HW does not poison the creatures used.

- Reducing volume Bioremediation can reduce volume as when certain plants and trees – in a process called phytoremediation – take up and concentrate within themselves a hazardous metal from soil or water. University of Washington scientists developed genetically engineered (GE) poplar trees that can break down many toxic industrial contaminants including benzene and the common groundwater contaminant trichloroethylene (TCE) into carbon dioxide, water, and salts.¹⁶ The poplars destroy TCE much more efficiently than do unmodified poplars. Moreover, their leaves also absorb pollutants from the air and degrade them. GE poplars have been extensively field tested, but remain controversial. Researchers must assure that GE trees don't spread into the environment; some say this can be prevented by harvesting the trees before they reach the age of flowering.
- Reducing toxicity Microbes reduce the toxicity of some organic chemicals by taking up and degrading them into less toxic chemicals. In one application, microbes are grown on filters and hazardous organic gases then passed through them. This destroys, in some cases 95–99% of the gases. Research to develop microorganisms bioengineered to specific uses is of great interest. More is seen below on using bioremediation to clean up HW sites.

Disposal

Unlike municipal solid waste, HW cannot legally be landfilled in the United States until it has been treated to destroy its toxicity, or stabilized to prevent its hazardous components

¹⁴ Resource Conservation and Recovery Act (RCRA) Subtitle C: managing hazardous waste from cradle to grave. *US EPA Region 10*, March 20, 2009, [http://yosemite.epa.gov/r10/OWCM.NSF/webpage/Managing+Hazardous+Waste+\(RCRA\)](http://yosemite.epa.gov/r10/OWCM.NSF/webpage/Managing+Hazardous+Waste+(RCRA)).

¹⁵ (1) Engelhaupt, E. Happy birthday, Love Canal. *Environmental Science & Technology*, **42**(22), November 15, 2008, 8179–8186. (2) Love Canal, public health time bomb. New York Office of Public Health, September, 1978, http://www.health.state.ny.us/environmental/investigations/love_canal/lctimbmb.pdf.

¹⁶ Superfund, Cleaning up the nation's hazardous waste sites. *US EPA*, March 9, 2009, <http://www.epa.gov/superfund/index.htm>.

Table 12.2 Treatments for hazardous wastes

Treatment	Examples
Chemical	<p><i>Neutralization</i> takes an alkaline or acidic substance, and converts it to a neutral form. Acid is neutralized with an alkali, and alkali with acid. After neutralization, the waste is no longer hazardous unless it has other hazardous constituents.</p> <p><i>Precipitation</i> is often used to treat a metal solution. A substance is added that leads to the metals becoming insoluble and precipitating out. The precipitate may be hazardous, but waste volume is much reduced. If enough metals precipitate from the solution and are carefully removed, the solution may no longer be hazardous.</p>
Physical	<p>In <i>filtration</i> a liquid is separated from a solid using a membrane. The liquid goes through membrane pores. The solid particles are retained on its surface. If enough hazardous material is filtered out, the liquid coming through the membrane (the filtrate) may no longer be hazardous.</p> <p><i>Distillation</i> is sometimes used to separate a mixture of liquids. The mixture is heated. Lower temperatures drive off the more volatile substance, leaving behind those with higher boiling points. Depending on the chemicals and the means of distillation, the waste remaining may or may not be hazardous. Volumes of some of the components can be reduced too.</p>
Thermal (also a physical treatment)	<p><i>Incineration</i> can destroy organic substances. If metals are present, the ash produced may be hazardous waste, but its volume has been much reduced. Incineration is often used to recover energy from organic substances.</p> <p><i>Stabilization</i> is a process in which a metal-containing waste is heated to high temperatures and melted. After it solidifies into a hard mass, it is difficult to leach metals from it. Thus, it may safely be placed in a landfill in many cases.</p>
Biological (bioremediation)	<p>Microorganisms degrade certain organic hazardous wastes using them as nutrients. Certain plants take up and concentrate metals from soil or water (<i>phytoremediation</i>). Some microbes also concentrate metals or change the metals to less noxious forms.</p>
Once chemicals are separated from one another they are more easily managed than if they remained in mixtures. However, the separated chemicals may still be hazardous waste, and need further treatment.	

from leaching. More than one treatment may be needed. ▪ Some HW is disposed of by injecting it into deep underground wells within well-understood geological formations. A permit to inject hazardous waste into a well requires that the waste not contaminate underground drinking water sources for 10 000 years. This of course cannot be proven, and concern remains that groundwater could become contaminated. Complex and costly regulations plus potential liability, limit such disposal.

Tracking hazardous waste¹⁷

In the United States, HW is regulated from *cradle to grave*. ▪ If a HW leaves the facility generating it an identifying document, a *manifest*, goes with it. ▪ If it goes to a storage facility, that facility receives a copy of the manifest. ▪ When the waste goes to a treatment facility, it receives a copy too. ▪ Finally, the disposal facility receives a copy and sends a copy back to the generator. The generator then sends a copy to the EPA or a state agency. ▪ This procedure assures that a paper trail documents the waste every step of its way, cradle to grave. In Chapter 18, you will see a new approach, *cradle to cradle*. Its intent is to assure that a material doesn't become waste.

SECTION III

Hazardous waste sites

A HW site is one where uncontrolled release of hazardous substances has occurred, or could occur. In the late 1970s, Love Canal became a notorious example of people and HW coming together (Box 12.2). Fortunately today a site is usually found and evaluated before a situation reaches such an extreme point.

Evaluating a newly identified site

Many questions need answering when investigating a HW site. What chemicals are present? What type of soil does it have? How does water drain from the site? Is there evidence that contamination of surface or ground water has occurred? How close is the site to human dwellings? Are there air, water, or food routes by which human exposure could occur? By 1997, more than 40 000 uncontrolled hazardous-waste sites had been reported in the United States. The EPA determined that most of these sites did not require federal action. These were left to states to remediate. The 1300 sites it deemed high risk, were placed on a *National Priority List* (NPL). The EPA oversees remediation of NPL sites such as Love Canal (Box 12.2).

Questions 12.1

1. Do you believe that the city of Niagara Falls bore any responsibility for what happened at Love Canal? Explain.
2. Should a business be held liable for a HW site cleanup even if the damage was caused by an earlier owner? Explain.
3. Superfund megasites such as Coeur d'Alene cannot realistically be completely cleaned up. Assuming that is true, make a proposal as to what cleanups should be done. Then answer the question: would this be acceptable to you personally if you lived near one of these sites?

¹⁷ Gustavson, K. E. *et al.* Superfund and mining megasites. *Environmental Science & Technology*, **41**(8), April 15, 2007, 2667–2672.



Figure 12.1 An infrared aerial view of Love Canal in 1978. Credit: New York State Department of Health

Health threat of hazardous-waste sites

Most-often-found chemicals¹⁸

Among the 10 most commonly found chemicals at HW sites are four metals (lead, arsenic, mercury, and cadmium) and four volatile organic chemicals (benzene, vinyl chloride, chloroform, and trichloroethylene). The other two are PCBs and BaP (benzopyrene), a PAH described in Chapter 14. The Agency of Toxic Substances and Disease Registry (ATSDR) has also identified more than 2000 other industrial chemicals at HW sites.¹⁹

How can exposure occur?^{20,21}

Human exposure to chemicals at HW sites may occur through air, drinking water, soil, or food. Look at Figure 12.2: notice the drums (one source) showing spilled chemical waste. Follow the possible exposure pathways.

¹⁸ Frequently asked questions about contaminants found at hazardous waste sites. *ATSDR*, October 7, 2008, <http://www.atsdr.cdc.gov/toxfaq.html>.

¹⁹ Each of these chemicals has at least one hazardous waste characteristic, i.e., it is toxic, corrosive, ignitable, or reactive. ATSDR was created by the Superfund law to deal with the risks posed by HW sites.

²⁰ Frequently asked questions about contaminants found at hazardous waste sites. *US ATSDR*, March 4, 2009, <http://www.atsdr.cdc.gov/toxfaq.html> (has a list of the many chemicals found at HW sites).

²¹ Public health assessment guidance manual. *US ATSDR*, March 12, 2009, <http://www.atsdr.cdc.gov/> (this site has much useful information for the newcomer to HW).



Source of pollutant

Hazardous waste spills from drums or from oil tankers, or it is dumped. It evaporates into air, runs off into surface water, or percolates down into groundwater, or absorbs into the soil

HOW EXPOSURE CAN OCCUR – INGESTION

Ingestion via WATER



Drinking water contaminated by pollutant (from surface water, well water, or bottled water)

Ingestion via FOOD CHAIN



Eating grain or produce contaminated by pollutant deposited from air, or taken up from soil or water



Eating meat, milk, and eggs polluted by deposition from air, or taken up from the soil or in the animal's food

HOW EXPOSURE CAN OCCUR – INHALATION



People or animals breathe in air contaminated by the evaporation of the waste

Figure 12.2

How exposure to hazardous waste can occur. Credit: US ATSDR

- Air If volatile organic chemicals (VOCs) were in the spilled waste, these can evaporate. Direct inhalation by humans would ordinarily be very small unless they live very near the site or they are unprotected on-site workers).
- Food Evaporated VOCs could condense onto vegetation such as the trees and corn plants shown in Figure 12.2. Animals may eat the contaminated vegetation or grain. Later, humans may eat contaminated meat, vegetation, or grain.
- Soil Although soil is not ordinarily a direct exposure source for humans, contaminated soil could affect plants and animals on site.
- Water A portion of the spilled waste could percolate into groundwater or – not shown – runoff into surface water. Groundwater used for drinking is the most likely exposure route for those living near sites.

Health-risk assessments

Before taking action to clean up a HW site, possible risks to people living nearby are assessed. To assess possible exposure, questions that need answers include: what is the route of exposure to the chemicals – ingestion (from food or water), inhalation (from air), or skin absorption? What is the

amount, frequency, and duration of exposure? Who is exposed? In particular, are children exposed? ■ If exposure is occurring, what are possible health effects of the conditions of exposure. About half the NPL sites evaluated since 1992 were deemed to pose a health threat to nearby persons. Another quarter was not believed to pose a threat. The remaining quarter had “indeterminate risk,” i.e. it wasn’t clear if they presented a risk. ■ ATSDR estimates that 20 to 40 million US residents live within 4 miles (6.4 km) of a HW site. About 4 million live within a mile. Many epidemiologic studies have been done on these people. Some indicated a small to moderate increased risk of cancer and birth defects, but others showed no adverse effects. Taken together, some researchers find study results troubling. However, all the studies were based on how close to HW sites the people lived, *not* on actual measured exposures to chemicals. Thus, current studies look at actual exposure by monitoring urine and blood samples for chemicals found at those sites. (Recall how CDC measures exposure to chemicals. See Chapter 4, Section I.)

Other hazardous waste sites

Underground storage tanks

Some HW sites were created by leaking underground storage tanks. Years ago, most storage tanks for petroleum and other flammable chemicals were above-ground. Because these posed fire hazards, underground tanks became popular. But over years of burial, tanks corroded and leaked, contaminating surrounding soil and, sometimes, groundwater. Many tanks are still underground, located beneath gas stations and industrial operations. The EPA has worked with states to remove leaking tanks, and to clean up the contamination they caused. To prevent future leaks the EPA now requires underground tanks to meet specific design, construction, and installation requirements and to have leak detection and leak prevention systems.

Federal sites

Sites on the NPL are only a portion of high priority sites. Of equal or greater importance are the 20 000 sites for which the federal government itself bears responsibility. Some were produced by US Department of Defense Operations (military bases) and many others by the Department of Energy (weapons complexes). The Departments of Agriculture and Transportation created a smaller number. Some of these are described as “toxicologically very complex” because they contain not just the usual HW, but radioactive wastes too. These pose difficult and expensive problems. Estimates of cleanup costs are staggering, perhaps a trillion dollars, spent over 30 years. It is unlikely that all can be entirely cleaned up. High-priority sites, those presenting risks to people living near them are dealt with first.

Questions 12.2

1. How does a hazard differ from a risk?
2. What are reasons that proximity to a HW site does not necessarily mean that a person is highly exposed to its wastes?
3. Only potential risks to human beings are discussed in this chapter. When is risk important to the surrounding wildlife or ecosystem?

SECTION IV

Reducing the risk of hazardous waste sites

You know that pollution prevention is the preferred step in the WMH. But once a spill has occurred it is too late for P². Nonetheless, spills can push companies to pursue P². This happens because of the cost, bother, and bad publicity that result from spills and HW sites. It also happens because companies, along with society at large, have become more aware of the results of indiscriminate disposal that characterized earlier years.

Immediate protections afforded to those living near a site

Of 1300 NPL sites, the US EPA concluded that 2% posed an imminent (urgent) hazard. An imminent hazard is dealt with quickly to avoid continuing exposure to nearby communities and to protect workers. Examples are explosives, or conditions that could lead to contamination of groundwater used for drinking. ▪ Even if a site poses no imminent hazards, actions may be taken immediately to limit possible exposure to waste-site chemicals. Among possible actions: restrict access to the site, provide a different source of drinking water, or issue fish consumption advisories.

Clean up

Once site characteristics are well understood, cleanup possibilities are evaluated. For a NPL site, EPA consults with other concerned parties to select a cleanup remedy from identified alternatives. ▪ The selected remedy must comply with federal, state, and local laws. It must also protect human health and the environment – a controversial requirement: must the site be returned to “pristine” conditions? If it’s to become an industrial site again or a parking lot, can the cleanup stop after 90 or 95% of the contaminants are removed (Box 12.3)? ▪ After selecting a remedy, an engineering design is prepared followed by the construction necessary to accomplish the cleanup. Finally, the remedy is carried out. These actions may require 10 years or more. After cleanup, monitoring must continue for years. If groundwater is being treated, the process could take many more years. Although EPA takes responsibility for the NPL sites, others may perform the actual cleanups. The public has a right to comment at all stages, although some believe their input is not always taken seriously. ▪ Funding cleanup Cleanup is funded in two ways: ▪ If parties responsible for creating the site are identified, they pay. ▪ If parties cannot be identified or if the sites are old ones such as abandoned mining areas or sites that once manufactured town-gas (some from the nineteenth century), *Superfund* pays for the cleanup. Superfund was created by a tax levied on oil, chemical, and manufacturing industries. If the company that was responsible for creating the site now has different ownership, its new owners must take responsibility. This has led companies to become very careful about properties they purchase. For example, Hooker Chemical

Box 12.3

Brownfields²²

A number of reasons exist to explain why a business might not buy a *brownfield* (an abandoned industrial site) to locate a facility. One reason for avoiding brownfields is that the buyer may be required to clean up the land. To avoid potential problems, a company usually prefers *greenfield*, land that is undeveloped. Inner-city Detroit, Michigan, has been devastated by large tracts of abandoned land, that some said resemble a war zone. Nationwide there are about 45 000 brownfields. Strict cleanup standards can inhibit land reuse and mean that undeveloped land is developed. To counter this trend, EPA funds brownfield redevelopment projects. *Site-specific standards* allow a brownfield to be cleaned up to standards consistent with its future use. For some brownfield sites, vegetation including native flora have been reintroduced providing greenery and parks to some urban areas. The city of Pittsburgh, Pennsylvania, sees itself as a national model for brownfield development.²³ It transformed what, for more than a century, were major industrial sites (including mammoth deserted steel mills) and the pollution associated with them into useful and attractive places that also generate tax revenue. Cleanup will be very thorough when reclaimed land is to be used for new housing, retail, entertainment, and research and development.

Company disposed of hazardous waste at Love Canal, but Occidental Chemical, the subsequent owner had to assume the responsibility of remediation. Cleanup of NPL sites has been slow mostly because there are many legal challenges. In 1995, the US Congress allowed the Superfund tax to expire and has not renewed it. Now, Superfund depends on an annual appropriation leading to concern that some sites may not be cleaned up properly or may have to be cleaned up at public expense. Nonetheless, cleanups still seem to be progressing.²⁴ The cleanup of many sites such as those contaminated by the military and the Department of Energy are already government funded.

Cleanup methods

You were introduced above to methods used to treat HW (Table 12.2). Methods used to clean up HW at abandoned sites are similar, but more complex. Consider the complexity of a Love Canal remediation or a cleanup made necessary by finding dozens or hundreds of drums of leaking chemicals.

²² Annual Superfund data shows continuing cleanup progress. *US EPA*, November 22, 2005, <http://yosemite.epa.gov/opa/admpress.nsf/0/177D956E79308A46852570C1006CD11C>.

²³ Brownfields and land revitalization, basic information. *US EPA*, April 23, 2008, http://www.epa.gov/brownfields/basic_info.htm.

²⁴ Dettore, J. N. Brownfield development in Pittsburgh, recycling and reuse of the steel industry's abandoned mills: the environmental transformation of an American industrial city. *Pittsburgh Green Story*, <http://www.pittsburgh-greenstory.org/html/brownfields.html>.

Cleaning up metal contamination

Soil contaminated with lead or other heavy metals is often found at HW and old mining sites.

- One way to deal with this is to excavate the soil, treat it and place it in a landfill dedicated to HW. This option is expensive, and simply moves the problem “away.”
- Another expensive option is to stabilize the metals on site by heating the soil to a temperature high enough to melt the soil into a hard mass (vitrification). Stabilized metals are much less likely to leach.
- A less-expensive on-site stabilization technique is mixing the soil with cement and letting it solidify.
- Or, metals can sometimes be removed from the soil. The method used depends on the metals involved. The *TerraMet* process is specific to lead.²⁵ (1) Separate the contaminated soil into its components (gravel, sand, silt, and clay). (2) Wash the gravel to remove most lead; then return it to the site. (3) Shake the sand in water. Because lead is denser than sand, it settles to the bottom and is removed. Treat the sand itself with a proprietary chemical that dissolves the remaining lead. Return the cleaned sand to the site. Treat the proprietary chemical solution to precipitate the lead from it; recover the lead for recycling. (4) Treat the silt and clay using methods similar to those for sand, and return these to the site.

Bioremediation

Recall the poplar trees capable of accumulating organic solvents. Other living organisms can sometimes be used to *bioremediate* HW sites contaminated with oil or munitions, or to clean up contaminated water or sediments. The microorganisms and plants used must concentrate the contaminant of concern, but not be poisoned by it.

Bioremediation using microorganisms

First, investigate the site as to pollutants present, characteristics of its soil and water, and microorganisms naturally present. Often site microbes have already slowly begun to degrade organic waste. Humans may work to speed up microbial action by providing fertilizer for the microbes. Oxygen may be added in some cases. ▪ A well-known use of bioremediation followed the Exxon Valdez Alaskan oil spill. First a physical cleanup method such as using high-pressure water to wash oil from rocks was used; this was not effective and may have caused harm. But bioremediation helped. Microbes naturally present along the shore had already begun degrading the oil’s hydrocarbons; tidal flux provided oxygen. A nitrogen fertilizer was added to speed the microbial action. Microorganisms that received fertilizer degraded surface and subsurface oil three to five times faster than microbes in unfertilized areas. Oil that could have taken 10 years or longer to degrade naturally broke down in 2–3 years. Microbes could not degrade those hydrocarbons that had become immobilized into an insoluble asphalt-like material. However, the immobilized hydrocarbons were not expected to affect biological systems.

²⁵ Terramet soil remediation system, COGNIS®, February 20, 1997, http://www.epa.gov/ORD/SITE/reports/540_MR-95_535.pdf.

Bioremediation at metal-contaminated sites

Microbes cannot destroy metals, but do sometimes convert them to less hazardous forms. ▪ They may cause reactions that lead to metal stabilization: at one site, microbes converted sulfate to sulfide. Sulfide reacted with metal contaminants to produce metal sulfides, very insoluble chemicals. Basically, the metals were immobilized in place. This is analogous to stabilizing metals in soil by heat or cement, but the microbial treatment is cheaper and more environmentally benign. ▪ In another case, microbes concentrated plutonium, a dangerous radioactive element present at a site. This ability has promise to help clean hazardous-weapons-production sites. ▪ Natural microbes are typically used in remediation projects, but effort is ongoing to bioengineer organisms capable of degrading specific chemicals. A bioengineered organism is one into which one or more genes have been introduced to make it capable of carrying out a task it previously was unable to accomplish. Natural microbes can degrade the persistent PCBs and dioxins, but do so very slowly. The challenge is developing organisms that rapidly destruct hazardous chemicals, while not themselves becoming a new environmental risk.

Phytoremediation

Hundreds of plants and trees have been identified that can accumulate metals from soil or water, sometimes to high concentrations – they are hyperaccumulators – and do so without ill effects to themselves. Plants hyperaccumulate metals such as nickel, zinc, copper, cadmium, selenium, and manganese. Some hyperaccumulate metals up to 40% of their weight. Why they hyperaccumulate is unknown except that it may give them a metallic taste, which insects that otherwise would feed on them do not like. Plants can subsequently be harvested and burned to recover the metals. One aquatic plant took water contaminated with the explosive TNT from a concentration of 128 ppm down to 10 ppm. Envision a HW site covered with attractive plants or trees that are cleaning it up and you see the appeal of phytoremediation. However, it is not yet widely practiced commercially.

Bioremediation's potential

The potential, whether with microbes or plants, is tremendous. It costs less than most other methods and it works with natural systems. Yet bioremediation raises a familiar problem – it cannot degrade or take up all the contaminant. ▪ Consider a microorganism that degrades an organic chemical. It does so because it uses it as a nutrient or as a source of energy to promote its own growth. When the concentration becomes low, the chemical no longer supports microbial growth. When growth stops or slows, so does the accelerated degradation of the chemical. ▪ Likewise, for a plant that hyperaccumulates, it does not use all the metal in soil or water.

Questions 12.3

1. Organic HW can sometimes be treated by spreading it on land and allowing natural processes to degrade it. (a) What natural factors contribute to such degradation? (b) What are the potential environmental health and safety shortcomings of land spreading?
2. Consider hazardous chemicals buried in sediment. What natural factors, available in the water itself, are not available in the sediment to assist in the degradation?

3. Bioremediation has great potential. What risks might it have?
4. Among methods used to remediate lead-contaminated soil are: (1) soil excavation and removal; (2) thermal stabilization; and (3) the TerraMet process. (a) What are the environmental impacts of each? (b) Which do you believe is preferable and why?
5. CERCLA or the Superfund law has stimulated more responsible waste disposal and more P² efforts. How did Superfund do these?

SECTION V

International transport of hazardous waste²⁶

Was it a criminal act for Taiwan to ship thousands of tons of concrete waste into Cambodia, an impoverished nation for disposal? Consider that the waste was heavily contaminated with mercury, but had no warning labels let alone any safeguards.²⁷ The waste reportedly caused the death of one person unloading it, and that of a villager who took a shipping bag home and slept on it. People panicked and as many as 10 000 left their homes. Other wastes transported into impoverished countries by more well-to-do nations include drums of HW, and medical wastes including hypodermic needles and used bandages concealed in containers identified as “paper” (for recycling). Moreover, even when waste is properly identified, impoverished nations ordinarily lack infrastructure to handle it safely or properly dispose of it. Waste is handled in a manner that the countries of origin wouldn’t allow to occur on their own soil. Figure 12.3 shows children next to smouldering electronic waste, which was illegally imported into Nigeria.

The Basel Convention^{28,29}

To address such problems, the UN negotiated a treaty, the *Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal*. ■ Its objectives are: (1) minimize hazardous waste generation; (2) dispose of hazardous wastes close to where they are generated; and (3) reduce the international movement of

²⁶ Caution: hazardous waste. *UNEP*, 2002, <http://www.grid.unep.ch/waste/html/file/34/35/hazardous/caution.html>.

²⁷ French, H. Can globalization survive the export of hazard? Toxic waste management. *USA Today*, May, 2001, http://findarticles.com/p/articles/mi_m1272/is_2672_129/ai_74572238/pg_2.

²⁸ (1) The Basel Convention at a glance. *UNEP*, <http://www.basel.int/convention/about.html>. (2) Origins of the Convention and questions and answers regarding it. *UNEP*, <http://www.basel.int/convention/basics.html>.

²⁹ Text of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal. <http://sedac.ciesin.org/entri/texts/basel.transboundary.hazardous.wastes.1989.html>.



Figure 12.3 Nigerian children next to smoldering electronic waste illegally imported. Credit: Basel Action Network

hazardous wastes. The Convention prohibits transboundary movements of hazardous or other wastes without *prior written notification* by the nation exporting the waste to authorities in the country importing it. Shipments must also be accompanied by appropriate documents. There are outright bans on the export of hazardous wastes to certain countries. The Basel Convention is a global agreement ratified by 170 countries and the European Union (EU). The United States is the only industrialized country not to have ratified it.

Reducing hazardous waste generation

The Basel Convention aims to minimize HW generation. Some steps taken in Europe and the United States specifically push P², Design for the Environment (DfE), or industrial symbiosis. ▀ Although an emphasis is placed here (below) on waste electronics (Box 12.4), keep in mind that many hazardous wastes exist. These include contaminated liquid organic solvents, and aqueous waste contaminated with metals, see Table 12.2. ▀ One approach used to minimize chemical HW is green chemistry, which is DfE directed toward chemicals. Green chemistry works to design chemicals more environmentally benign than the chemicals they replace, but performing the same functions, and to produce them more safely and in ways that produce less HW (see Chapter 18).

Box 12.4

Electronic waste

An Ocean of Electronic Discards

Each year individuals and businesses buy many millions of computers, televisions, and other electronics. Typically, these are not durable, and it is often less expensive to buy a new device than repair the old. Even when repair is possible, it is often expensive. Also, as better and faster computers and other electronics are created, people often prefer these over what they already have. Hundreds of millions of obsolete computers have been discarded, and computers are but one product among many electronic products. Electronic waste volume is growing three times faster than MSW as a whole. The US EPA reports that Americans removed more than 300 million electronic devices from their homes in 2006. ■ Discarded electronics are difficult to disassemble, and increasingly uneconomical to recycle because their valuable metal content has been decreasing.³⁰ Silicon chips were previously gold backed, but no longer. Metals in printed wiring boards have decreased too. Once-valuable steel computer housing is now plastic. ■ Most discarded US computers, monitors, printers, and other electronics go to landfills. A few states including Massachusetts and California have banned cathode ray tubes (CRTs) from landfills. ■ Only 15–20% are “recycled.” Several state governments subsidize electronic collection and recycling. Because this is expensive, some lower costs by using prison labor.

Illegal movements

Private US companies may sponsor collection events: citizens wanting to recycle waste electronics take them to these events. Some reputable recyclers do actually repair the newer electronics that they collect for reuse and recycle materials from older electronics. However, perhaps 80% of collected electronics are exported to less-developed nations, especially China³¹ where it costs only 10% as much to process waste electronics as in the United States. Labor costs are very low, safety and environmental regulations ignored. See Figure 12.4. The US Government Accountability Office found many “recyclers” cultivate an “environmentally responsible” image, some even holding Earth Day events to collect the e-waste they export.³² However, the EU and other industrialized countries have ratified the Basel Convention, which forbids EU countries from making such shipments.

How to Make a Computer Hazardous

Discarded electronics provide a vivid illustration of what can happen when wastes are sent to nations lacking the infrastructure to handle them: even a non-hazardous product can become

³⁰ Computers do contain tiny amounts of valuable metals, cadmium, chromium, lead, beryllium, mercury, even bits of gold. These are recoverable, but not simply so, and components contain too little of the metals to make recycling economical in industrialized countries. Electronics also contain brominated flame retardants, and billions of pounds of plastics. However, some P² has occurred: a computer or television CRT previously contained several pounds of lead, now three out of four manufacturers are producing lead-free panels for CRTs.

³¹ Following the trail of toxic e-waste by CBS’ 60 Minutes. *Toxic Trade News* (BAN), November 9, 2008, http://www.ban.org/ban_news/2008/081109_following_the_trail.html.

³² Johnson, J. Passing the recycling buck, federal investigators find recyclers willing to ship hazardous electronic waste to world’s poor. *Chemical & Engineering News*, **86**(39), September 29, 2008, 30–32.



Figure 12.4 Woman prepares to smash a computer monitor cathode-ray tube to recover the copper-containing yoke. Credit: Basel Action Network

hazardous. In several Asian countries, adults and children work under primitive conditions to “recycle” electronics. Hundreds work in sheds or outdoors, hammering computers to recover wires, metals, and other components. Unprotected workers are exposed to acid and coal-burning fumes as they dip electronics into hot acid baths fueled by coal to recover tiny amounts of gold. Other salvage metals including copper from wires, mercury from batteries and switches, and a bit of beryllium from computer motherboards. Workers are fully exposed to emissions from these operations. Electronics’ plastic casings are burned, shredded for use in new low-quality products,

or just dumped. Guiya, a Chinese town, is littered throughout with piles of motherboards, hard drives, keyboards, and glass from monitors. Runoff carries contaminants into local rivers and rice paddies. A river runs through Guiya that has lead levels many times greater than World Health Organization (WHO) health-based standards. This river, black with pollution also carries pieces of plastic and shards of glass. Drinking water must be trucked into Guiya. Workers want these jobs although they suffer burns, skin injuries that heal improperly, and hacking coughs resulting from poor ventilation. Some children work full time. Those remaining in school are affected by the air pollution. China has banned these imports, but importers bribe customs officers. As of late 2008, the trade continues. China has requested that countries discontinue shipping electronic waste because otherwise – even if China successfully stops the imports – wastes will just go to another impoverished country. However, there are a few responsible operations: Samsung Corning has a CRT recycling operation in Malaysia which safely recycles the glass.

Responsible management of electronic waste

▪ As signatories to the Basel Convention, 179 countries have banned hazardous waste shipments into less-developed countries except under carefully defined conditions. ▪ The EU took another very significant action by passing a Waste Electrical and Electronic Equipment Directive (WEED). Starting in 2005, WEED mandates a *take-back* program (also called *extended producer responsibility*, EPR): manufacturers must take back and recycle their own products. For 10 years, they are allowed to charge consumers a fee to pay for recycling older electronics manufactured before the law's passage. WEED's purpose is to promote recycling and reuse of electrical and electronic products. It also asks manufacturers to phase out lead and other hazardous substances, especially certain fire retardants, in electronics. Japan has taken similar actions. DfE efforts by individual companies are not well developed, but meaningful changes have begun. ▪ To enhance worldwide electronics management, the UN along with government agencies and industry, is undertaking StEP (Solving the E-Waste Problem): it intends to develop worldwide policies stimulating the redesign of electronics for reuse and recycling.³³ StEP is pledged to help poor nations develop the ability to manage discarded electronics because handling discarded electronics has the potential to provide *good* jobs.

United States

Environmental organizations want the United States to also have mandatory take-backs. They ask too for a system to collect used electronics while assuring environmentally-sound recycling. ▪ United States industry does not want take-back mandates, instead advocating shared financial responsibility among companies, consumers, and government. Consumers could pay a fee when buying electronic equipment to assure money for proper recycling. ▪ The US EPA urges manufacturers to view "waste" electronics as a raw material source and to begin to

³³ Burger, A. Taking on the e-waste problem, *Environmental News Network*, December 31, 2007, http://www.enn.com/top_stories/article/28393.

consciously use DfE to move toward less or even zero waste.³⁴ Maine, Washington, California, and Maryland have laws requiring manufacturers to pay for recycling old computers, monitors, and TVs. As more states develop requirements, manufacturers may come to prefer a uniform national law.

Corporate actions³⁵

▪ *Panasonic* has taken steps to design-for-disassembly, and design-for-recycling. It has cut the number of plastic types in its television sets from 13 to 2, and labels each to allow easier separation during disassembly and subsequent recycling. It cut the time to disassemble its TVs from 142 to 78 s. It uses 10% recycled glass in its CRT (the funnel-shaped glass in monitors) and plans to make TVs with lead-free solder.³⁶ ▪ *Sony* has a national system to collect and recycle old electronics responsibly: "We don't allow recyclers to export to developing countries. We do our own audits, but need the help of the federal government" so as to have a uniform nationwide system." *Hewlett-Packard* has a Product Take Back operation, recycling more electronics than any other company in the United States.

Technology

Processes to manage discarded electronics are not simple. Electronics must be collected, sorted, and disassembled. Recovering metals from complex electronics requires large-scale, high technology processing. Printed circuit boards (PCBs) are the most valuable component; they are mainly composed of copper, lead, and tin. Although there is technology to do so, it is still a challenge to recover PCBs as they must be separated from many other electronic components. Work is ongoing to improve the efficiencies of such separations.³⁷ However, the ultimate goal is not to waste electronics management, but DfE – producing electronics that are straightforward to disassemble and reuse. Such electronics would not become waste, but become an important contribution to closed cycle operations.

³⁴ (1) Promoting and practicing environmental stewardship for electronic products wastes. *US EPA*, December 4, 2008, <http://www.epa.gov/epawaste/partnerships/stewardship/products/electronics.htm>. (2) Green electronics. *US EPA*, December 24, 2008, <http://www.epa.gov/oaintrnt/practices/electronics.htm>. (3) Wastes. Partnerships, product stewardship: electronics. *US EPA*, December 4, 2008, <http://www.epa.gov/epawaste/partnerships/stewardship/products/electronics.htm>.

³⁵ One company, Redemtech's Sustainable Computing Initiative helps businesses extend the life of purchased equipment, and not just buy newer technology. They work to redeploy technology within a firm or as donations or remarketing. They advocate a zero-landfill disposal policy and have a tracking system to fully account for every item received. It supports high standards for e-waste recycling through the Basel Action network. Moreover, it claims significant savings for the businesses with which it works. <http://www.greenercomputing.com/news/2008/10/08/redemtech-launches-sustainable-consulting-initiative>.

³⁶ Greenpeace developed a Guide to Greener Electronics, how the companies line up. *Greenpeace*, August 2006, <http://www.greenpeace.org/international/campaigns/toxics/electronics/how-the-companies-line-up>. Greenpeace ranks 18 manufacturers of personal computers, mobile phones, TVs and games consoles according to policies on toxic chemicals, recycling, and climate change.

³⁷ A good description of ongoing work to improve technologies is: Betts, K. Producing usable materials from e-waste, new technologies being developed in China and Eastern Europe may create usable materials from e-waste. *Environmental Science & Technology*, **42** (18), September 15, 2008, 6782–6783.

Other life-cycle issues

Manufacturing an average 53-lb (24-kg) desktop computer plus its monitor requires at least 10 times its weight in fossil fuels and chemicals. Pound for pound this is much more than required for an automobile or refrigerator, which require one-two times their weight in fossil fuels.³⁸ These factors must be considered too when doing DfE.

Questions 12.4

1. The EU expects that the Waste Electrical and Electronic Equipment Directive to stimulate DfE among those who manufacture electronics – explain why this is likely to happen.
2. Explain how DfE lead to closed-cycle operations or to industrial symbiosis.
3. (a) The United States has no take-back directive. Do manufacturers of electronics nonetheless have ethical responsibilities for their products? Explain what that responsibility might look like.
4. Itaru Yasui of the UN University has stated: “Collectively, the role of consumers is enormously important to the world environment, whether purchasing, using or disposing of electronic equipment.” Explain what this could mean in actions that you yourself could take.

Box 12.5

“Throwing away” a ship³⁹

Shipbreaking is the dismantling of old ships for scrap metal and other valuables.⁴⁰ It was once carried out in the United States and Europe. In the 1970s as labor costs and environmental regulations increased, the industry moved to Korea and Taiwan. Lastly, it moved to the poorest countries including India, Bangladesh, and Pakistan. About 90% of the 700 end-of-life ships a year end up in impoverished countries. Hazardous substances in the ships include asbestos, PCBs, and heavy metals such as lead, mercury, and cadmium. Workers, often barefoot, dismantle ships by hand using tools such as hammers and blowtorches. They are exposed to toxic fumes, excessive noise, and heat and have no occupational safety and health regulations.⁴¹ Accident rates are high and there is much pollution around the operations. Bangladesh wants the steel that the ships contain, steel that is several times cheaper to produce by re-rolling from dismantled ships than milling it from fresh ore. Ore must be imported because the country “is a river delta with no mineral deposits, just sand and earth.”

Figure 12.5 shows a step far along in ship dismantlement, recovering copper from wiring by burning off its rubber casings. Photographer Claudio Cambon comments that this sight is

³⁸ Kuehr, R. and Williams, E. (eds.) Computers and the environment, understanding and managing their impacts. In *Eco-Efficiency in Industry and Science Series (ECOE 14)*. Dordrecht/NL: Kluwer Academic Publishers & United Nations University, October 2003.

³⁹ Breaking more than ships. *UNEP*, 2002, <http://www.grid.unep.ch/waste/html/file/40-41/shipbreaking.html>.

⁴⁰ Ship dismantling. *European Commission, Environment*, January 1, 2009, <http://ec.europa.eu/environment/waste/ships/index.htm>.

⁴¹ Langewiesche, W. The shipbreakers. *Atlantic Monthly*, **286**(2), August, 2000, 31–49.



Figure 12.5 Shipbreakers burning rubber casing of copper wire in Chittagong, Bangladesh. Credit: Claudio Cambon, Marina Del Rey, Calif. (Copyright 1998)

common in shipbreaking yards. This “dramatically-polluting activity . . . sadly typifies the level of safety and protection available to workers and the environment not only in shipbreaking, but in all of Bangladesh, a poor country with little infrastructure of any sort.” Although the work is dangerous and polluting, the jobs are wanted. Referring to hazardous materials in the ships that could affect their health, workers told Cambon “Why worry about what might kill me 20 years from now when I can’t see from here to 1 month from now, because I can’t feed myself and my family without this job?” Cambon was last in Bangladesh in 2004, but keeps in touch with the beaching master. In 2009 he noted that “the industry is still unregulated, the government gets to buy cheap steel and charge a lot of taxes on the industry.” Everything remains “low tech” in how ships are dismantled, the workers are unprotected, and suffer in the short and long term. Cambon asks: “Where is the compassion? . . . This is what things will always look like unless there is a compelling reason to change.” ■ More broadly, shipbreaking remains controversial. In 2006, India refused to accept an arriving French warship because it contained almost 50 tons (45 tonnes) of asbestos. It returned to France and, eventually, ended up in Britain to be broken up.⁴² The EU in 2008 proposed measures to make ship dismantling safer both for workers and the environment.⁴³

⁴² Toxic French warship to be dismantled in Britain. *AFPGoogle*, July 1, 2008 <http://afp.google.com/article/ALeqM5iOEsl8VqfzzyzvqNjDvCYN0PzAjw>.

⁴³ EU: safer ship dismantling. *MarineLink.com*. November 21, 2008, <http://www.marinelink.com/Story/ShowStory.aspx?StoryID=213635>.

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Society can move to the next phase of the industrial revolution that runs without fossil fuels, or it can ignore the problem, sentencing humanity and other creatures to struggle on an increasingly desolate planet.

Dr. James E. Hansen, director of the National
Aeronautics & Space Administration's Goddard
Institute of Space Studies

Chapter 13 provides an overview of energy production and use as a major source of pollution, and how that pollution may be alleviated. Section I surveys world demand for energy. Section II concentrates on motor vehicle pollution and how we can reduce that pollution. Section III delves into pollution from electricity generation and use and means to reduce that pollution. Section IV briefly examines nuclear power. Section V summarizes renewable sources of energy. Finally Section VI looks at plans directed toward sustainable energy generation.

SECTION I

Energy demand, usage

Overviewing world energy use

The continuing increase in world energy demand is being viewed with alarm. Between 1970 and 1997 world energy consumption nearly doubled, and is projected to grow 57% between 2004 to 2030 (Figure 13.1).¹ Worldwide, total energy use is projected to grow from 447 quadrillion British thermal units (Btu) in 2004 to 702 quadrillion Btu in 2030.² In less-developed countries energy consumption is projected to rise three times as fast as in OECD countries. And as energy use increases, so does pollution. ■ Consumption would be higher still except that *energy intensity*, the amount of energy used to per dollar of gross domestic product (GDP) produced is declining, especially in less-developed countries. The United States uses about a quarter of the world's energy, almost twice more than Japan on a

¹ International Energy Outlook, DOE/EIA-0484, Chapter 1: World energy demand and economic outlook. *EIA*, 2008, <http://www.eia.doe.gov/oiaf/ieo/world.html>.

² International Energy Outlook. Washington, D.C.: US Department of Energy, May, 2009, <http://www.eia.doe.gov/oiaf/ieo/world.html>.

Table 13.1 Energy use in selected countries (tonnes oil equivalent/person)

United States	7.8
Russia	4.5
Japan	4.2
OECD, Europe	4.1
China	1.3
India	0.5
IEA data for 2005	
OECD is an organization of 30 mostly prosperous countries.	

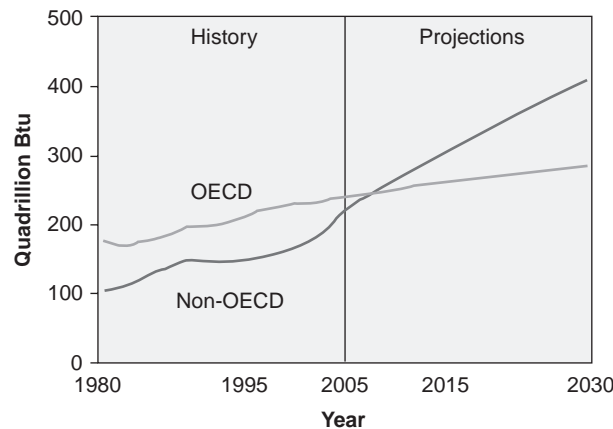


Figure 13.1 Increase in world energy consumption. The OECD countries are the world's well-to-do countries; non-OECD are the rest. Credit: US DOE/Energy Information Administration

per capita basis and many times more per capita than in less-developed nations (Table 13.1). Fossil fuels furnish about 90% of the world's energy (Figure 13.2). The planet has abundant coal resources, but oil reserves are decreasing. Although expert opinion differs, most agree that we are uncomfortably close to having used half the world's oil. Thereafter, oil prices are expected to rapidly rise. Other sources of oil such as oil shale are more environmentally damaging and more expensive.

Up to half the world's population doesn't even buy fossil fuels or else buy very small amounts. Impoverished individuals do not contribute to fossil-fuel pollution. They rely, as did their and our ancestors, on wood, if available, for cooking and some warmth. Even now over 60% of the wood consumed in the world is used as fuel. Other fuels used by those using little or no fossil fuels are agricultural wastes and dried manure. In China, people burn coal, but its quality is often poor and responsible for human poisonings and environmental ills. Coal mining and oil recovery operations can ruinously impact local environments and, when burned, pollute, sometimes heavily. Table 13.2 reviews the major environmental impacts of burning fossil fuels – global climate change, acid deposition, ambient air pollution, and eutrophication. Continued fossil fuel burning raises the question, how much more pollution can our environment absorb? When projections are made to year 2020, it appears that only

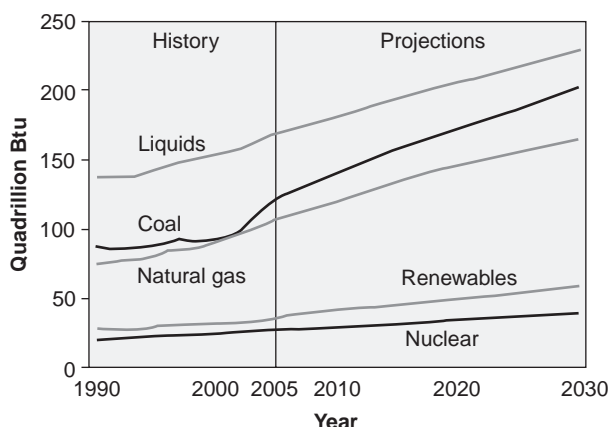


Figure 13.2

Fuels burned around the world and demand for them (1990–2030). Credit: US DOE/EIA

Table 13.2 Review of air pollutants resulting from fossil fuel burning*

Issue and pollutants produce	Fossil-fuel responsible ¹
Global climate change	
Carbon dioxide (CO ₂)	Coal burning produces more CO ₂ than petroleum, and petroleum more than natural gas
Methane	The methane that arises from fossil-fuel use primarily comes from coal and petroleum recovery and natural gas pipeline leaks.
Acid deposition	
Sulfuric acid and sulfate	Sulfuric acid and sulfate are formed in the atmosphere from SO ₂ .
Nitric acid and nitrate	Nitric acid and nitrate are formed in the atmosphere from NO _x .
Ambient air	
Sulfur dioxide (SO ₂)	SO ₂ is emitted in especially high amounts by coal-burning facilities, and to lesser extents by burning oil and natural gas.
Nitrogen oxides (NO _x)	NO _x forms – not from the fuel – but from a reaction between nitrogen and oxygen during high temperature combustion. Motor vehicles predominate in urban areas. Power plants are also important
Carbon monoxide(CO) Ozone (O ₃)	CO is a product of incomplete combustion. In urban areas, up to 90% is from gasoline combustion.
Particulates	O ₃ is not a primary pollutant, but is formed from precursors. Motor vehicles are a major source of NO _x and VOCs, which lead to O ₃ . Particulates are emitted during coal burning and to a lesser extent from oil burning. ▪ Metals are emitted as particulates (excepting elemental mercury). ² ▪ The particulate, carbon soot results from incomplete combustion. Most PAHs are emitted as particulates.
VOCs	
Hydrocarbons PAHs	Hydrocarbons are the major VOCs emitted from gasoline-burning vehicles. Some PAHs are volatile. ³

Table 13.2 (cont.)

Issue and pollutants
produce

Fossil-fuel responsible¹

Eutrophication

Nitrogen oxides (NO_x)

Although fertilizer is the greatest source, motor vehicles contribute increasing amounts.

¹ Fossil-fuel burning is not the only source of many of these pollutants, but is a major source.

² Coal and oil burning emit trace amounts, but metals are persistent and can build up in the environment.

³ PAHs are incomplete combustion products from burning coal, oil, or other carbon-containing fuel. Heavier PAHs are not VOCs, but are found in soot.

about 6% of the energy used within the OECD nations will come from renewable sources such as solar or wind.

SECTION II

Motor vehicles

In the New York City of 1900 horses deposited several million pounds of droppings each day, filling the air with pungent fumes; dried droppings entered the air as pathogen-carrying dust. When motor vehicles displaced horses, tuberculosis rates fell dramatically. Today we depend almost entirely on gasoline-powered motor vehicles, and it is they that pollute. In 1990, US motor vehicles emitted 65% of the country's carbon monoxide (CO), a third of the nitrogen oxides (NO_x), and 29% of the volatile organic chemicals (VOCs). They also emit soot-containing particulates, PAHs, and metals (Table 13.2). Motor vehicle emissions are higher in urban areas: in the San Francisco of 1990, cars emitted 75% of the city's CO, 58% of NO_x, and 38% of VOCs. Auto pollution pulls many US cities out of compliance with federal air quality standards, most often in summer months. In the United States, automobiles also generate about 25% of the country's greenhouse gases; an average vehicle produces its own weight in carbon each year.

Pollutants and problems³

In the United States and Canada, over half the cars sold – until very recently – were Sports Utility Vehicles (SUVs), minivans, and light trucks. In 2008, US motor vehicles averaged

³ As of 2009, much of the information in this paragraph is in transition as economic conditions have inhibited car purchases and, to some extent, traveling.

21 mpg (8.9 km/l),⁴ about 6% lower than the high point attained in 1987 – and that was only 22 mpg (9.3 km/l). Until late 2008, many more cars were being sold than at any previous time; for many years auto ownership grew six times faster than the population. And each car traveled more miles than did those of earlier years.⁵ Considering these facts, it was not surprising that a UN study showed that US and Canadian citizens use nine times more gasoline than the global average. All forms of transport put together consume about a third of the energy used in the United States. More roads continue to be built to “solve” the congestion created by the increasing millions of vehicles. Roads add to the burden of impervious surfaces and thus to polluted runoff to water, and to disruption of wildlife habitat. And adding roads doesn’t solve congestion. As University of California Professor M. Wachs notes, “You can never build enough roads to keep up with congestion. Traffic always rises to exceed capacity.” ■ Many European cities have population densities four times greater than American cities. Shopping and other facilities are close enough to homes that individuals can make up to 50% of their trips on foot or bike. About 10% use energy-efficient public transit. Trains are, per passenger, six times more energy efficient than automobiles. In contrast US individuals make 87% of their trips by car and only 3% via public transit although, as fuel prices have risen, that percentage is growing. Author Molly Sheehan states, “US drivers consume roughly 43% of the world’s gasoline to propel less than 5% of the world’s population.”⁶ Burning gasoline exerts a heavy environmental price, and dependence on foreign oil threatens national energy security. Nonetheless, gasoline use has continued to grow. Manufacturing and fueling cars is the world’s biggest industry, and a vehicle can produce as much pollution during its manufacture as over its driving lifetime. ■ And remember the whole life cycle: In 1995, a car used nearly 1800 pounds (820 kg) of steel, 398 pounds (180 kg) of iron, 188 pounds (85 kg) of aluminum, and 246 pounds (112 kg) of plastics. Thereafter, as Americans bought larger vehicles, resource use has become higher still. ■ And beyond cars are trucks, farm machinery, snowmobiles, all-terrain vehicles, and gasoline-driven appliances of all types, including lawn mowers and leaf blowers. As with multiplying brooms in the story of the Sorcerer’s Apprentice, petroleum-powered vehicles and appliances have multiplied out of control.

Reducing air pollution from motor vehicles

Recommendations include: mandating that cars have greater fuel efficiency and use less polluting fuels; raising fees charged on cars; and aggressively promoting carpooling.

⁴ Cars and light trucks, fuel economy trends, 1975–2008. *US EPA*, January 14, 2009, <http://www.epa.gov/otaq/fetrends.htm>.

⁵ In what author Hertsgaard says “must rank as the great corporate crimes of the century, General Motors secretly joined with Standard Oil of California, Firestone Tire and Rubber, Phillips Petroleum, and Mack (Truck) Manufacturing in 1932 to form National City Lines . . .” This syndicate bought about 100 railways and trolley lines in 45 US cities, shut them down and tore out their tracks. Their “punishment” was a \$5000 fine in 1949. Meanwhile, highways were being built, and it was to private cars – exactly as the conspirators desired – that Americans turned.

⁶ O’Meara Sheehan, M. *City Limits: Putting the Brakes on Sprawl*. Worldwatch Paper 156. Washington DC: Worldwatch Institute, 2001, <http://www.worldwatch.org/node/834>.

Reducing or eliminating auto emissions is discussed below. Remember that cars also pose other major problems. Roads destroy communities when high-speed, high-traffic roads bisect them, and disrupt wildlife habitat and destroy farmland as people leave cities.⁷ Beyond more air pollution from increased driving, is increased runoff of polluted water containing oil, chemicals, tire shreds, and the like.

Reducing air pollution from cars

By mandate The 1990 US Clean Air Act Amendments (CAAA) mandated steps to reduce motor vehicle pollution from cars, buses and trucks, non-road vehicles, boats, farm equipment, bulldozers, lawn and garden devices, and construction machinery. Tailpipe emissions were tightened. Cities not in compliance with EPA standards were expected to reduce hydrocarbon emissions 25–29%, toxic emissions 20–22%, and NO_x emissions 9–10%. Many approaches were used to accomplish this. ▪ By conservation The CAAA asked the smoggiest cities to encourage alternatives to people driving alone. In especially polluted areas, businesses employing more than 100 people were asked to find ways to increase the number of passengers per vehicle commuting to work and in work-related trips, and, to further reduce car use, encourage carpooling and provide incentives to carpool. To encourage biking, provide bike paths and a place to shower after bikers get to work. Most important in the long run is redesigning cities to make walking, bicycling, and use of public transport more convenient.

Methods used to reduce air pollution

- Carbon monoxide (CO) Motor vehicles are the major source of CO emissions. Two CAA programs addressed this problem. 1. Greater CO emissions occur in cold weather when fuel burns less efficiently and pollution control equipment works less well. Cold-engine emissions may represent 75% of emissions on short trips. Manufacturers had to modify vehicles to lower cold-engine emissions. 2. Because CO is a product of *incomplete* combustion, the EPA asked cities out of compliance with CO standards to use gasoline to which an oxygen-containing chemical was added; more oxygen assists in converting carbon *monoxide* to carbon *dioxide* and thus reduces CO in the exhaust.⁸
- Ozone (O₃) The EPA characterizes ozone as the United States's most serious and persistent air quality problem. Thus, restrictions were placed on the pollutants, hydrocarbon, and

⁷ A US Union of Concerned Scientists evaluation concluded that, among our personal habits, it is transportation – and driving cars in particular – that is most environmentally destructive. Moreover, 40 000 Americans die in accidents each year. Worldwide, about 900 000 a year die. Many recommend the re-urbanization of America, i.e., moving back into more compact communities. This would benefit public transport, and increase walking and biking to get groceries and other necessities. Professor Tim Gutowski of Massachusetts Institute of Technology notes that the automobile even threatens itself. This is true because infrastructure and roadway construction cannot keep pace with ever-increasing auto use especially in locales with already high population densities.

⁸ Previously, the UNITED STATES used methyl tertiary butyl ether (MTBE) to provide oxygen, but MTBE proved more water soluble than expected and became a widespread water contaminant. The oxygen-containing chemical, ethanol (common alcohol) is now used to furnish oxygen.

NO_x emissions, which lead to ozone formation. To reduce hydrocarbon evaporation from gasoline an EPA program required gasoline be reformulated to contain hydrocarbons less likely to evaporate; mandated devices that trap gasoline vapors from the engine and fuel system; and trap emissions that humans are exposed to during refueling.

- **Inspecting and maintaining vehicles** About 10% of vehicles emit 50% of car emissions in the United States. This 10% includes old vehicles plus improperly maintained vehicles of all ages. Some locales, out of compliance with the federal ozone standard, must have inspection and maintenance programs to identify vehicles that emit VOCs and NO_x above specified levels. Owners must repair or take these vehicles off the road. On occasion, a company will pay to repair cars that flunk the test or to buy and scrap the vehicles. Sunoco did this in Philadelphia to achieve a partial offset against its own increased emissions when it expanded its refineries.

Modifying Vehicles for Better Fuel Economy

European cars have better average fuel economy than North American ones, and additional directives will continue to increase their efficiency. Japan too has passenger cars getting higher, sometimes much higher, miles per gallon. However, US manufacturers have resisted mandates to make cars that have better fuel economy. Until very recently, many Americans continued to buy large vehicles regardless of fuel economy. Moreover, the US Congress has barely improved national fuel economy standards over many years, which many consider astonishing considering that the United States in 2008 had to import about two-thirds of the petroleum that it uses⁹, and despite fears of instability in oil-rich Mid-Eastern countries.

Low-emission and zero-emission vehicles

- Because California has suffered severe air pollution from cars for many years, its Air Resources Board has been at the forefront of setting lowered emissions standards, and a number of other states accept California mandates as their own. In 1990, California adopted a zero-emission mandate requiring 10% (about 150 000) of new cars sold in the state each year be zero emission by 2003. However, the Board, under pressure later ruled that gas–electric hybrid cars (see below) and vehicles burning cleaner gasoline were acceptable toward meeting state goals. In 2008, it scaled this back to only requiring 7500 zero-emission vehicles (to be powered by electricity or hydrogen fuel-cells) by 2014. However, the Air Board is still requiring automakers to sell 60 000 plug-in hybrid vehicles in California while developing the technology to meet a zero-emission standard.
- Meanwhile, some newer car models have reduced emissions 90%. Most significantly, in 2001, the Honda Insight and the Toyota Prius entered the US market. These are powered by hybrid electric–gasoline engines. Pure electric vehicles are limited in the distance they

⁹ *The World Factbook, United States*. Central Intelligence Agency, updated biweekly, <https://www.cia.gov/library/publications/the-world-factbook/fields/2175.html?countryCode=us&rankAnchorRow=#us>.

can drive between recharging. However, hybrids are partially fueled by gasoline and their (lightweight nickel–metal hydride pack) batteries are charged in a totally different manner; batteries charge via regenerative braking, i.e., the electric motor harnesses kinetic energy from the forward momentum of the vehicle whenever the car decelerates. Moreover, hybrid bodies and frames are made of lightweight materials designed to keep drag low. Depending on several factors, they obtain 50 to more than 60 mpg, and are served by the gasoline infrastructure already in place. ▪ Purely electric vehicles don't pollute at all although the electric power plants recharging them do. However, society controls emissions from a limited number of electric power plants more efficiently than emissions from millions of individual vehicles; also, electric power plants are usually found outside the most polluted urban areas thus relieving urban pollution. ▪ Solar-powered vehicles are zero-emission vehicles too, but are a long way from reaching commercial status.

Alternative motor fuels to lower emissions

The CAA did not address *flexibly fueled vehicles* (FFVs); these don't use gasoline, but different less-polluting fuels such as natural gas, propane, electricity, biodiesel,¹⁰ and potentially hydrogen. ▪ Propane fuels hundreds of thousands of US vehicles, still only a tiny percentage of the total cars. Vehicle maintenance costs and engine wear are lowered because the clean-burning propane leaves no lead, varnish, or carbon deposits, and has lower emissions of ambient air pollutants. And because propane and natural gas contain less carbon than gasoline, emissions of the greenhouse gas, CO₂ are reduced. ▪ A major advantage to those driving gasoline-powered cars is an established service infrastructure, fueling stations, mechanics, etc. So, if FFVs are to succeed, an infrastructure must be available to fuel and service them. To prod infrastructure development, the US Energy Policy Act of 1992 required that 75% of the light duty fleet owned by federal agencies be FFVs. However, compliance has been spotty. Some local and state governments and private companies have bought a limited number of propane-fueled buses. ▪ A tiny but important set of FFVs are those powered by hydrogen fuel cells.

Hydrogen fueled cars for zero emissions?

A zero-emission vehicle of great interest is the hydrogen fuel-cell powered auto, which emits little more than hot water, and no CO₂. A fuel cell converts chemical energy directly to electric current (Figure 13.3). Its engine makes little noise, and has low maintenance costs.¹¹

¹⁰ One definition of biodiesel comes from the web: biodiesel is a type of biofuel made by combining animal fat or vegetable oil (such as soybean oil or recycled restaurant grease) with alcohol. It can be directly substituted for diesel as a stand-alone fuel (called B100, for 100% biodiesel) or be used as an additive. <http://www.mtpc.org/cleanenergy/energy/glossarytechfuels.htm>.

¹¹

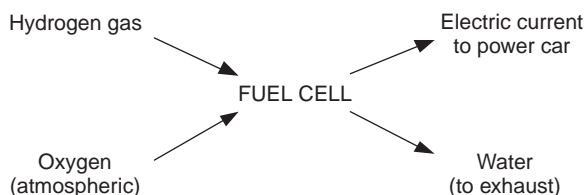


Figure 13.3

Hydrogen reacts with oxygen in a fuel cell to produce electric power

However, the quote “Hydrogen is the fuel of the future and it always will be” reflects the lack of enthusiasm that some have regarding hydrogen fuel. A little history first: the Partnership for a New Generation of Vehicles (PNGV) was a cooperative effort between the US government and the auto industry. Its goals were to triple vehicle gas mileage while maintaining safety. By 2001, PNGV had not produced marketable vehicles, but did have prototypes getting up to 70 mpg; these were lighter weight vehicles with sleek designs exhibiting less drag when driven. However, in 2001, a new presidential administration in Washington cancelled the program. It instead supported a “Freedom Car” powered by a hydrogen fuel cell. ▪ Hydrogen fuel-cell cars represent an ideal non-polluter emitting only water. However, major problems must be solved to make them practical and affordable. How can hydrogen be generated cheaply and sustainably? How can hydrogen, an explosive and flammable gas that may have to be stored in pressurized tanks be used safely? (But recall that gasoline and natural gas are also hazardous.) How will the expensive infrastructure be developed to fuel and maintain the vehicles? ▪ How the hydrogen is generated is critical to analyzing the life of a fuel-cell car. Hydrogen is now made from natural gas – a fossil fuel. For hydrogen to be effective, we must use renewable energy sources such as solar or wind to electrolyze water into oxygen and hydrogen.¹² Critics say that, at least currently, the “hydrogen fuel cell just shifts pollution from vehicles to the hydrogen manufacturing facility,” or to an in-car reformer using fossil fuel. Supporters believe fossil fuels will be used only during a transitional phase. ▪ In 2002, Toyota began leasing hybrid fuel-cell SUVs to facilities in California and Japan that could access hydrogen. The vehicles use compressed hydrogen and, like other hybrids generate electricity through braking mechanisms. Toyota will assess vehicle performance, and hopes to stimulate an infrastructure for fuel-cell cars. A consortium of European automakers is working to make hydrogen-powered vehicles available commercially and develop an infrastructure for them including hydrogen fuelling stations.¹³ Several individual carmakers have active programs. Hydrogen-fuelled buses are available in several cities. ▪ By the time petroleum becomes prohibitively expensive, hydrogen may come into its own.

¹² Levy, D. Researchers envision a hydrogen economy, fueled by wind and new technology. *Stanford Report*, June 24, 2005, <http://news-service.stanford.edu/news/2005/july13/hydrogen-071305.html>.

¹³ Day, R. Hydrogen projects, from Iceland to Italy. *E The Environmental Magazine*, January, 2007, <http://www.emagazine.com/view/?3519>.

Lowering emissions using biomass fuels?

- Interest in using biomass such as ethanol from corn or biodiesel from soybeans as motor-vehicle fuel is partially driven by an interest in lowering greenhouse gas emissions, especially CO₂.¹⁴ A biomass fuel, when burned produces CO₂, but *if* grown sustainably, the next generation of plants takes up as much CO₂ as was released when the biofuel was burned. Thus, ideally, cycling through the generations, no more CO₂ is released than is taken up. Unfortunately, there are many problems with producing and using biofuels.¹⁵
 - In the United States there is a push to grow more corn to produce ethanol. However, many analysts – examining the whole life cycle – have concluded that growing, harvesting, and then fermenting cornstarch to produce ethanol may require almost as much fossil fuel energy as the fuel value of the ethanol being produced. And, growing more corn, an open-row crop leads to more soil erosion and more runoff of fertilizer and pesticides.^{16,17} Corn is also water intensive to grow, especially irrigated corn; in addition it takes several gallons of water to produce one gallon of ethanol. A major ethical concern is: in a world where producing enough food is an ongoing problem, to use corn, soybeans, and other food crops as fuel is considered questionable.¹⁸
- Professor L. Lave of Carnegie-Mellon University and others propose that we produce ethanol from switchgrass or various agricultural *wastes*. This poses other problems. It means that instead of using, as an ethanol source, corn starch, which is quite easily degraded into glucose, we use cellulose. Cellulose is much more difficult to degrade into glucose; it is also a more expensive process. However, agriculturally undesirable land can be used to produce grasses and trees, and agricultural waste could be used, thus avoiding the major impacts of growing corn (or even of growing sugarcane in Brazil). Nonetheless, as stated by Jeffrey Fox, vice president of a biorefinery, “It will be a huge issue just getting cellulosic material to the biorefinery.” And using crop residues, which would otherwise remain on and nourish the soil, may be shortsighted.
 - Although still believing that producing biofuels is important, Europeans and, more slowly, Americans are developing standards as to what constitutes sustainably grown biomass, and to also think of how food prices might be impacted.¹⁹
- One non-controversial biomass source is – very specifically – biodiesel made from the billions of gallons of waste oil produced in countless restaurants that deep fry food.
 - A much bigger source potentially that some believe may approach fruition within a decade is growing large quantities of algae and extracting oil from them from which to

¹⁴ Equally, if not stronger, reasons for the interest in biofuels include lowering the amounts of imported petroleum and providing another means to farmers to make a more profitable livelihood.

¹⁵ Schultz, W. The costs of biofuels. *Chemical & Engineering News*, **85**(51) December 17, 2007, 12–16. (This article presents two points of view on using corn ethanol and, eventually, ethanol made from cellulosic biomass.)

¹⁶ Biofueling water problems. *Environmental Science & Technology*, **41**(22), November 15, 2007, 7593.

¹⁷ Engelhaupt, E. High corn demand could harm US waters. *Environmental Science & Technology*, **41**(19), October 1, 2007, 6635–6635.

¹⁸ Exploding US grain demand for automotive fuel threatens world food security and political stability. *Earth Policy Institute*, November 06, 2006.

¹⁹ Widenoja, R. and Halweil, B. Banning “bad” biofuels, becoming better consumers. *Worldwatch Institute*, January 23, 2008, <http://www.worldwatch.org/node/5587>.

produce biodiesel. Algae grow “almost everywhere there is water and sunlight, and under the right conditions . . . is the ultimate fast-growing organism;” it also happens to be rich in oil.²⁰

Dr. J. L. Schnoor, Editor of *Environmental Science and Technology*, comments: “If every motorist properly inflated their tires several times a year, it would improve gas mileage by 3.3%. And, if the US government increased the gas mileage required of our autos as little as 6 miles per gallon (2.55 km per liter) that alone could meet the goal for the amount of biofuel production that the US DOE envisions for 2017.”²¹ Schnoor asks: “Why shouldn’t we as our first policy instrument, emphasize energy efficiency? Why aren’t we conserving energy rather than flailing about trying to produce it from grain?”

Questions 13.1

1. (a) The United States consumes 25% of the world’s petroleum, but has less than 3% of the reasonably recoverable reserves in the world. Is the United States likely to find enough petroleum within its borders to increase production to meet its consumption? Explain. (b) What steps could the United States take to remedy this situation in the short run? (c) In the longer run?
2. Fuel-economy measures focus on manufacturers. The US Office of Technology Assessment stressed that to reduce energy use and traffic congestion we must focus on how *individuals* buy and use motor vehicles. (a) How can society raise the consciousness of car owners on this issue? (b) What should be the balance between manufacturer and individual responsibility? (c) What changes would you personally be willing to make in how you buy, use, and maintain a motor vehicle? (d) Under what circumstances might you voluntarily give up your vehicle?

SECTION III

Electricity production and use

We use electricity for a multitude of purposes including home and commercial lighting, heating and cooling, household appliances, and countless industrial needs. ▪ The US Department of Energy’s EIA forecasts that American electricity use will grow from 16 424 billion kW h in 2004 to 30 364 billion kW h by 2030 –almost a doubling of use. ▪ Worldwide, electricity consumption may grow an additional 76% by 2020 as compared

²⁰ Green energy: cost-efficient process expected to turn algae into fuel. *Associated Press*, September 28, 2008, http://www.huffingtonpost.com/2008/09/28/green-energy-cost-efficie_n_130073.html.

²¹ Schnoor, J. L. Ethanol and water use. *Environmental Science and Technology*, **41**(19), October 1, 2007, 6633.

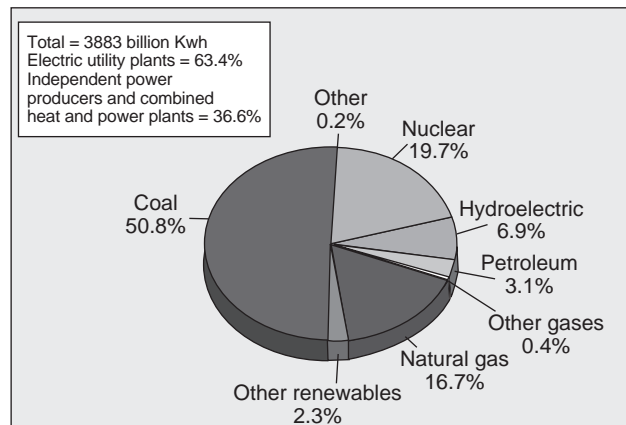


Figure 13.4

Sources of power for US electricity, 2003. Credit: US DOE/EIA

to 1997. Electricity use – along with all types of energy use – continues to increase relentlessly.²²

Generating Electric Power

Worldwide 90% of the energy powering the turbines that produce electricity comes from burning fossil fuels, coal, oil, and natural gas. In the United States about 75% comes from fossil fuels, mostly coal. Data from the EIA in 2007 indicate that the United States generates 49% of its electric power from coal; 22% from natural gas; 2% from oil; 19% from nuclear; 6% from hydroelectric; 1% from wind; 2% from biomass plus a tiny percentage from solar and geothermal. See Figure 13.4.

Coal

Coal provides half of US electricity. In Europe, the heavy use of coal began in the eighteenth century as wood became increasingly scarce. Coal's use increased about 500-fold over the years as western economies industrialized. *Western civilization was built on the energy of coal*, the dirtiest fossil fuel. Coal remains so plentiful it may continue to be used for many years. Coal is also cheap – but is that really true? The market price of coal, as for most products, doesn't take its environmental impacts into account, so-called *externalities*. Add these in and coal is very expensive. Below are some of the pollution and environmental degradation problems caused by coal mining, refining, burning, and ash disposal.

²² International Energy Outlook. Washington, D.C.: US Department of Energy, May, 2009, <http://www.eia.doe.gov/oiaf/ieo/world.html>.

- **Air pollution:**
 - **Sulfur** The sulfur content of coal ranges from 1% to 5%. Industrialized countries often remove the water-soluble portion of sulfur in high-sulfur coal before burning it. The sulfur that is part of coal's matrix is insoluble and cannot be washed out. During burning, sulfur is converted to the major pollutant, sulfur dioxide (SO₂). Modern equipment can capture most SO₂, but many facilities lack good controls.
 - **Nitrogen oxides** Another major pollutant formed during burning coal and other fossil fuels is NO_x. Low-NO_x burners, when used, can remove most.
 - **Metals** Coal has only trace amounts of metals, but a billion tons (0.91 billion tonnes) a year is burned in the United States alone.²³ Without good controls to remove these persistent pollutants, environmental levels build over time. Coal also contains radioactive elements, uranium (~1.3 ppm) and thorium (~3.2 ppm). People living near coal-burning power plants have higher potential exposure to ionizing radiation than those living near nuclear-power plants because emissions from the latter are better controlled.
- **Water pollution** Many air pollutants result from burning coal, which are either particulates to begin with such as metals or are converted to particulates such as acids. These settle onto water bodies as well as land.
- **Coal's life cycle:**
 - Mining** Surface mines can ruin local environments. One particularly destructive form is the mountain-top removal of coal (Chapter 1). Underground mining poses dangers to workers, and until modern workplace protections, coal dust often caused deadly black-lung disease. Both surface and underground mining lead expose sulfur-containing rocks to water and air, which oxidize the sulfur to sulfuric acid. Moreover, the acid dissolves metals in rocks, which with the acid run off to local water bodies.
 - Processing** As coal is crushed, sized, and (sometimes) washed, scarce water may be polluted. Coal mining and processing produce large quantities of waste and air pollutants.
 - Water use** Coal cleaning and burning require large amounts of water.²⁴
 - Burning** Although coal burning releases significantly fewer pollutants than a generation ago, power plants in the aggregate still produce significant pollution, even in developed nations.
 - Ash** About 100 million tons (91 million tonnes) of ash results from burning a billion tons (0.91 billion tonnes) of coal a year in the United States. About 40% of this is used in road beds and to make cement, wallboard and other products. Once organic matter is burnt away, ash has a high metal content. Stored above ground, ash can result in acid and metal runoff into area waters. Some ash is disposed of in old mines. Much, sometimes decades of accumulation, is stored in "ponds" where the ash is kept wet. A billion-gallon (3.8 billion liters) spill of coal ash sludge and water occurred in 2008. This happened when the dam on a coal-ash pond failed, greatly damaging a river and a Tennessee community.
- **Coal reserves** Tremendous reserves of coal exist around the world, especially in the United States, China, and India. Challenging questions include: can coal be mined in less destructive ways? Can it be burned cleanly? Can the ash be either beneficially used or safely disposed of? How possible is the addition of the very expensive technology needed for carbon capture and sequestration (CCS)?

²³ US to burn 1.2 pct less coal for power in 2009, EIA. *Reuters*, February 10, 2009, <http://uk.reuters.com/article/oilRpt/idUKN1029694020090210>.

²⁴ Frazer, L. Low water consumption: a new goal for coal. *Environmental Health Perspectives*, April, 2004, A296–299.

Natural gas²⁵

- Compared to coal and oil, natural gas has fewer contaminants, burns more cleanly, and generates only about half as much CO₂ per unit of energy as coal. However, as with coal and oil, burning natural gas produces NO_x. Low-NO_x burners are necessary to control it. The primary component of natural gas is a different greenhouse gas, the potent methane, which

Box 13.1

Energy and pollution in China

Figure 13.1 indicates that energy use in less-developed (non-OECD) countries will likely grow even faster than in OECD countries. The two countries with the largest populations, China and India, have between them about 2.3 billion people. Both have abundant coal, and use it heavily; however, China currently uses about five times more coal than India.²⁶ Coal supplies about 70% of China's energy needs as compared to a world average of less than 30%.²⁷ And 80% of China's electricity is fueled by coal. Thus, not surprisingly China's CO₂ emissions have outstripped US emissions, and will continue to grow as it builds about one new coal-burning power plant a week.²⁸ ▪ China's economy is projected to grow 6% per year in the coming years, twice the rate as the world as a whole.²⁹ Air and water pollution is already at painful levels, and one wonders how China will cope if pollution increases in step with energy use,³⁰ especially as officials in Beijing are not successful in controlling provincial officials who won't curb local industry. China has a huge heavy industry sector making products such as steel and cement. But even its newest factories and plants are energy inefficient. Moreover 95% of its new buildings require twice the energy to heat and cool as do United States and European buildings. ▪ More positively, China is investing heavily in renewable energy. By 2020, it intends that 15% of its energy be from solar, wind, and hydro-electric dams. Although still building huge hydroelectric dams, many small dams are also being built. And the government in 2007 started a public education drive.³¹ It gives citizens information on ways they can significantly reduce energy use by using CFL light bulbs, choosing energy-efficient appliances, using public transport instead of cars, etc. The advice is, not surprisingly similar to that given in Western countries. ▪ The challenge says an IEA report "is for all countries to put in motion a transition to a more secure, lower-carbon energy system, without undermining economic and social development. Nowhere will this challenge be tougher, or of greater importance to the rest of the world, than in China and India. Vigorous, immediate, and collective policy action by all governments is essential to move the world onto a more sustainable energy path."

²⁵ Note that oil is not covered here because only 2% of US electricity is generated by burning oil.

²⁶ Coal and climate change facts. *Pew Center on Global Climate Change*, 2007, <http://www.pewclimate.org/global-warming-basics/coalfacts.cfm>.

²⁷ World Energy Outlook, 2007, China and India insights. *IEA*, 2007, <http://www.iea.org/Textbase/npsum/WEO2007SUM.pdf>.

²⁸ China's future in an energy-constrained world. *World Resources Institute*, December 12 2008, <http://earthtrends.wri.org/updates/node/274>.

²⁹ As with any current projection (2009), it is not clear how the worldwide economic downturn will impact growth.

³⁰ Kahn, J. and Yardley, J. As China roars, pollution reaches deadly extremes. *New York Times*, August 26, 2007, <http://www.climateark.org/shared/reader/welcome.aspx?linkid=82634>.

³¹ Li, L. China launches energy conservation guide for citizens: *WorldWatch Institute and Global Environmental Institute* (Beijing), September 13, 2007, <http://www.worldwatch.org/node/5346>.

poses concerns when gas leaks. ▪ Because of its relative cleanness, natural gas is a fast growing means of producing electricity worldwide. Its use may double by 2020 as compared to 1997 although the United States still produces about four times more electricity from coal than from gas. Like coal, natural gas is nonrenewable. ▪ Several sources of natural gas exist. Accessing these can pose serious environmental problems. Periodically, leaks happen during recovery, transportation, and use of natural gas; these can result in destructive explosions. In the United States hundreds of carbon monoxide deaths occur each year in private homes due to malfunctioning natural-gas furnaces. These occur with oil furnaces too, but more frequently with natural gas.

Conservation and efficiency

Energy conservation – using less energy – is pollution prevention (P^2). It lessens the pollution associated with using fossil fuels and conserves valuable resources. As Peter Robertson (Chevron) states, “The best source of new energy is efficiency and conservation.” Jim Rogers (Duke Energy) observes, “Energy efficiency . . . is the lowest-cost alternative and is emissions free. It should be our first choice in meeting our growing demand for electricity, as well as in solving the climate challenge.”

Practicing efficiency at home

Before noting ways to reduce energy use at home, see Figure 13.5 ▪ Worldwide, electric lighting for homes and industry consumes about 19% of electricity; in the United States

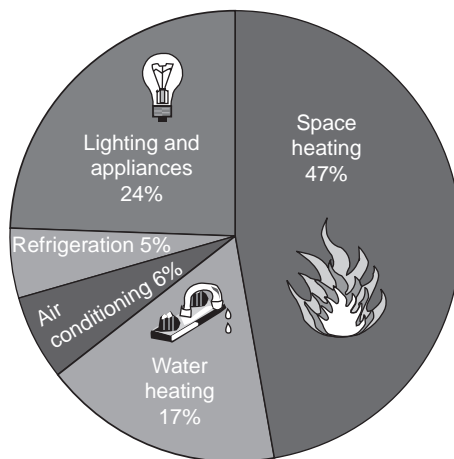


Figure 13.5

How energy is used in US homes. Credit: US DOE/EIA



Figure 13.6

The EnergyStar® logo

the figure for lighting and appliances is 24%³² (plus another 5% for refrigeration and 6% for air conditioning). An average home uses 1500 kilowatt hours/year (kW h/year) for lighting, 40% more than in 1970. ■ An incandescent light bulb uses only 10% of the energy that it consumes to produce light; the rest is given off as heat. Replace a quarter of your incandescent bulbs with compact fluorescents lights (CFLs), and cut your lighting bill as much as half. CFLs cost more, but use two-thirds less electricity and last up to ten times longer. ■ About half of an American home's energy use is for space heating. One-third of a typical home's heat loss is through doors and windows. If you can't put in double-pane windows, buy plastic kits to install plastic over the glass. The air trapped between the plastic and glass can reduce heat loss 25–50%. And check that doors are sealed tightly to prevent air leaks. ■ A home's water heater uses about 17% of its energy, so use less hot water. Install low-flow showerheads. Their cost will be repaid in energy savings in three to four months. ■ Buy energy star appliances (Figure 13.6), those identified by the US EPA and DOE as the most energy-efficient products in their classes. Other good suggestions are found at a number of web sites.³³

Becoming more energy conscious

All these suggestions require a small up-front investment, which is paid back with interest. There are other simple conservation measures with no upfront cost. ■ Turn off unneeded lights. ■ Turn down the thermostat at night. ■ Turn down the temperature of your water heater. ■ Use cold water to wash clothes. ■ Don't wash clothing more often than necessary. Clothing driers, in particular, are large energy users.

³² Johnson, J. The end of the light bulb. *Chemical & Engineering News*, **85**(49), December 3 2007, 46–51.

³³ (1) Vogel, J. Ten simple ways to save energy. *E The Environmental Magazine*, XVI(2), March/April, 2005, <http://www.emagazine.com/view/?2313>. (2) A consumer's guide to energy efficiency and renewable energy. *US Department of Energy*, March 12, 2009, <http://apps1.eere.energy.gov/consumer/>. (3) Creating an energy-efficient world. *Alliance to Save Energy*, 2009, <http://www.ase.org/>.

Questions 13.2

1. Why is coal ash stored in wet “ponds”?
2. Some believe that coal can be burned cleanly. Others say clean-coal is a myth. With which of these two statements do you most tend to agree and why?
3. One American uses twice as much energy as a European or Japanese person, 15 times as much as an Indian, etc. Above and beyond environmental impacts, what other impacts of this high energy use should Americans consider?
4. Cutting greenhouse gas emissions also reduces emissions of SO_2 , NO_x , and particulates. How?
5. What are three energy-conservation steps a business or institution can carry out without cost?
6. What are three ways of conserving energy that have upfront costs, but will pay for themselves?

Conservation in industry

Manufacturing consumes about half of the world’s energy, and US facilities use a third of the nation’s total energy. Joseph Romm’s book, *Cool Companies* notes that companies – even after having already gone through a careful examination of energy-saving opportunities – can repeat the process and find additional ways to conserve energy. John Browne, CEO of BP-Amoco, stated that BP had by 2002 voluntarily cut its greenhouse gas emissions 10% below 1990 levels at no net cost to the company. Browne said this was “the product . . . of hundreds of different initiatives carried through by tens of thousands of people across BP.” Notice Browne’s point: conservation and efficiency measures were accomplished not by one big step, but by multiple small ones. ■ However, companies often hesitate to make upfront investments in energy saving features, especially if the payback time on the investment is years.

- In the United States industrial motors consume two-thirds of the electricity used by industry, about 50% of the electric power produced in the United States. Motors are often inefficient and bigger than necessary for their particular job. The DOE is working with companies to stimulate their use of efficient motors. In one audit of a dozen industrial sites, they found that – by installing motors more appropriate to the job – energy use could be cut by a third with a payback time of 18 months.
- Generating steam is another energy hog, and the steam’s energy is often not fully used. This contrasts with Kalundborg (Figure 2.2) where the power plant passes unused steam on to other facilities or to to warm households. This “district heating,” where an electric power plant forwards steam to central city buildings is often used in Europe; a limited number of US industrial generators do likewise. In Jay, Maine, Androscoggin Energy operates a natural gas power plant, which is co-located with a pulp and paper mill owned by International Paper. The power plant generates electricity for sale elsewhere, and sells part of its steam to the mill. Thus, the mill and power plant both use energy more

efficiently and save money. This is called *cogeneration* or, recently, *recycled energy*.^{34,35} Unfortunately, the EPA found that only a small percentage of the waste energy produced by 16 American industries was being used, although the EPA had calculated that energy could have provided power for 48 million homes.³⁶ However, more industries are now looking into the potential that energy offers them.

- The US DOE in 2005, developed computer software to help plants assess where energy savings in their facilities can be made.³⁷ An 800 acre (324 hectare) chemical plant owned by Rohm and Hass is one among hundreds of beneficiaries of DOE's effort. The plant already had a team that had worked for ten years on energy use and pollution abatement and believed it had found all the "low hanging fruit" energy savings. But the DOE audit coupled with the energy team resulted in seeing the plant with fresh eyes and yielded "astounding" results. "Ten years of looking at this plant – we'd never seen this situation," said Frederick Fendt, a systems engineer. One audit finding was that they could have been using previously wasted heat for many applications that only needed low-pressure steam. DOE's Scheiwing noted the program was "a crash course in educating manufacturing managers . . . in what this fruit looks like."

Burning cleaner fuel

▪ Natural gas is the cleanest burning (generates less pollution) of the fossil fuels. Petroleum is intermediate. Coal is the least clean-burning although the most-advanced coal-burning plants reportedly burn much more cleanly. ▪ CO₂ emissions from gas burning are lower because natural gas contains less carbon. ▪ Low-sulfur coal produces less SO₂ when burned than higher sulfur coals. Some coals from western US states have as little as 0.3% sulfur.

Adopting clean-coal technology

- Scrubbers are commonly used to capture SO₂ and particulates (including metals and soot). Although 100% of pollutants cannot be captured, advanced technologies capture almost all. Low-NO_x burners cut NO_x emissions as much as two-thirds, and newer technology much more.
- One P² method involves washing crushed coal with water to remove the soluble sulfur so that the coal has lower SO₂ emissions when burned. Another P² approach is burning coal on a *fluidized bed*: coal is pulverized and burned together with ground limestone on a

³⁴ Another natural gas power plant, a two hour drive from the one in Jay vents its lower-energy steam (which cannot drive a turbine) into the atmosphere. Especially on cold days, big clouds of steam (wasted energy) hang over the area.

³⁵ Combined heat and power partnership. *US EPA*, March 18, 2009, <http://www.epa.gov/CHP/index.html>.

³⁶ Johnston, M. W. Considering cogeneration: clean power whose time has come back. *E The Environmental Magazine*, January–February, 2008, <http://www.recycled-energy.com/newsroom/news/emagazine-jan-feb2008.html>.

³⁷ Johnson, J. Ending plants' wasting ways. *Chemical & Engineering News*, **86**(02), January 14, 2008, 37–38. (2) Energy trends in selected manufacturing sectors: opportunities and challenges for environmentally preferable energy outcomes. *US EPA*, February 17, 2009, <http://www.epa.gov/sectors/energy/index.html>.

screen. Air currents keep the coal particles in constant motion, giving the appearance of a boiling (fluidized) bed. The limestone captures SO_2 as it is formed. A fluidized bed also allows more efficient burning with fewer by-products of incomplete combustion.

- Carbon is an integral part of coal's chemical matrix and cannot be washed out like inorganic sulfur. Also, CO_2 is not ordinarily captured from flue gas.³⁸ As discussed in Chapter 7 major problems remain with finding efficient affordable techniques to capture and sequester CO_2 emissions. Meanwhile, we depend on conservation and efficiency to reduce CO_2 emissions, and on greater use of renewable energy sources.
- Modern clean-coal technology can burn coal efficiently, capture SO_2 , metals, and other particulates, and has greatly lowered NO_x emissions.³⁹ Compare three pictures: 1. If no coal-burning plants in the United States had controls, they would emit 20 million tons (18 million tonnes) of SO_2 . 2. With the controls that plants actually use now, they emit about 12 million tons (11 million tonnes). 3. If all plants used state-of-the-art technology, they would emit only 2 million tons (1.8 million tonnes). But many companies resist spending large sums for major retrofits to reduce pollution, and resist building expensive new plants. Thus, many dirty facilities remain in operation. These were “grandfathered” in under the first CAA of 1970, and so chose not to install modern controls. Many still exist, producing a disproportionate amount of pollution. At the other end of the spectrum, the Bruce Mansfield Power Plant in Pennsylvania spent almost a third of its construction budget on environmental technologies, and built a state-of-the-art plant that burns coal much more cleanly. ▪ In poor countries the situation is typically worse. In China and especially India, air-emission controls are poor and sulfur often not removed. And because pollutants travel, SO_2 emitted in China can impact Japan, a country that uses modern controls.

SECTION IV

Electricity from nuclear power

In 2007, nuclear power generated 16% of the world's electricity and 19% in the United States. In the EU as a whole, nuclear power provides 34% of the electric power, but some EU countries don't use nuclear at all, whereas France generates a remarkable 78% of its electricity from nuclear. Nuclear power plants produce no air pollution. Some nuclear waste

³⁸ Small amounts are captured for such uses as carbonating beverages or making the calcium carbonate used in paper making.

³⁹ A technology being tested in demonstration projects is coal gasification, which converts coal to *syngas*, then burned to produce electricity. Gasification is not incineration, the whole process is changed. Almost all the sulfur in Syngas can be recovered as elemental sulfur, a salable commodity. Mercury can be contained within the system. Carbon monoxide (CO) can be converted to carbon dioxide (CO_2) before it reaches the flue gas. So pollutant emissions are low. Gasification technology is also more energy efficient than a traditional coal-burning plant. It may be commercialized in a decade. However, it is more expensive than building a traditional electric power plant.

components are very long-lived or highly radioactive, but waste volume is small and solid. Consider arguments⁴⁰ against and for nuclear power. ■ An argument in favor of nuclear power is that modern nuclear reactors are much safer than those involved in the 1986 Chernobyl accident; one is the pebble bed modular reactor.⁴¹ ■ Opponents argue that even if plants are operated safely, radioactive wastes cannot be safely disposed. Disposal is so controversial that, many years after selecting a burial site in the United States, it may be many more years before it is used, if ever. Meanwhile, waste is stored at the sites where it is generated. Proponents point to France a country that recycles its spent fuel. Eighty percent of the fuel actually remains after being “burned.” France recovers this to reuse in the power plant.⁴² It vitrifies the other 20%, which greatly reduces the risk of radionuclides leaching out. The process is expensive, but no more than the long-drawn-out approaches that the United States has used to find and prepare acceptable storage. Proponents point to the Oklo “natural reactor” in the Republic of Gabon. Starting about two billion years ago and continuing over a 500 000-year period, natural uranium fission reactions occurred that created hundreds of tons of nuclear fission products. In 2 billion years no radioactive materials has migrated from the rocks. Opponents say there is no assurance that other storage sites would be equally safe. ■ Many believe that our energy needs and the pollution from burning fossil fuels are so great that we cannot discard nuclear power. Kurt Yeager of the US Electric Power Research Institute observed, “I believe it would be a tragedy for future generations if we outlaw nuclear power because the current generation of engineering doesn’t meet our standards.”

Coal versus nuclear

Nuclear proponents compare a 1000-megawatt nuclear-power plant to a 1000-megawatt coal-burning power plant.

- Coal A coal-burning plant emits up to 35 000 tons (32 tonnes) a year of SO₂ (although good controls can much reduce this). Metals, although emitted in small quantities build up in the environment. Uranium and thorium are radioisotopes emitted at levels greater than those permitted for a nuclear reactor. Current environmental controls cannot reduce the 4.5 million tons (4 million tonnes) of CO₂ that a coal-burning plant may emit. It also produces 3.5 million cubic feet (0.1 cubic meters) of ash a year. Mining coal often entails great environmental damage.

⁴⁰ Sovacool, B. K. Think again: nuclear energy. *Foreign Policy*, September 22, 2005, http://news-nuclear.blogspot.com/2005/09/foreign-policy-think-again-nuclear_22.html.

⁴¹ Schmidt, C. The next generation of nuclear power? *Environmental Science & Technology*, **40**(5), March 1, 2006, 1382–1383. In addition to being safer, this reactor operates at a high temperature of 1652°F (900°C), which could be used to electrolyze water to obtain hydrogen gas. This could assist society in its transition to a hydrogen economy.

⁴² During recycling, some plutonium is produced. If this fell into the wrong hands it could be used in the building of nuclear weapons. Another concern relates directly to nuclear installations. There has been fear since the 9/11 attacks on the United States, that attacks from the air could result in widely broadcast radioactive chemicals. Not all consider this a concern.

- **Nuclear** The nuclear plant produces only 70 cubic feet (2 cubic meters) of high-level radioactive waste.⁴³ There is no CO₂ or other emissions during operations, except for hot water. However, a life-cycle analysis indicates carbon emissions are involved because much energy is required to mine and mill uranium. Moreover, a large amount of electricity is necessary to enrich uranium. And, pollution is a concern when the plant is dismantled.

Questions 13.3

1. Put yourself into the world of 1945. World War II has just ended after nuclear bombs were dropped on Japan. Your country strongly desires to use nuclear energy for peaceful purposes, and especially to produce nuclear electric power. Consider that you know problems that can arise with using nuclear power to produce electricity: ionizing radiation can harm life, and nuclear reactors may not always be safe. Even if reactors are fail-safe, human operators are not. Some nuclear waste components remain radioactive for many thousands of years, and disposing of them raises perplexing and expensive problems. Nuclear power technology can sometimes be used to develop nuclear weapons. Your nation nonetheless believes that nuclear power is desirable. If your country knew in 1945 what we know now, how would it have developed nuclear power in a more environmentally and socially responsible way?

Nuclear Fusion

Nuclear *fusion* does not use radioactive chemicals and produces no air pollution.⁴⁴ The process produces neutrons, and it is the capture of these neutrons that produces heat. The reaction vessel becomes radioactive during this process, but remains so for a much shorter time than do isotopes produced by nuclear fission. Research and development on nuclear fusion has been ongoing for decades and has been extremely expensive. Congress has supported nuclear fusion research done in cooperation with the EU, Japan, and Russia intended to demonstrate self-sustaining fusion, and to eventually operate a reactor. Some scientists consider the likelihood of successful nuclear fusion dim. Others say progress has been steady, and that “despite enormous hurdles, the most promising long-term nuclear power source is still fusion.” They believe that we may see a commercial fusion reactor in a decade.⁴⁵

⁴³ The great majority of radioactive waste needing to be dealt with in the UNITED STATES is not from commercial reactors, but from old military and US DOE operations. Thus, even if no new nuclear plants are built, this waste needs action. Unlike civilian power-plant waste, which is solid, much military and DOE waste is liquid, is complex, and often mixed with other hazardous waste. The military and DOE sites containing this waste present tremendously expensive and technologically challenging cleanup problems.

⁴⁴ How is nuclear fission different from nuclear fusion? *WikiAnswers*, 2008, http://wiki.answers.com/Q/How_is_nuclear_fission_different_from_nuclear_fusion.

⁴⁵ Kanellos, M. Nuclear fusion is coming. *Green Tech*, February 7, 2008, http://news.cnet.com/8301-11128_3-9866626-54.html.

SECTION V

Electricity from renewable sources^{46, 47}

With the exception of nuclear and geothermal power, renewable energies all depend directly or indirectly on the sun. The Earth's surface yearly receives sunlight with energy equivalent to 10 times more than that stored in all known reserves of coal, oil, natural gas, and uranium combined. And were we capable of harnessing 40 minutes of sunlight, it could satisfy global energy needs for a year.

- We use solar energy *indirectly* when we burn wood and other biomass fuels or when we burn fossil fuels, which are organic material stored beneath Earth's surface eons ago. ▪ Energy represented by the flow of water over dams originates from the sun's energy (which evaporates the water that subsequently falls onto the Earth). ▪ The energy of the wind that drives wind turbines comes from the sun. So does sea wave power.
- We *directly* use solar power when we use photovoltaic cells, solar concentrators, or passive solar. The solar power industry currently supplies less than 0.1% of US electricity, but that figure may grow to 10% by 2005.

Solar, photovoltaic (PV)⁴⁸

The term *solar energy* as applied to electric power generation refers to either photovoltaic cells or thermal-solar systems. *Photovoltaic* (PV) cells directly generate electricity from light. ▪ Solar power does not directly pollute, but remember life cycle issues (see Box 13.2). ▪ Location Solar power plants are located in areas when sunlight is plentiful but, to be useful on a large scale must be transported to less-sun rich locales. ▪ Storage Because solar energy is generated only when the sun shines, storage is necessary to have it available for other times.

PV operations

- Small⁴⁹ You are probably familiar with *very* small-scale applications such as powering a calculator or, recharging batteries with a solar-powered charger.⁵⁰ Solar panels on a roof

⁴⁶ Alternative energy: biofuels, fuel cells, geothermal energy, hydropower, solar energy, wind power. *National Geographic*, <http://environment.nationalgeographic.com/environment/global-warming/alternative-energy/>.

⁴⁷ Renewable energy sources: a consumer's guide. *EIA*, 2004, <http://www.eia.doe.gov/neic/brochure/renew05/renewable.html>.

⁴⁸ Exploring ways to use solar energy. *US DOE*, September 12, 2005, http://apps1.eere.energy.gov/consumer/renewable_energy/solar/index.cfm/mytopic=50011.

⁴⁹ HomePower Magazine (wind, solar and other micropower sources), <http://www.homepower.com/home/>.

⁵⁰ More recently small lamps, powered by small solar panels are beginning to be used in less-developed counties as affordable electricity; they can be charged by several hours of sunlight. They are also useful for camping trips.

Box 13.2

Pollution from making polysilicon

Overall, life-cycle assessment (LCA) of PV is very favorable, cutting pollution by 90% as compared to burning coal. Pollution can be even lower if rooftop panels are used to eliminate the need for the electric grid.⁵¹ Manufacturing the polysilicon (from highly purified and processed sand) needed for the panels, was previously done in developed countries. For each ton of polysilicon produced, about four tons of a hazardous waste containing silicon tetrachloride is also produced. Through an energy-demanding process, manufacturers destroy this waste, and recycle recovered polysilicon. Also, workers are protected from the hazardous chemicals used. ▪ But, a few years ago as interest in solar PV increased, demand for polysilicon increased too beyond the supply available. At this time, Chinese companies began making it at a fraction of the cost in developed countries. To keep costs low, many dump the hazardous waste, untreated.⁵² In one village near a polysilicon plant, trees and grass at the dumping site have died as did nearby crops. When the air is moist, the waste reacts to form and release hydrogen chloride, an irritating acid gas which, at higher levels is corrosive. The factory chimneys also release pollutants, which villagers call “poison air.” It has been pointed out that a manufacturer doing this in the United States would be arrested. One suggestion to correct this situation is that Germany and Spain (the main buyers) not allow their PV producers to purchase polysilicon from companies that can’t prove their entire supply chain is environmentally responsible.

can also partially or totally fill the electricity needs of individual homes or buildings. Households in remote locations or those wanting to live “off the grid,” can use PV setups especially in sunny locations. ▪ Even a few residents of the northern US state of Maine install PV systems for part, sometimes all, of their electric power. They use battery arrays to store energy for when the sun isn’t shining. ▪ The Japanese developed a “solar roof” in which PV cells replace ordinary shingles on part of the roof. In the United States some federal buildings are retrofitted with solar shingles. A major example of these still-expensive shingles is the Pentagon roof.

- **Medium** The sunny city of Los Angeles (LA), California, began providing financial assistance to households installing PV grids several years ago for systems to generate 60–80% of an average home’s electricity needs. Still, as of 2008 solar generated less than 1% of LA’s energy needs; most power is still fossil-fuel generated. So LA developed plans to obtain 10% of its energy by solar:⁵³ it will install enough solar panels on household roofs to generate 380 megawatts of power, use city solar-power plants to generate 500 megawatts, and generate another 400 megawatts from panels installed on the roofs of city-owned property. The project, planned for completion by 2014 will cost between \$1.5 and 3 billion. Once installed, the system will cost each LA resident about an extra \$2 a month.

⁵¹ Lubick, N. New photovoltaics change solar costs. *Environmental Science & Technology*, 42(6), March 15, 2008, 1816.

⁵² Cha, A. E. Solar energy firms leave waste behind in China. *Washington Post*, March 9, 2008, A01. <http://www.washingtonpost.com/wp-dyn/content/article/2008/03/08/AR2008030802595.html>

⁵³ Los Angeles boasts world’s largest solar energy plan. *ASH Institute*, December 3, 2008, http://www.enn.com/top_stories/article/38778.

- Large PV systems can run electric power plants, a feat already accomplished in several nations, e.g., Spain. ■ It is envisioned that electric energy sufficient for the whole United States could be generated in the southwestern US states. ■ EU scientists foresee a solar system in the North African desert where the sun is particularly intense; by 2050, all of Europe's electricity could be provided from the Sahara.⁵⁴ Algeria is already setting up a power grid to begin exporting some electricity to Europe by 2020. New and modern transmission lines will be needed both in the United States and Europe for these schemes to reach fruition. ■ Germany, although not receiving great amounts of sunlight, has PV solar electric plants; one generates power for 10 000 homes. However only 0.5% of Germany's power is from solar. Its major interest is in solar research and development, and in selling abroad the technologies that they develop.⁵⁵

Storing PV energy

Solar energy is not generated at night and less is made on days with weak sunlight; solar energy must be stored if it is to be available at any time. There are several incompletely developed technologies to store energy on a large scale. ■ Batteries are commonly used for small applications, but the UK has developed a "giant battery" with a "secret combination of chemicals," expected to be operational in 2009, which will store either solar or wind power.⁵⁶ Other efforts are also underway.⁵⁷ ■ Ken Zweibel writing in *Scientific American* notes another possible system: solar electricity can be used to compress air, which is kept in compressed-air facilities. Then, at any hour, air is released to turn a turbine and generate electricity.⁵⁸ ■ Others don't like the idea of large facilities – whether solar or wind. They believe that local and individual power will become increasingly important. However, there are advantages to large facilities; one is, if society wants to have power available at any time, it needs to be able to draw on power at a distance. Then, when the sun is not shining or the wind not blowing in one place, it is shining or the wind is blowing in another. Elaborate controls would be necessary to integrate all sources and their power offerings.

Solar, concentrated solar power

Concentrated solar power (CSP) functions differently than PV. CSP focuses sunlight falling on mirrors onto a tube filled with oil. The hot oil is run through a heat exchanger and in the process heats water to steam, which runs a turbine to generate electricity. The electricity is then

⁵⁴ Jha, A. Solar power from Saharan sun could provide Europe's electricity, says EU. *The Guardian*, July 23, 2008, <http://www.guardian.co.uk/environment/2008/jul/23/solarpower.windpower1>.

⁵⁵ Whitlock, C. Cloudy Germany a powerhouse in solar energy. *Washington Post*, May 5, 2007, A01, <http://www.washingtonpost.com/wp-dyn/content/article/2007/05/04/AR2007050402466.html>.

⁵⁶ Harrison, P. UK plans giant battery to store wind power. *Reuters*, September 14, 2007, <http://www.planetark.com/dailynewsstory.cfm/newsid/44343/story.htm>.

⁵⁷ (1) Sharp to make solar power storage batteries. *Reuters*, February 26, 2008, http://www.enn.com/top_stories/article/31783. (2) Bland, E. Pourable Batteries Could Store Green Power. *Discovery News*, April 8, 2009, http://www.enn.com/top_stories/article/39620.

⁵⁸ Zweibel, K., Mason, J. and Fthenakis, V. A solar grand plan. *Scientific American*, January, 2008, <http://www.sciam.com/article.cfm?id=a-solar-grand-plan>.

fed to the power grid.⁵⁹ Energy expert Joseph Romm recognizes that there is no magic bullet to replace fossil fuels and that we must use many technologies, but nonetheless refers to CSP as “the technology that will save humanity.”⁶⁰ ■ Storing CSP An important attribute is – because CSP generates energy as heat – the heat can be stored many times more cheaply and efficiently than electricity generated by PV. To store it: allow CSP to heat oil or molten salt, which then retain enough heat so that energy can be released for a number of hours to generate electricity.

Solar, passive⁶¹

Passive solar usually requires some up front costs in a home or building. Costs can be small unless solar is expected to supply a large percentage of heating. Even in cloudy or northern locations homes can be built to capture solar energy to help meet daytime heating needs. Or the sun can warm building material, dark flooring, or walls within the structure, or to heat large containers of water; these release their warmth at night. There are many examples of passive solar. Most are much more economical than using PV.⁶² ■ Another practical use of passive solar is to provide hot water; water is pumped through black roof pipes exposed to the sun. The amount of hot water produced depends on the amount and intensity of sunshine. In Bogota Columbia the hot water in many apartment buildings is generated this way. Even in cloudy or northern locales, there is often enough sunlight to heat part of a household's water.

Questions 13.4

Author Andrew Leonard asks, “Who is responsible for the poisonous silicon tetrachloride liquid waste being dumped, untreated in open fields near the town of Gaolong, in Henan province, China?”⁶³ Is it the polysilicon foundry creating the waste? The government, which does not enforce its own regulations? The European buyers of polysilicon? The foreign governments that subsidize the purchase of PV panels after they are produced? Respond to these questions individually or as a class exercise.

Wind Power^{64, 65}

Wind machines (turbines) are located in areas with dependably strong winds. Because people often don't want to live near turbines, European nations have begun building them

⁵⁹ Schmidt, C. Sunlight on mirrors. *Environmental Science & Technology*, **42**(19), October 01, 2008, 7031.

⁶⁰ Romm, J. The technology that will save humanity. April 14, 2008, http://www.salon.com/news/feature/2008/04/14/solar_electric_thermal/print.html.

⁶¹ Siliski, A. Everyday environmental stewardship: passive heating. http://www.mipandl.org/ees/EES_PassiveSolarHeat.pdf.

⁶² Solar do it yourself space heating projects. http://www.builditsolar.com/Projects/SpaceHeating/Space_Heating.htm.

⁶³ Leonard, A. Paying the polysilicon piper. *How the World Works*, March 10, 2008, http://www.salon.com/tech/htww/2008/03/10/polysilicon_pollution/.

⁶⁴ Exploring ways to use wind energy. *US DOE*, September 12, 2005, http://apps1.eere.energy.gov/consumer/renewable_energy/wind/index.cfm/mytopic=50014.

⁶⁵ Motavalli, J. Unplugging: living off the grid. *E The Environmental Magazine*, July, 2005, <http://www.emagazine.com/view/?2650>.

offshore anchored to the sea floor and taking advantage of strong winds. ■ Wind machines don't directly pollute, but as with solar generate pollution when manufactured; unlike solar, no highly toxic chemicals are associated with their manufacture. Pollution is associated with their transportation, and building access roads for them. ■ As with solar, much land is needed to generate electricity on a large scale. However, except for surfaces covered by machines and access roads, the land can simultaneously be used for crops or trees. Locations and orientation of wind farms must be planned to avoid killing bird and bats.⁶⁶ Some believe the future will see turbines, not clustered on large wind farms, but dispersed among many small farms as an extra "cash crop," and possibly in urban settings too where they would need to be smaller and less noisy. Storing wind power Because winds are not constant, the power generated must be stored. Active research on projects such as having turbines force air into underground pipes, aquifers, or caves is ongoing; the pressurized air is released to the surface as needed to generate electricity.^{67,68} Also, recall UK's "giant battery" expected to store power. Small operations Recall that windmills were used for centuries in the Netherlands, and were also common on American Midwestern farms. In both cases, they pumped water. Today, some households use a turbine to generate electricity.

Increasing usage of wind power

■ Europe now has two-thirds of the world's wind-generated electricity, supplying about 3% of its energy needs this way.⁶⁹ Germany gets 6% of its electricity from wind, Spain 8%, and Denmark 20%. However, there must be strong ties to the larger electric grid to avoid the vagaries of wind. The European Wind Energy Association has a goal of supplying 23% of Europe's electricity by 2030. ■ The United States generates about 1% of its electricity from wind although wind power is growing rapidly. And several states, California, Iowa, Minnesota, Colorado, and Oregon already get a higher percentage of their power from wind. The US DOE believes that, by the year 2030 wind power will supply 20% of US energy, and that it will cost 6–8.5 cents/kWh, unsubsidized, including the cost of the new transmission lines needed to access existing power lines.⁷⁰

Producing electricity from biomass⁷¹

Biomass is any natural organic material such as wood, crop wastes or other vegetation, animal dung, or fuel such as charcoal derived from organic material. Billions of people burn

⁶⁶ Anderson, L. Big California wind farm wrestles with bird deaths. *Reuters*, May 16, 2005, <http://www.planetark.com/dailynewsstory.cfm/newsid/30802/story.htm>.

⁶⁷ Romm, J. Winds of change. *Salon*. May. 17, 2008. http://www.salon.com/news/feature/2008/05/17/wind_power/.

⁶⁸ LaMonica, M. Compressed air storage coming to wind power. *GreenTech*, August 27, 2008, http://news.cnet.com/8301-11128_3-10026958-54.html.

⁶⁹ Global wind power expands in 2006. *Earth Policy Institute*, June 29, 2006. http://www.enn.com/press_releases/1561/print.

⁷⁰ 20% Wind Energy by 2030: increasing wind energy's contribution to US electricity supply. *US Department of Energy*, January 8, 2009, http://www1.eere.energy.gov/windandhydro/wind_2030.html.

⁷¹ Exploring ways to use biomass energy. US DOE, September 12, 2005, http://apps1.eere.energy.gov/consumer/renewable_energy/biomass/index.cfm/mytopic=50001.

Box 13.3

Using biomass energy

- Use biomass directly as a fuel ▪ When large amounts of biomass are available, it can be burned to power electricity-producing turbines. Crops that can be used include switchgrass, or agricultural waste such as stover (dried stalks and leaves of a crop). ▪ One type of biomass is available as a liquid: used vegetable cooking oil from restaurants. This, after simple processing, can be used to power motor vehicles.
- Ferment biomass to obtain fuel Biomass contains polymers. ▪ The major polymer in corn is cornstarch, which can be treated to release glucose. The glucose is fermented to *ethanol*, which is burned as fuel. ▪ Cellulose is the major polymer in switchgrass or other grasses and in agricultural waste. Cellulose gives up its glucose with more difficulty than is the case for starch, but intensive ongoing research strives to find means to do so economically. Once obtained, it is fermented to ethanol. ▪ Any of these approaches *can* be viable, but would need careful monitoring to prevent adverse impacts. One potential problem relates to taking biomass from the land, and depleting the soil's organic material and minerals. A possible solution is, after fermenting the glucose, to compost the resulting waste. Likewise, when biomass is burned, a mineral-rich ash is produced; this too can be returned to the soil.
- Fermentation of manure Manure is animal, not plant matter, but can be used in similar ways. In countries as different as the United States and Nepal, manure is sometimes fermented to generate methane, which can be burned as a cooking fuel. When larger quantities are generated, it can be burned to generate electric power. In the United States, New York State is subsidizing farmers to purchase digesters to ferment manure, and use the methane generated to produce electricity for their farms. ▪ In the poor country of Nepal, harvesting wood as cooking fuel aggravates deforestation. Fermenting manure and human waste partially solves this problem: it provides clean-burning methane as a cooking fuel. Residues remaining from fermentation can be composted.

biomass in developing nations, as has happened for eons to generate heat and light. Biomass can be used directly to produce electricity when it is burned, or used indirectly to produce fuels including biodiesel, ethanol or methane (Box 13.3). ▪ One example that many people know is generating electricity from burning the biomass in our municipal solid waste. *If* grown in a sustainable manner, biomass has no net CO₂ emissions. Many of the problems associated with using biomass as a fuel were noted above when considering its use to make biofuels for motor vehicles. ▪ If grown sustainably, biomass can provide new markets to farmers for their crops. If row crops (corn) are avoided, it can sometimes lead to more environmentally sound land management. Biomass can create new technologies and contribute jobs to local economies. In some cases, it could provide fuel to generate electricity in local economies. And *if* used in a sustainable manner to produce ethanol, biomass may lessen dependence on foreign petroleum imports. Some optimistically assert that biomass could provide 8–16% of US electricity without displacing critical food crops. ▪ Over many years economies that are now industrial evolved from using biomass to using fossil fuels. Now, some visualize a return to biomass, but a return based upon sound environmental principles.

Geothermal energy⁷²

Geothermal refers to the heat below the Earth's surface. The deeper into the Earth's interior one goes, the higher is the temperature.

- In volcano-rich Iceland and some parts of California, hot water and steam are found close to the Earth's surface. If the temperature is at least 302°F (150°C), these can be used to generate electric power. Unlike wind or solar it's always available. It's as much as 80% less expensive than fossil fuels, and involves only about a sixth as much CO₂ as compared to a natural-gas-fueled power plant. But some foul-smelling highly-toxic hydrogen sulfide gas is released. There are also geothermal fluids with toxic substances which must be disposed of. And, overdrawing local geothermal supplies is sometimes a problem.
- A different technique called heat mining is useful in many places where steam is not near the surface. Wells are drilled to reach hot rocks in the Earth's crust, which are then connected to an area of fractured rock through which water is allowed to flow. This water becomes heated and, carried to the surface provides the hot water or steam able to run an electric generator. Energy is needed to do the drilling but once the hot rocks are accessed, no further fuel is needed. Environmental impacts are low as operations are underground except for the power plant at the surface. However, the power plant needs water, sometimes a problem. An MIT panel studying heat mining concluded that, when developed, it could supply 6% of US electric energy.⁷³
- There is no need to drill into hot rocks when the intention is simply to obtain warmth for space heating in a home or other structure. The Earth starting within a few feet (about a meter) below the surface has a temperature of 45–70°F (7–21°C), considerably higher than above-ground winter temperatures. To warm a home, fluid is circulated (using a geothermal heat pump) into a well dug several feet down; the fluid becomes warmed and its warmth is transferred into the home. The home temperature obtained may be lower than desired, and an electrically operated surface heat pump is used to raise the temperature further. However, the amount of electricity used is much less than would be the case without geothermal heat. In the summer, the geothermal pump can be operated in reverse to cool the home. The system is significantly more expensive to install than a conventional heating/cooling system, but can pay back the investment within a few years.⁷⁴

Hydrogen⁷⁵

Hydrogen fuel cells were discussed above as a means to power cars. However, they can be scaled to many sizes to provide electricity for a house or building, or to power an

⁷² Geothermal heat pumps. *US DOE*, May 1, 2008, http://apps1.eere.energy.gov/consumer/your_home/space_heating_cooling/index.cfm/mytopic=12640.

⁷³ MIT-lead panel. The future of geothermal energy: impacts of enhanced geothermal systems (EGS) on the United States in the 21st century. *US Department of Energy*, January 22, 2007, <http://web.mit.edu/newsoffice/2007/geothermal.html>.

⁷⁴ Geothermal heat pump. *Wikipedia*, November 30, 2008, http://en.wikipedia.org/wiki/Geothermal_heat_pump.

⁷⁵ Exploring ways to use hydrogen. *US DOE*, September 2, 2008, http://apps1.eere.energy.gov/consumer/renewable_energy/hydrogen/index.cfm/mytopic=50005.

electric-power plant. In fact, using hydrogen to provide electricity for stationary uses is easier than using it in a vehicle. Some buildings that need totally dependable electric power already use hydrogen – however, hydrogen is produced by using fossil fuels. ▪ In a demonstration project,⁷⁶ Maine’s Chewonki Foundation placed solar panels on its Education Center roof to provide the power to electrolyze water and obtain hydrogen ($\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$). In this case, the energy used to produce the hydrogen comes from a renewable source. The hydrogen generated is piped into the building, where fuel cells convert it into electricity, which is then available to supply power to the building for 4 days in the event of a power outage. A company involved in the project, Maine Oxy, uses solar energy on a larger scale to produce hydrogen and oxygen, which it sells. ▪ Iceland heats 90% of its buildings using hydroelectric and geothermal energy. It also uses geothermal energy to electrolyze water into hydrogen: it is making hydrogen from a renewable source. Iceland plans to fuel all its vehicles with hydrogen, and end fossil fuel use by 2030. The city of Reykjavík already has hydrogen-powered buses. Other countries lack Iceland’s geothermal supplies. However, other means of generating geothermal as described above may be able to do so in the future.

Harnessing the ocean’s energy^{77, 78}

The oceans provide several opportunities to generate electrical energy.

- Wave energy technologies make use of devices placed on the water’s surface that convert wave movements into mechanical energy, which is used to drive a turbine. Wave energy is already used in Portugal on a small scale.⁷⁹ As of 2008, this country obtains 42% of its electricity from renewable resources, mostly solar and wind. Now “sea snakes” offshore, using wave energy are connected to the commercial grid and supply electricity to 1500 homes. Many more snakes are planned. Other nations are also actively exploring wave energy’s potential. Because it is variable, it would need to be part of a mix of energy sources.
- Tidal energy harnesses energy from the difference between high and low tides; that difference must be at least 16 ft (4.9 m), which limits its use in the United States to Maine and Alaska.⁸⁰ One means to trap tidal energy is by building a dam across an estuary. As the tide changes, it forces water through turbines in the dam to turn a generator. In 2008, the UK built a commercial marine turbine in Northern Ireland powering about a thousand homes. It has plans to build many more. For example, Scotland is moving toward

⁷⁶ Harkavy, J. Chewonki’s renewable hydrogen center. *Chewonki*, August 28, 2006, http://www.chewonki.org/news_detail.asp?news=11.

⁷⁷ Exploring ways to use the ocean’s energy, *US DOE*, September 12, 2005, http://apps1.eere.energy.gov/consumer/renewable_energy/ocean/index.cfm/mytopic=50007.

⁷⁸ Harnessing the ocean’s energy. *Environmental Health Perspectives*, **112**(5) April 2004, 1, <http://www.thefreelibrary.com/The+state+of+the+oceans,+part+2:+delving+deeper+into+the+sea%27s+bounty-a0137505234>.

⁷⁹ Durham, N. The little nation that could go green. *CBC News*, October 20, 2008, <http://www.nowpublic.com/environment/little-nation-could-go-green-and>.

⁸⁰ Johnson, I. “Saudi Arabia of renewable energy” off Scotland’s coast, June 22, 2007, <http://news.scotsman.com/index.cfm?id=982522007>.

commercial development. Some fear that deriving power from tides could disrupt whole ecosystems.

- Ocean thermal energy conversion, which works in warm climates, takes advantage of the differences between the solar-warmed surface waters and the colder deep waters.

Hydroelectric dams⁸¹

Hydroelectricity is often referred to as a renewable source of electricity. A dam does have many advantages: it produces little air pollution, uses few nonrenewable resources, generates needed electricity, prevents floods, and provides irrigation water. However, large dams⁸² flood agricultural land, displace people from their homes and communities, disrupt ecosystems and wildlife habitats up and downstream, interfere with fish migration, and deprive downstream recreational users of water. Moreover, on occasion changes in water flow can lead to catastrophic floods. The irrigation water a dam provides can waterlog the land where it is used and saturate it with salt. Dams have safety concerns. Their lifetimes are limited by a buildup of silt. And dams are not pollution free: decomposing organic matter in reservoirs generates methane, and reservoir bacteria are unusually active in converting elemental mercury to methylmercury. Dams, even within one country, and much more often when on international rivers, can cause severe tensions.⁸³ ■ *Small* dams, depending on the characteristics of each, avoid the worst of these problems.

Obstacles to renewable energy sources

Fossil fuels receive government subsidies in many parts of the world. Eliminating these subsidies is widely seen as a step that would promote wider use of renewable energy sources and a number of countries have begun to do so. Another barrier to renewable energy is that the environmental damage caused by fossil fuels is not accounted for in their price. Coal, especially, remains cheap.

Promoting conservation

Governments could provide incentives to conserve energy, regardless of where the energy comes from. EU countries already consume less energy than North Americans, but believe

⁸¹ Exploring ways to use hydropower, *US DOE*, September 12, 2005, http://apps1.eere.energy.gov/consumer/renewable_energy/hydropower/index.cfm/mytopic=50006.

⁸² A large dam is one almost 50-ft (more than 15-meters) high or one with a reservoir holding more than 106 ft³ (3 million m³) of water. There are over 45 000 large dams in the world. China, which already has a great many of these has built the biggest dam of all, the Three Gorges Dam on the Yangtze River, displacing two million people in the process.

⁸³ The World Commission on Dams in 2000 presented a decision-making framework to guide dam construction. This analyzes whether another option could meet the same goal as a dam, evaluates the impacts the dam will have, and makes recommendations to assure that benefits would not be appropriated by only a few individuals. It also recommends providing for people whose livelihoods and homes are destroyed.

they can make further reductions. Toward this end, they may reduce taxes on energy-efficient products and buildings; implement stricter building codes that promote energy-efficient buildings; promote co-generation; and promote renewable energy sources. ■ California is among the US states passing legislation to promote renewable energy use. Already 12% of California's electric power comes from wind, solar, geothermal steam, small hydroelectric plants, and biomass plants burning waste wood or other biomass. In 2002, California passed legislation requiring utilities to increase their purchase of renewable power by 1% a year until they reach 20%. ■ Considering the 29 OECD countries as a whole, it appears that no more than 6% of the energy used by the year 2020 will come from renewable sources such as solar or wind. However, the pace of new development is increasing to an extent that this situation could change.

The promise of micropower

Micropower refers to buildings or individual households off the central grid, providing their own electric power. Some banks, high technology firms or sensitive government operations that cannot tolerate even momentary disruption in electric supply sometimes use micropower. Some of these use fuel cells, although the hydrogen is not from renewable energy sources. Micropower can be provided by a microturbine fueled by natural gas, which is less expensive than hydrogen, and some of the steam generated can heat water or be used for space heating. ■ Micropower is not limited to special circumstances. Individual households can use many of the renewable energy sources just discussed. For those wanting to pursue one of these options many sources of information are available.⁸⁴

Questions 13.5

1. Having examined the variety of renewable energy sources available, pick two that sound most promising to you. Explain why.
2. If you wanted to micropower your own new home, which energy sources would you choose to research? Explain. How would your thinking differ if you were going to retrofit a pre-existing home?
3. Which form of solar energy do you believe is most feasible for large-scale applications? Explain.
4. For hydrogen to become a means of lowering the pollution now generated by fossil fuels, it *must be produced by renewable energy sources* and affordably so: explain what source you see as most likely to serve this purpose, and how soon it might happen.
5. Fossil fuels can power a plant generating electricity around the clock. Excepting geothermal, renewable sources don't provide round-the-clock power. (a) Do you believe storage

⁸⁴ A consumer's guide to energy efficiency and renewable energy. *US DOE*, November, 2008, <http://apps1.eere.energy.gov/consumer/>.

technologies have evolved far enough to solve this problem? Explain. (b) Does the energy necessarily have to be stored – how else can these energies be used without disrupting consumer supply?

6. Consider PV solar and solar-thermal. (a) Which of these is *less* likely to be useful in powering a private home or building and why? (b) For providing power to a national network of customers, which of the two sources do you consider superior and why?
7. Compare the environmental impacts of a coal-burning power plant and a large hydro-electric dam. (a) Give at least two reasons why it is difficult to directly compare the two. (b) The difficulty you had in answering this question also comes into play when comparing other sources of energy. How then can society make decisions on how best to produce energy?

Delving deeper

1. An estimated 2 billion of the world's people don't have electricity. Using web-based and other information, find the obstacles to serving the rural poor with electric power from a central grid. Secondly, find out how else this population can obtain electric power. What is being done to solve this problem, e.g., the World Bank has a large project toward this end – what do you think are its attractive features? Its shortcomings? By yourself or in cooperation with a partner or the class, propose a feasible means to provide electricity to a large numbers of people (on an individual household or village scale).
2. Go to the web to learn more about one of the items in Section VI: Re-power America, the Apollo Project, or Stabilization Wedges. After being clear in your own mind that you understand your selection, critique it in a written or verbally presented report. Make your own recommendations as they relate to the item you chose.
3. Investigate how heat can be recovered from each of the following sources in useful amounts and the uses to which it can be put: sewage effluent; a power plant's air stacks; methane in a landfill; and regenerative braking. Why aren't these being used more widely?

SECTION VI

The future

For most of the first decade of the twenty-first century the US government did little to manage an evolving energy crisis. The result is that, in 2009 the United States has a sense of urgency in moving toward renewable sources of energy. ▪ Cutting greenhouse gas emissions is cited as a major reason for renewable energies. ▪ However, also consider the rampant air pollution and other environmental degradation that are a part of burning fossil fuels. The United States, humanity more generally must find means to eliminate *most* pollution resulting from energy use. ▪ Energy security is also widely cited as a major reason

for finding realistic renewable energy sources within one's own border especially if those sources also provide good jobs and enhance a nation's infrastructure. ■ There must be a mix of renewable energy sources so that when, e.g., wind is not working, solar and other renewable energy sources are on line. And we need to develop means to efficiently store renewable energies using a "smart grid"⁸⁵ to assure that the national electric grid is flexible.

A number of plans have been proposed to move the United States toward renewable energies while also stabilizing and reducing greenhouse gas emissions. Following are three plans that, with variations, are applicable to many countries.

- Former US Vice President Al Gore supports *Re-power America*, a plan to reach 100% carbon-free sources of energy within 10 years.⁸⁶ This plan assumes that the government would be actively involved in providing incentives for concentrated solar-thermal plants and wind farms; planning and constructing a new "smart grid" to transport renewable electricity from its rural sites of production to cities where it is needed; converting our car fleet to plug-in hybrids; retrofitting buildings to make them more energy efficient⁸⁷; and taking a leading role in developing a post-Kyoto treaty to cap global CO₂ emissions while encouraging nations to come together in investing in means to reduce greenhouse gas emissions and deforestation.
- The *Apollo Project*⁸⁸ aims to integrate social goals (increasing jobs, technological innovation, and economic opportunity) with energy efficiency and conservation, and greater use of renewable energies. The program includes accomplishing all of the following by 2025: reducing by 30% the energy used in new and existing buildings; producing 25% of US electric power from renewable and recycled (now wasted) energy resources; modernizing the power grid; improving by 20%, the efficiency in existing power plants and industries; and connecting neighborhoods and cities with world-class public transit systems.
- In 2004, two Princeton University scientists presented a case for *Stabilization Wedges*. They state that "Humanity already possesses the fundamental scientific, technical, and industrial know-how to solve the carbon and climate problem for the next half-century."⁸⁹ These scientists propose taking the next 50 years to *stabilize* CO₂ in the atmosphere at no higher than 500 ppm⁹⁰ using already established technologies, which they describe. Concurrently, we must immediately pursue research and development to develop the "revolutionary technologies" required to actually make *steep* cuts in the amount of

⁸⁵ Charles, D. Energy: Renewables test IQ of the grid. *Science* **324**(5924) April 10, 2009, 172–175.

⁸⁶ Repower America, 100% clean energy within 10 years. <http://www.repoweramerica.org/>.

⁸⁷ Keep in mind that buildings use over 70% of US electricity and account for 40% of CO₂ emissions.

⁸⁸ The new Apollo program. *Apollo Alliance*, 2008, <http://apolloalliance.org/apollo-14/executive-summary/>.

⁸⁹ Pacala, S. and Socolow, R. Stabilization wedges: solving the climate problem for the next 50 years with current technologies. *Science*, **305**(5686), August 13, 2004, 968–972. One stabilization wedge equals what it would take to keep a billion tons of carbon from being emitted every year by 2054.

⁹⁰ 500 ppm is less than double the pre-industrial level of 280 ppm CO₂. 500 ppm is considered a "tipping point" beyond which humanity must not allow itself to go before irrevocable changes could take place in our climate. Stabilizing CO₂ at 500 ppm would be accomplished by energy efficiency and conservation; replacing many coal with gas power plants; using CO₂ capture and sequestration; adding more nuclear power plants; using more wind, solar, and biomass to replace coal; and reducing deforestation while working toward reforestation and using conservation tillage for agriculture.

atmospheric CO₂. The methods that they propose, not surprisingly, include energy conservation and efficiency, and making use of a number of renewable energy technologies already available or rapidly developing.

Japan has already taken major energy-saving steps.⁹¹ After the energy crises of the 1970s, the government mandated conservation and energy efficiency, placed high taxes on petroleum, and maintained a steady government investment in energy research and development. Japan's energy intensity (the amount of GDP produced per unit of energy) was, in 2005, more than twice that of the United States and the EU, and eight times that of China and India. Consider steel-making, a heavy user of energy. Japan invested large amounts in energy-savings technologies for this industry. An example of rewards for this effort is the Keihin steel mill on Tokyo Bay: it captures waste heat and gases so efficiently that the mill can generate 90% of its own electricity. However, Japan still uses a great deal of coal and has significant CO₂ emissions; it is now targeting reductions in CO₂ emissions from industry. Japan now sells its energy-saving technologies around the world.

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⁹¹ Fackler, M. Japan sees a chance to promote its energy-frugal ways. *New York Times*, July 4, 2008, <http://www.nytimes.com/2008/07/04/world/asia/04japan.html>.

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“Sustainable development simply means ‘treating the Earth as if we intended to stay.’”

Crispin Tickell, British Ambassador to the United Nations

Section I of this chapter examines general characteristics of those chemicals that are *persistent, bioaccumulative, and toxic* (PBT). We see that even at low environmental levels, they can present problems. Section II looks at actions society is taking to reduce the risk of PBTs. Because all the PBTs we examine in this chapter are organic, the acronym POPs (persistent organic chemicals) is also used in this chapter. Section III examines three families of PBT chemicals: one polychlorinated, one polybrominated and one polyfluorinated (Box 14.1).

SECTION I

Tens of thousands of chemicals are in common commercial use. Of these, the US EPA has identified 31 as PBTs (28 organic chemicals plus three metals and their compounds).¹ Other PBTs may be identified in future screenings. Thirty-one out of thousands is a small number, but given their ability to cause problems we can be grateful there are relatively few. Industrialized countries banned the worst polychlorinated chemicals such as DDT and PCBs in the 1970s and 1980s. Over time, the levels of persistent chemicals have slowly fallen. But hot spots remain, and advisories exist not to eat fish caught in the Great Lakes and certain other waters. The US EPA continues to develop action plans to reduce the levels of specific PBTs.² The Stockholm Convention of 2000 banned or greatly restricted 12 polychlorinated chemicals, dubbed the “dirty dozen.” PBTs³ also often move among air, water, and land, and cross human boundaries. Most are organic chemicals so, in this chapter, you often also see a second acronym used, POP (persistent organic chemical). The few PBTs that are metals are covered in Chapter 15.

¹ (1) Priority chemicals. *USEPA*, November 19, 2008, <http://www.epa.gov/epawaste/hazard/wastemin/priority.htm>. (2) Environmental hazard lists, *Scorecard*, 2005, http://www.scorecard.org/chemical-groups/one-list.tcl?short_list_name=pbt. This site lists 30 priority chemicals. (3) PBT Chemical List (1998 draft list of 53 chemicals). *US EPA*, November, 1998 <http://p2pays.org/ref/02/01851.pdf>.

² PBT National Action Plans. *US EPA*, January 15, 2008, <http://www.epa.gov/pbt/pubs/epaaction.htm>.

³ Other useful US EPA websites on PBTs: (1) PBTs, Frequently asked questions. *US EPA*, January 15, 2008, <http://www.epa.gov/pbt/pubs/faq.htm>. (2) PBT profiler. *US EPA*, January 15, 2008, <http://www.epa.gov/oppt/sf/tools/pbtprofiler.htm>. (3) About PBTs, general information. *US EPA*, January 15, 2008, <http://www.epa.gov/pbt/pubs/aboutpbt.htm>.

Box 14.1

A bit of chemistry

- Look at Figure 19.2, the periodic table of the elements. Go to column 17 and you will see the halogens, a family of five elements with related chemical properties. Note that the column begins with F (fluorine). The element below it is Cl (chlorine), and below Cl is Br (bromine).
- A *polyhalogenated* chemical is one that contains several halogen elements in its structure, e.g., CFCs contain the halogens, fluorine, and chlorine.
- An *organochlorine* is an organic chemical that contains chlorine. All 12 of the chemicals banned by the Stockholm Convention (described later) are polychlorinated.
- An *organobromine* is an organic chemical that contains bromine.
- An *organofluorine* is an organic chemical that contains fluorine.

Red-flag characteristics

Persistence

A persistent chemical⁴ – one that does not readily degrade – raises a red flag. In the laboratory, a POP (persistent organic pollutant) is more soluble in *octanol* (an oily substance that stands-in for fat) than in water, i.e., a POP favors a fatty environment and bioaccumulates in fatty tissues. A POP has an environmental half-life greater than a month, sometimes much greater. Thus, even low emissions of a POP, if they continue, allow it to build up in the environment. As its level increases, the possibility of harm to wildlife or humans exposed to it increases too. Most POPs are polyhalogenated; that is, they contain a number of halogen atoms (Box 14.1).

Nature produces thousands of chemicals that contain halogens but these ordinarily have only one or two halogen atoms⁵ – they are *not* polyhalogenated. Humans have synthesized many polyhalogenated chemicals. These can degrade, but only slowly over, sometimes, many years. If emissions continue environmental levels build up and the POP may bioaccumulate in animals. Depending on the specific pollutant and the conditions involved, POPs can take months, years, or decades to degrade. At the poles, buried in ice they may never degrade. See Box 14.2.

Bioaccumulation and biomagnification

- Another red flag is raised if a chemical *bioaccumulates*, i.e., builds up to levels in living organisms higher than those in the environment. This happens when a microbe, plant, animal, or human only very slowly breaks down a chemical, or if the chemical finds sites

⁴ Chemical reactivity as a tool for estimating persistence. *Environmental Science & Technology*, **39**(230), December 1, 2005, 480A–486A.

⁵ One exception is thyroxine, a hormone produced by the thyroid gland, which contains four iodine atoms.

Box 14.2

PBTs often present multiple problems

- If a pollutant has a short life span in the environment, hours, days, or weeks, then we may only need to limit current emissions to avoid a problem. However, in the case of a PBT we must deal with the PBT already in the environment from earlier emissions. This is the case with polychlorinated biphenyls (PCBs).
- Many PBTs are emitted *dispersively*: spraying a pesticide into the air is a dispersive use. The lead that for many years was added to gasoline was dispersively emitted in the exhausts of many millions of vehicles; the lead particles fell over wide areas. Power plants burning fossil fuels can be a major means of dispersing PBTs, hundreds even thousands of miles.
- A hazardous waste site can be difficult and expensive to clean up but, at least the chemicals are often concentrated on site and can be partially, sometimes almost totally cleaned up. Examples: PCBs leaked from electrical equipment dumped at a site, or lead that accumulated on site from an old lead-acid battery recycling site.
- The polychlorinated insecticide, DDT (dichloro-diphenyl-trichloroethane)⁶ has five chlorine atoms. Their arrangement in the DDT molecule hinders the ability of enzymes from living creatures to degrade them. (Figure 16.1)
- A notorious family of POPs is the dioxins.⁷ Figure 14.1 shows the most toxic dioxin: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (also just called dioxin). It is one of the most toxic chemicals known.
- A chemical family related to the dioxins is the PCBs (polychlorinated biphenyls).⁸ Several are as toxic as some of the dioxins. Banned more than 30 years ago, they still circulate in the environment.

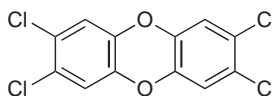


Figure 14.1

The structure of “dioxin” (2,3,7,8-tetrachlorodibenzo-*p*-dioxin)

within the plant or animal that firmly bind it. In such cases, its level increases, it bioaccumulates. Example ▪ PCBs accumulate in fatty tissues.

- More generally, polychlorinated chemicals only slightly dissolve in water, but are soluble in the fat of animals and humans, and in the fatty cuticle of plants: thus they accumulate in fat to levels higher, sometimes far higher, than those found in the environment. PCBs are a well-known example. A chemical is said to undergo *biomagnification* if its level becomes progressively higher moving through the food web (See Figure 3.3).

⁶ PBT chemical program, DDT. *US EPA*, January 15, 2008, <http://www.epa.gov/pbt/pubs/ddt.htm>.

⁷ (1) PBT chemical program, dioxins and furans, *US EPA*, January 15, 2008, <http://www.epa.gov/pbt/pubs/dioxins.htm>. (2) Dioxin. *US EPA*, June 29, 2007, <http://cfpub.epa.gov/ncea/CFM/nceaQFind.cfm?keyword=Dioxin>.

⁸ Polychlorinated biphenyls (PCBs). *US EPA*, January 15, 2008, <http://www.epa.gov/pbt/pubs/pcbs.htm>.

Toxic

Specific toxic effects vary with the particular POP in question. Many POPs (including dioxins, DDT, and PCBs) are environmental hormones (Chapter 3). Depending on the POP in question, it can impact the nervous system, reproduction and development, or is sometimes linked to cancer. Dioxins, DDT, and PCBs can act as environmental hormones, but they also demonstrate other toxic behaviors. POPs also vary as to whether they cause acute or chronic effects. Illustration DDT is not acutely toxic in mammals, but dioxin (2,3,7,8-TCDD) is acutely toxic.

PBTs often travel⁹

An example of how pollutants travel, in this case dust or smoke particulates is shown in Figure 14.2. PBTs are often trapped on dust or smoke particles and sometimes can be carried thousands of miles. They would present fewer problems if they did not travel. See Box 14.3. Many polychlorinated chemicals show *volatility*, i.e., they evaporate from land or water. Or, in the case of some pesticides sprayed into the air they may, caught in wind currents travel a few miles, or hundreds or thousands of miles from the point of emission, crossing human-made borders as they go. A polychlorinated pesticide sprayed into the air in Latin America may travel thousands of miles north from its point of use via a grasshopper effect (Chapter 1), and a portion ends up in Earth's polar region. Polychlorinated chemicals also move in migrating fish, animals, and birds. ■ The result is that polychlorinated PBTs are found concentrated in the fat of Arctic seals and other marine mammals, and Arctic people as well. Although polychlorinated chemicals were not used in the Arctic, the blood of the Inuit, indigenous people of northern Quebec contain levels of these chemicals up to 70-times greater than found in individuals living in southern Quebec. However, levels have recently begun to fall.

SECTION II

Reducing the risk of PBTs¹⁰

Reducing risk through information

- Remember the Toxic Release Inventory (TRI) from Chapter 2: just being required to report chemical releases can often get facilities to find ways to reduce emissions.

⁹ The Plain English guide to the Clean Air Act. *US EPA*, April 2007, <http://epa.gov/air/caa/peg/peg.pdf> (see page 19 of this site for "Persistent, bioaccumulative toxics").

¹⁰ PBT chemical program: preventing new PBTs, policy statement. *US EPA*, January 15, 2008, <http://www.epa.gov/pbt/pubs/prevent.htm>.

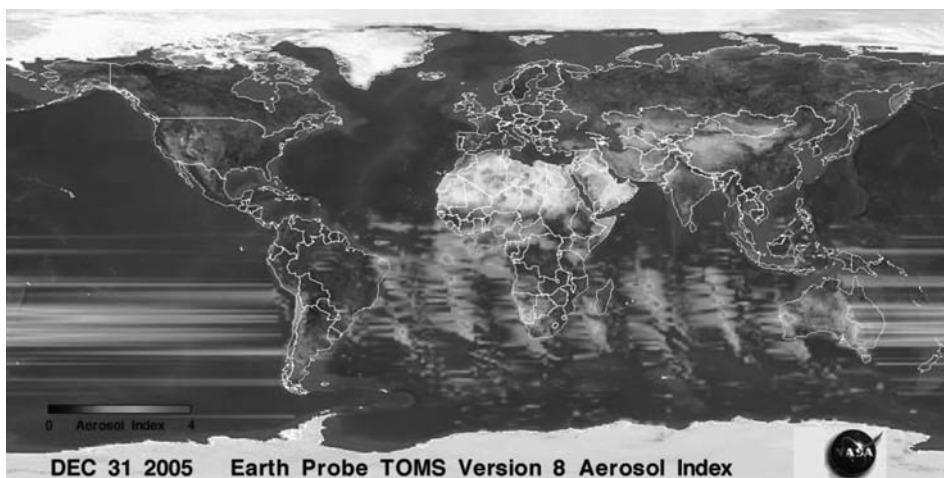


Figure 14.2 Airborne aerosol particles (microscopic dust/smoke) blowing out to sea from North Africa Credit: Earth Probe TOMS Aerosol Index. Credit: US NASA

Box 14.3

A bit of chemistry

Phthalates are small chemicals, often incorporated into plastics as *plasticizers*. Their function is to soften plastics, make them pliable. Another group of small chemicals (often PBDEs) are incorporated into products as fire retardants. Because plasticizers and fire retardants are not chemically bonded within these products, they are not held in place – they can volatilize or leach out. This can lead to both human and wildlife exposure. Sometimes it is possible to chemically bond flame retardants or plasticizers to the products. Bound chemicals won't leach out unless the chemical bond is broken.

Previously, US facilities did not need to report POP emissions as none were released in the large quantities characteristic of other TRI chemicals. However, in the year 2000 the US EPA began requiring businesses to report if they make, use or release 10 pounds (22 kg) or more of any of 27 specified PBTs.

Screening chemicals before they are produced¹¹

- The US EPA developed a *PBT Profiler*¹² to screen chemicals and identify those with PBT properties.¹³ The EPA also has National Action Plans to minimize the use of several PBTs

¹¹ (1) Chemical reactivity as a tool for estimating persistence. *Environmental Science & Technology*, **39**(230), December 1, 2005, 480A–486A. (2) Renner, R. Bioaccumulation assessments point to pressing data gaps. *Environmental Science & Technology*, **39**(13), July 1, 2005, 278A.

¹² PBT Profiler. US EPA, January 14, 2008, <http://www.epa.gov/oppt/sf/tools/pbtprofiler.htm>.

¹³ Ritter, S. K. Crystal ball on the environment: detective work and expertise are used to evaluate environmental contaminants of emerging concern. *Chemical & Engineering News*, **84**(5), January 30, 2006, 37–40.

including dioxins/furans, hexachlorobenzene, mercury, and benzo[*a*]pyrene. ▪ Large chemical companies including DuPont, Proctor & Gamble, and Dow had already begun to screen chemicals for PBT properties whenever they began developing new chemical products. They work to design chemicals without such properties. This represents “green chemistry,” deliberately designing chemicals or processes to make them more environmentally benign.

Reducing the risk worldwide¹⁴

In December 2000, after years of negotiation representatives of 122 countries finalized a treaty, the Stockholm Convention on Persistent Organic Pollutants (POPS).^{15,16} This banned or greatly limited 12 chemicals, called the “dirty dozen.” It was agreed that these 12 posed greater risks than other POPS. This treaty was the first-ever global agreement to abolish a class of chemicals. ▪ All 12 chemicals are *polychlorinated*.¹⁷ Nine are pesticides: aldrin, chlordane, DDT (notorious for greatly damaging populations of bald eagles, ospreys, and other predatory birds), dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene. Two are industrial chemicals, PCBs and hexachlorobenzene. Two are by-products of combustion and industrial processes, dioxins and furans. ▪ Most had already been banned in industrialized countries, but were still used elsewhere as in India and Latin America. For the treaty to work, industrialized nations had to assist less-developed nations. They provide \$150 million a year plus technical assistance to help phase out production and use of the dirty dozen, destroy existing stockpiles and, sometimes to help set up the production of alternatives. Delegates continue working on additional chemicals that may be banned in the future.¹⁸

Exceptions to the treaty

- DDT was banned many years ago in Western countries. However, at the urging of malaria experts, the treaty allows poorer countries to continue using DDT to control malaria-bearing mosquitoes. They spray DDT on the walls of homes,¹⁹ a procedure which repels or kills mosquitoes entering a home.

¹⁴ (1) Persistent organic pollutants (POPS): a global issue, a global response. *US EPA*, October 2, 2008, <http://www.epa.gov/oia/toxics/pop.pdf>. (2) International agreements and treaties. *US EPA*, October 16, 2008, <http://www.epa.gov/oppfead1/international/agreements/index.html>.

¹⁵ Ridding the world of POPS: a guide to the Stockholm Convention on persistent organic pollutants. *UNEP*, April, 2005, http://www.pops.int/documents/guidance/beg_guide.pdf.

¹⁶ Hogue, C. No vote for US in chemicals treaty. *Chemical & Engineering News*, **83**(18), May 2, 2005, 26–27. (The US signed the treaty, but has not passed enabling legislation so is not yet a party to the treaty.)

¹⁷ (1) UN to review “dirty dozen” chemicals. *Reuters*, May 2, 2005, <http://www.planetark.com/dailynewsstory.cfm/newsid/30639/story.htm>. (2) A longer description is: The Foundation for Global Action on POPS: a US perspective. *US EPA*, March 2002, <http://www.epa.gov/ncea/pdfs/pops/POPsa.pdf>.

¹⁸ (1) Governments take decisive action to rid world of POPS: four new chemicals proposed for phase-out. *UNEP*, May 6, 2005, www.pops.int/documents/meetings/cop_1/.../pr5-05POPsCOP1.pdf. (2) Arnaud, C. Persistent Organic Pollutants, more chemicals may be flagged as risky. *Chemical & Engineering News*, **85**(26), July 16, 2007, 6.

¹⁹ Handwerk, B. DDT to return as weapon against malaria. *National Geographic*, August 1, 2006, <http://news.nationalgeographic.com/news/2006/08/060801-ddt-malaria.html>.

- PCBs are still found in old electrical equipment. The treaty allows the equipment's continued use through 2025 if maintained to prevent leaks.
- For dioxins, the treaty has "the goal of their continuing minimization and, when feasible, ultimate elimination." Dioxins and furans cannot be banned because, except for laboratories making tiny amounts for research work, no one deliberately makes them. We can modify the processes that produce them to often virtually eliminate emissions: pesticide production processes that once produced dioxin by-products have been modified or eliminated. Current means of bleaching wood pulp has eliminated or greatly lowered the formation of dioxin by-products. Some of these reductions were started decades ago and, over the years environmental levels and body burdens of dioxins have decreased. Combustion remains their major source.

The Stockholm Convention may be working

The Stockholm Convention may be showing results. PCBs, DDT, chlordane, and toxaphene levels in Canadian Arctic animals have leveled off or fallen.²⁰ ■ PCBs in beluga, narwhal, walrus, and ringed seal decreased by an of average 43% since 1997. The exposure of the Inuit, the Arctic's indigenous people dropped about 20% this past decade. In pregnant women PCB blood levels fell 24% between 2000 and 2007. Because the Inuit body burdens of PCBs had been among the highest in the world, this finding is welcome, but results need to be confirmed. ■ Mercury, a metal to be discussed in Chapter 15 has not decreased. Moreover, not all POPs were examined in this study and, as seen below, levels of polybrominated fire retardants may still be increasing.

SECTION III

Three families of POPs

Three families of POPs are discussed below. The first, PCBs, have been frequently mentioned in this text. The second, polybrominated fire retardants, are still in use. Production of the third family, perfluorooctane sulfonates is being phased out and may be eliminated.

²⁰ Toxic chemical levels finally dropping in Arctic animals. *The Canadian Press*, July 14, 2008, <http://www.panna.org/files/CanadianPressArcticToxicsDrop20080714.pdf>.

Family one: the ubiquitous and long-lasting polychlorinated biphenyls (PCBs)

The PCBs are a family of 209 chemicals.²¹ Each PCB varies in the number and location of its chlorine atoms. These chemicals banned 30-years ago in the United States still pose problems because of their longevity. Those with the most chlorine atoms are the most persistent, and they are the ones that concentrate most heavily in fat. A major use of PCBs (sold as the mixture, Aroclor) was insulation of electrical-equipment. This use resulted from the fact that PCBs are nonflammable even at high temperatures. Safety codes once mandated their use. PCBs were also used in paints, inks, adhesives, newsprint, carbonless duplicating paper, even deep-fat fryers. But after it became clear that PCBs were persistent, bioaccumulative, and harmed wildlife, the United States banned them. ■ By that time, the late 1970s, the United States had manufactured about 1.4 billion pounds (over 600 million kg). Several hundred million pounds (about 200 million kg) had become environmental pollutants in various ways as when they leaked from electrical equipment. In earlier years, manufacturers legally released PCB-containing wastes, and New York's Hudson River suffered heavy pollution. Contamination was even worse on a land site near Anniston, Alabama, where PCBs were manufactured for 40 years.²² Many locales around the Great Lakes and marine coasts were also heavily polluted. PCBs are major pollutants in 20% US Superfund sites. PCB manufacture continued until 2001 in less-developed countries until the Stockholm Convention was passed.

- PCBs cycle in the environment PCBs concentrate in sediments from which they slowly move into the water above. From water some escape to air, become windborne, deposit into water again, and concentrate in sediments again. PCBs can also leave their sediment sink when bottom-feeding organisms take them up, and once again they begin moving through the food web. They also escape during dredging operations.
- PCBs toxicity²³ The toxicity of a few PCBs is comparable to the more toxic dioxins. Depending on dose and the particular PCB, they can damage the nervous and immune systems, the liver, and thyroid gland. They can profoundly affect fetal brain development. Many workers, heavily exposed to PCBs over years, developed liver damage. Many also developed *chloracne*, a form of acne resulting from prolonged contact with organochlorine chemicals, especially PCBs and dioxins. Chloracne can be severe and last for years. Moreover, the US EPA and the World Health Organization (WHO) classify PCBs as probable human carcinogens.
- Today's exposure Although environmental levels are much lower than in the 1970s, PCBs remain ubiquitous contaminants in the United States and worldwide. PCB

²¹ (1) Polychlorinated biphenyls (PCBs). *US EPA*, August 8, 2008, <http://www.epa.gov/opptintr/pcb/>. (2) PCBs toxicity exposure pathways. *ATSDR*, September 30, 2000, http://www.atsdr.cdc.gov/csem/pcb/exposure_pathways.html.

²² (1) Anniston, Alabama. *Wikipedia*, March 18, 2009, http://en.wikipedia.org/wiki/Anniston,_Alabama. (2) Grunwald, M. Monsanto hid years of pollution. *Washington Post*, January 1, 2002. <http://www.commondreams.org/headlines02/0101-02.htm>.

²³ The health effects of PCBs. *US EPA*, August 8, 2008, <http://www.epa.gov/epawaste/hazard/tsd/pcbs/pubs/effects.htm>.

exposure occurs today mainly via eating fatty meat, milk, milk products, and fish. Since PCB production was banned in the United States, PCB levels in Great Lakes fish fell up to 90%. However, many fish still exceed 2 ppm, the US Food and Drug Administration (FDA) standard for PCBs in commercial fish; above 2 ppm they are considered unsafe to eat. Nonetheless, people still catch and consume fish from the Great Lakes; for these people, fish are the major source of PCB exposure. PCBs still rank as high-risk chemicals in the Great Lakes, the Arctic, and several other locales.

A half-billion dollar risk-reduction project

From 1947 to 1977 two General Electric (GE) plants on New York's Hudson River manufactured PCB-containing electrical equipment, meanwhile releasing over 1 million pounds (454 000 kg) into the Hudson. Fish in the Hudson's most contaminated section had 2–41 ppm PCBs in their flesh. Some fish showed obvious harm: 90% of one codfish variety developed liver tumors by adulthood. Other fish suffered DNA damage similar to that seen in some human tumors. In 1984 the US EPA declared a 200 miles (322 km) section of the Hudson River a Superfund site. GE officials insisted that the river had been cleaning itself and was continuing to do so. In 2000, the EPA did find it cleaner than in earlier years. But PCBs in fish were still above levels considered safe for women of childbearing age and small children. Consideration was given to capping heavily contaminated sections with clean sediments culled from elsewhere, but the EPA believed these sections were too turbulent for capping. In 2001, after ten years of research costing \$25 million and exhaustive scientific review, the EPA ordered GE to dredge sediments from a 40-mile (64-km) long section of the Hudson at an estimated half-billion dollars cost. GE called the plan "absurd," and claimed that dredging would only stir up contaminated sediment. In response, the EPA noted it would regularly evaluate PCB levels in water and sediment to decide whether to continue dredging. In 2005, GE committed to dredging 43 miles (72 km) of the river²⁴, but as of late 2008, little progress had been made.²⁵

Questions 14.1

Obvious versus subtle toxicity²⁶

Japan and Taiwan In the 1960s and 1970s, respectively, many individuals were poisoned after ingesting cooking oil accidentally contaminated with PCBs and furans.²⁷ Researchers followed the development of children born within 7 years to women who had been poisoned. The children showed abnormal skin pigmentation, impaired mental development, impaired muscle movements, and slower growth. The severity depended on how much oil their mothers were estimated to have eaten. Some children were clearly poisoned.

²⁴ DePalma, A. GE commits to dredging 43 miles of Hudson River. *New York Times*, October 7, 2005, <http://www.nytimes.com/2005/10/07/nyregion/07pcb.html>.

²⁵ Hudson River PCBs. *US EPA*, December 1, 2008, <http://www.epa.gov/hudson/>.

²⁶ Barry L. Johnson, B. L., Hicks, H. E. *et al.* Public health implications of exposure to PCBs. *ATSDR*, <http://www.atsdr.cdc.gov/DT/pcb007.html>.

²⁷ Furans are close chemical relatives of dioxins.

United States Now consider children born to mothers eating large amounts of PCB-contaminated fish from the Great Lakes. Epidemiological studies examined these infants and small children for possible developmental defects correlated to their mothers' exposure. Trained observers detected small differences in the learning ability and memory of the infants as compared to control children, and also reported that the infants were more easily distracted, and their muscle tone poorer.

Commenting on these studies, one researcher stated, "The literature on prenatal exposure to PCBs and developmental neurotoxicity is one of the strongest bodies of evidence of human health effects in low-level environmental exposure." Yet others, analyzing the same studies remained unconvinced that the reported effects were even real. Because the United States has not used PCBs since the late 1970s, and they are now banned worldwide, some believe PCBs are no longer important. For adults, exposure to PCBs at current environmental levels is not considered a threat.

1. On the basis of this limited information, explain whether you believe that women of childbearing age should be warned not to eat sports fish from the Great Lakes. Read "Contaminants in Great Lakes sports fish," which points out the benefits of eating fish as well as the contaminants in Great Lakes fish including PCBs.²⁸
2. What if family income is low and the fish are an important dietary source of protein and other nutrients – would this affect your response?
3. PCBs, dioxins, and furans concentrate in fat. How could fish be prepared or cooked to remove or reduce a portion of the fat-soluble chemicals?
4. Was the US EPA justified in demanding that more than 40 miles (64 km) of the Hudson be cleansed of PCBs? Explain.

Family two: polybrominated fire retardants

With PCBs, the concern is for chemicals that have persisted for many years after they were banned. We now consider *PBDEs* (*polybrominated diphenyl ethers*), another family of over 200 analogues; with PBDEs, the concern is right now. PBDEs are incorporated, often in large amounts into electrical equipment, electronics, plastics within television sets, automobiles, furniture foam, textiles, upholstery, and carpets. PBDEs serve the important function of preventing or retarding fires.

- How PBDEs become pollutants They represent 5–30% by weight of the products into which they are incorporated. Although not very volatile, they do slowly outgas. Discarded into landfills, PBDEs in products may leach out. Moreover, high levels of PBDEs are being found in discarded electronics and in shredded auto waste,²⁹ from which they could enter the environment. ■ Not surprisingly considering the many home products containing PBDEs, they are found in house dust in US homes, sometimes at

²⁸ Contaminants in Great Lakes sports fish. *US EPA*, March 9, 2006, <http://www.epa.gov/gllndicators/fishtoxics/sportfishb.html>.

²⁹ Betts, K. S. A new record for PBDEs in people. *Environmental Science & Technology*, **39**(14), July 15, 2005, 296A–298.

high levels.³⁰ They are also found in all US marine waters as well as the waters of the Great Lakes.³¹ Young children are exposed to much higher levels of house dust than adults. In Norway children under four-years old were found with levels of PBDEs in their blood several times greater than adults. This is a double concern because they may also have received PBDEs in breast milk.

- Toxicity³² The offspring of laboratory animals, exposed during gestation to high doses of PBDEs, were born with damaged thyroid and nervous systems. An impact on thyroid function may not be surprising because PBDEs are structurally similar to the hormone, thyroxine – so PBDEs may be acting as environmental hormones.³³ Cats are an animal population exposed to high levels of house dust, especially because of their careful self grooming habits. A study of household cats found them to have blood serum levels 20–100 times greater than adult humans in North America. Of 23 cats studied, 11 had feline hyperthyroidism, a sometimes-fatal disease not reported in cats at all 35-years ago.³⁴ Whether current PBDE levels are high enough to be toxic to humans is unknown. However, increased hyperthyroidism in house cats is not reassuring. Likewise, the ubiquitous environmental presence of PBDEs and their rising levels pose real concern.
- Increasing contamination Canadian scientists report that PBDEs are reaching the Arctic more quickly than did dioxins or PCBs, and accumulating in seals and other wildlife. Levels also continue to rapidly rise in fatty tissues of fish as far apart as Lake Ontario and the Baltic Sea, and in the fat of marine mammals. Japanese, Israeli, and Spanish investigators report increasing levels in human fat, and blood. Swedish researchers found PBDEs in women's breast milk at levels in 1999 that were 60-times higher than those in 1972. And PBDEs taint foods such as fish, milk and eggs. PBDE levels are *increasing* just as PCBs, dioxins, and DDT levels are *decreasing*.

Reducing the risk of PBDEs

Several years ago the EU and several US states banned two PBDEs, a penta-BDE and an octa-BDE. They banned them because they are persistent, toxic, and tend to bioaccumulate – they are PBTs.³⁵ Although not among the dirty dozen banned by the Stockholm Convention, some PBDEs are candidates for future banning. The EU recently also banned deca-BDE. Deca-BDE may break down in the environment into the more troublesome penta-BDE. However, deca-BDE is still used in most US states. Some industrial users believe no good substitute is available for their particular products.

³⁰ Betts, K. S. The risk of PBDEs in dust. *Environmental Science & Technology*, **41**(5), March 1, 2007, 1505–1506.

³¹ Hogue, C. Flame retardants found in all US coastal waters. *Chemical & Engineering News*, **87**(14), April 6, 2009, 22.

³² The Danger of PBDEs, *Environmental News Network*, December 25, 2007, <http://www.enn.com/wildlife/article/28141>.

³³ Betts, K. Unexpected human impact on Antarctica. *Environmental Science & Technology*, **42**(5), March 1, 2008, 1390–1391.

³⁴ Betts, K. PBDEs, cats, and children. *Environmental Science & Technology*, **41**(18), September 15, 2007, 6319–6320.

³⁵ Betts, K. Does a key PBDE break down in the environment? *Environmental Science & Technology*, **42**(18), September 15, 2008, 6781.

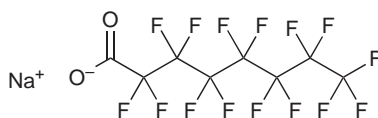


Figure 14.3

Structure of sodium perfluorooctanonate

Box 14.4

A bit of chemistry

The *per* in *per*fluorooctane sulfonates indicates that these chemicals contain as many fluorine atoms as the molecules can accommodate, i.e., they are fully fluorinated. The fluorine-carbon bond is extremely stable, one of the strongest chemical bonds known. This accounts for its great usefulness. It also accounts for its great persistence.

Family 3: a polyfluorinated mystery

In May 2000, 3M Corporation took a surprising action. It withdrew its popular fabric stain repellant, ScotchgardTM from the market. Scotchgard contained *perfluorooctane sulfonates* (PFOS), see Figure 14.3. PFOS are a family of about 300 *polyfluorinated* chemicals (Box 14.4). By 2002, 3M had phased out PFOS use in fire-fighting foams, mining and oil well surfactants, herbicides and pesticides, and products preventing food from sticking on paper surfaces such as pizza boxes and popcorn bags. Withdrawals occurred after researchers found PFOS at trace levels in human blood. This included the blood of 3M's own managers, who had not been directly exposed to PFOS. Trace amounts were also found in humans and wildlife around the world. How this widespread exposure to PFOS has happened is a mystery although explanations have been proposed.

One researcher said that fluorine was introduced into chemicals although “what we know about fluorine chemicals in the environment is less than what we knew about chlorine chemicals in the 1950s.” What we do know raises concerns.

- **Persistence** PFOS are extremely difficult for living organisms to degrade. Some believe they “will redefine persistence,” making PCBs and DDT seem comparatively easy to degrade.
- **Bioaccumulative** In a year 2000 accident near Toronto, Ontario (Canada), a spill of fire-fighting foam containing PFOS chemicals occurred. Researchers took advantage of the spill to study fish in a contaminated stream. They found PFOS in fish livers at concentrations 6300 to 125 000 times over the concentration in water. PFOS is clearly bioaccumulative.
- **Toxicity** Rats and rabbits exposed to high doses ate less, which resulted in reduced body weights. Their litters were smaller and their fetuses gained less weight. Because PFOS chemicals are chemically inert, this toxicity was unexpected. More recently health impact have been observed at low levels: the immune systems of mice fed PFOS at levels found in human blood showed suppression of antibody production.³⁶

³⁶ Cooney, C. M. PFOS alters immune response at very low exposure levels. *Environmental Science & Technology*, 42(10), April 16, 2008, 3486–3487.

- Traveling PFOS. How the non-volatile PFOS ended up in birds in the Pacific Ocean, and in animals in other isolated locations is a mystery.

Reducing the risk of PFOS chemicals

3M Corporation phased out production of PFOS chemicals while, meanwhile developing a non-fluorinated Scotchgard. It also reformulated many other products. The new products have undergone extensive environmental, health and safety testing, and reportedly have little to no environmental impact. They are manufactured and sold under consent orders with the US EPA.³⁷ The EPA believes that the quick phase out of PFOS chemicals will result in a quick decrease in exposure. ■ Government of Canada scientists concluded that current levels of exposure to PFOS would not adversely affect human health, but were concerned that some wildlife, such as polar bears or fish-eating bird species, might be near potentially harmful levels. ■ Canada will eliminate PFOS use by 2009,³⁸ and the EU by mid-2008. ■ In both places, there are limited exemptions for products without substitutes such as PFOS in aviation hydraulic fluids. ■ In May, 2009, there will be a vote under the Stockholm Convention to classify PFOS as a POP. If that happens, there could be a global ban on PFOS and PFOS-related compounds

Questions 14.2

1. Why are small children exposed to greater levels of house dust than adults?
2. (a) Why do POPs (including PCBs and PBDEs) concentrate in breast milk? (b) Does this mean mothers should avoid breast feeding? You may want to examine a respected site on the web such as that of the Centers for Disease Control and Prevention³⁹ before answering this.
3. (a) Manufacturers state that PBDEs should not be banned because fire prevention is so important. Is this reasoning legitimate? Explain. (b) What if no suitable substitutes are available for certain products and we continue to sell PBDEs – are there ways to lessen the risk?
4. Consider the PFOS story. What went wrong here? How can we prevent such happenings in the future?

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³⁷ PFOS/PFOA information: what is 3M doing? http://solutions.3m.com/wps/portal/3M/en_US/PFOS/PFOA/Information/Action/#top.

³⁸ Perfluorooctane Sulfonate (PFOS). *Government of Canada*, December 30, 2008, http://www.chemicalsubstanceschimiques.gc.ca/interest-interet/pfos_e.html.

³⁹ Breastfeeding, exposure to environmental toxins. *US Centers for Disease Control*, http://www.cdc.gov/breastfeeding/disease/environmental_toxins.htm.

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“Society is a partnership not only between those who are living, but between those who are living, those who are dead, and those who are to be born.”

Edward Burke, 1790

All metals are persistent, but not all fit the other two PBT criteria. ▪ Ability to bioaccumulate limits the list of PBT metals to three: lead, methylmercury, and cadmium. Notice that the element, mercury is not a PBT, but rather *methyl*mercury, which can bioaccumulate in living creatures and biomagnify in the food web a million-fold or more. ▪ Also remember that many metals are nutrients, and that exposure to metal nutrients at normal levels is not toxic. It is the metals that are not nutrients, especially the so-called “heavy” or hazardous metals that can be toxic even at relatively low concentrations. ▪ Another factor in toxicity is the chemistry of the metal’s compounds.¹ ▪ The US EPA now has only three metals on its PBT list: mercury, lead, and cadmium.² Section I of this chapter is a metal primer, providing information on metals and metal pollution regardless of whether they are PBTs. Section II details the three especially troublesome metal PBTs, lead, mercury, and cadmium plus one metalloid that is not a PBT, arsenic.

A metal primer

Metals are *elemental* and cannot be chemically destroyed (Chapter 19). But a metal does bond to other elements to become part of a compound. The compounds of a metal show properties different from the parent metal. Consider three examples.

¹ This is illustrated by the metal chromium. For compounds in which chromium has a valence of three, it is a nutrient. However, industrially important compounds with *hexavalent* chromium are toxic, carcinogenic, and mutagenic. Thus, chromium can be a necessary nutrient or a hazard, depending on its chemical state. Valence has to do with the number of electrons in the outer shell of an element, and are very important in determining how an element will react with other atoms, see Chapter 19. (1) Chromium. *Micronutrient information center*, Linus Pauling Institute, September, 2007, <http://lpi.oregonstate.edu/infocenter/minerals/chromium/index.html>. (2) Biedermann, K. A. and Landolph, J. R. Role of valence state and solubility of chromium compounds on induction of cytotoxicity, mutagenesis, and anchorage independence in diploid human fibroblasts. *Cancer Research*, **50**, December 15, 1990, 7835–7842, <http://cancerres.aacrjournals.org/cgi/reprint/50/24/7835>.

² In an earlier draft list of PBTs, <http://p2pays.org/ref/02/01851.pdf>, the US EPA evaluated 53 chemicals as possible PBTs including 11 metals (some of which were nutrients). However, there are only 30 chemicals in EPA’s final PBTs list, and only three metals. See: http://www.scorecard.org/chemical-groups/one-list.tcl?short_list_name=pbt.

- Elemental lead is a solid, but the lead compound, *tetraethyl lead* an antiknock agent is an oily liquid. The lead is still there, but bonded to carbon in a molecule. The molecule has very different properties than does lead itself.
- When elemental iron reacts with other elements to become a compound, its properties change too. A common iron compound is iron oxide (*rust*, a reddish substance) formed when iron reacts with atmospheric oxygen and forms a compound. You have probably observed rust on a bridge.
- Consider metal pollutants in soil at levels too high for safe agriculture. They may be present in compounds that plant roots can take up. Sometimes, it is possible to add lime (calcium oxide) to the soil. The polluting metals react to become metal oxides, which are insoluble and not easily taken up by plant roots. However, if the treated soil later becomes acidic – perhaps after a prolonged period of acid deposition – the metal may again become soluble.

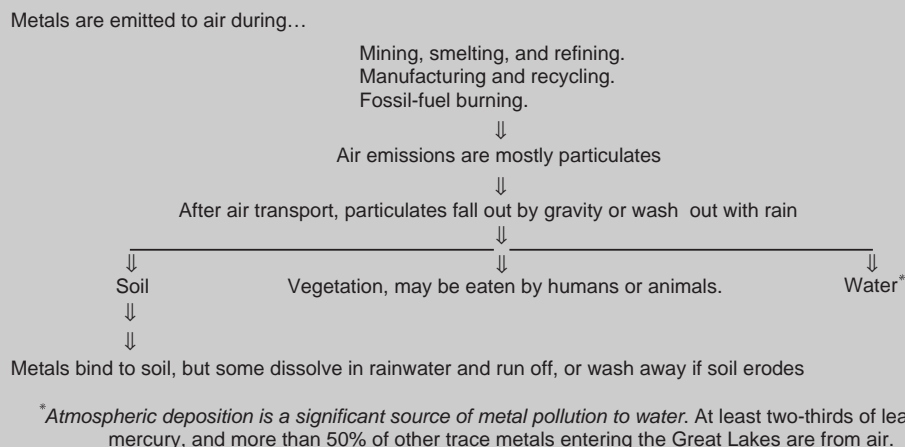
Movement of metal pollution

Excepting mercury, metals are usually emitted to air as particulates. In Table 15.1, notice that the particles don't stay airborne, but fall out to water and land. Much of this atmospheric deposition occurs near emission sources, but metal particulates can travel with the wind, some for long distances before fallout. In the 1950s, pilots flying in the Arctic in winter saw a haze so heavy it obscured visibility. Later, the haze was found to be composed of particles transported by winter winds from industrialized regions in Europe and Asia. The haze contained soot, soil particles, POPS, and metals.

Metals in soil and sediment

Because metals are natural substances, they are found in soil, usually at low levels. However, metals emitted during fossil fuel combustion, mining, or other industrial processes and falling on soil and water can increase metal concentrations. Because metals don't degrade, they can remain in the soil. However, concentration can be lowered: contaminating metals in surface soil are buried by the slow buildup of overlying soil. Rain may partially leach out soluble metals from surface soil and carry them away in runoff. Or water may erode and carry away the soil itself including its bound metals. ▪ In a water body, metals bind to sediment and may become more deeply buried as overlying sediment builds up. They may be buried deeply enough to no longer pose a problem – unless the sediment is stirred up as when a harbor or river is dredged.

▪ Especially near the sediment's surface though, problems can arise. Bottom-dwelling creatures can take up some metals as well as other chemicals from the sediment. Most problematic, however, is what happens to mercury: some sediment bacteria can convert it to the more toxic methylmercury, which can be absorbed into organisms and then through the food web.

Table 15.1 Fate of metals emitted to air**Box 15.1****An ambiguous term**

The term *heavy metal*³ is often used to refer to problematic metals such as lead, mercury, and cadmium. But this term is imprecise, and perhaps shouldn't be used at all.⁴ Recently, the alternative term *toxic element* has been used. However, as you saw in Chapter 3 toxicity depends on many factors. *Hazardous metal* may be a better designation – recall the difference between a hazard and a risk.

Metals in food and water

Metals are naturally found to varying extents in food and drinking water. Indeed nutrient metals (iron, chromium, copper, cobalt, manganese, molybdenum, nickel, selenium, vanadium, and zinc) are needed. However, at higher doses, metals can be toxic (Figure 3.2.) Think of iron, a nutrient. Iron still occasionally kills small children who find and eat their parents' iron supplement capsules. Natural metal levels can also pose risks when levels are unusually high; arsenic is found naturally at high levels in some soils and waters. ▪ However, human activities are responsible for the dramatic twentieth-century increases in metals in the environment. That century saw the mining of about 90% of all cadmium, copper, lead, nickel, and zinc ever mined. The metals, lead,

³ If you have lifted a lead brick you can understand the term, heavy metal (as compared to a light metal such as aluminum). A metal is sometimes considered heavy if it has a density greater than 5 g/cm³. Several nutrient metals such as iron are "heavy" too. Some metalloids such as arsenic have a density high enough to be called heavy.

⁴ Duffus, J. H. "Heavy metals"—a meaningless term. *Chemistry International*, 23(6), November, 2001, <http://old.iupac.org/publications/ci/2001/november/heavymetals.html>.

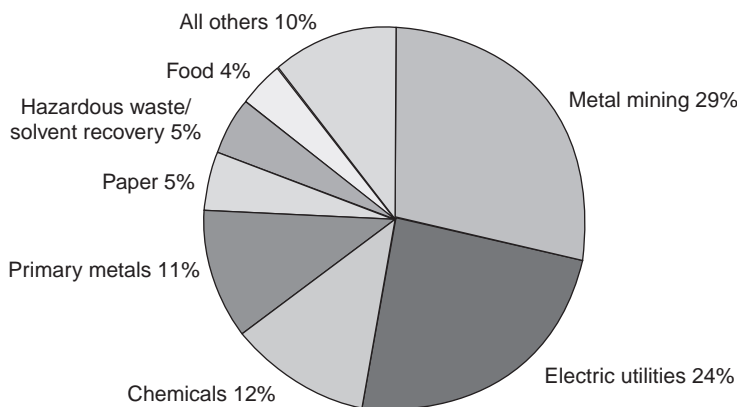


Figure 15.1

TRI disposal and other releases in 2006 by sector. Credit: US EPA

cadmium, and mercury pose special concerns. Others that sometimes present problems include antimony, cobalt, copper, manganese, molybdenum, nickel, selenium, vanadium, and zinc.

Metal pollution sources

Mining⁵ and metal product fabrication, use, and disposal

Mining operations produce major quantities of overburden (material previously overlying the ores). Metals leached from overburden and other mining wastes by rainwater can be carried in runoff to local waters. Mining wastes are often rich in sulfur. If moisture and oxygen are present, sulfur is oxidized to sulfuric acid; and acid dissolves additional metals to be carried away. Metals can foul streams and rivers for many miles downstream. Unless land is properly managed during mining, and carefully reclaimed afterwards, which usually doesn't happen, it may be useless for other purposes. The pollution is often significant: recall the TRI (Toxic Release Inventory) from Chapter 2. In 2006, metal mining was responsible for 29% of all US industrial emissions to land, water, and air (Figure 15.1). Notice in the same figure that primary metals represent another 11% of TRI releases.⁶ To get a sense of pollution associated with metal mining

⁵ (1) Profile of the metal mining industry. *US EPA*, November 18, 2007, <http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/mining.html>. (2) A guide to the toxic release inventory for Nevada. *State of Nevada*, <http://ndep.nv.gov/bwm/lication.pdf>. (This document overviews pollutants released from mining operations.) (3) Mining and metals, Environmental Social Management System. *UNEP*, http://www.unepfi.org/fileadmin/toolkit/Mining_Metals_ESRBN_amended180806.pdf.

⁶ The primary metals industrial sector is divided into three types of operations: metal fabrication, metal preparation, and metal finishing. See: Metals. *US EPA*, March 4, 2009, <http://www.epa.gov/compliance/assistance/sectors/metals.html>.



Figure 15.2 A coal-burning power plant. Credit: Phillip J. Redman, photographer, US Geological Survey

and metal product use, *remember LCA* (life-cycle assessment). ▪ Mining, smelting (melting an ore to separate out desired metals), and refining (purifying the metal) represent the first stages of a metal's life cycle. All produce some pollution. Manufacturers use the refined metal to produce metal-containing products. Depending on what products the metals are in, they may or may not be recycled at the end of their useful lives. The metal in a car is likely to be recycled. The metals contained in small products such as toys or even metal cans are often thrown away. Combusting municipal solid waste with metal-containing products may lead to metals particulates escaping into air. Discarding waste metal products leads to their corrosion and slow dissolution, which also pollute. It would be necessary to look at a specific product to become more specific in each of these steps.

Fossil fuel combustion

Later in this chapter you will see that coal-burning power plants are the major remaining source of mercury emissions. These same plants are a source, sometimes a major one, of a number of other metals (Figure 15.2). Emissions from coal have metals ranging from less than 1 ppm for silver, to 10 000 ppm for iron and aluminum.⁷

⁷ Vock, V.B. and Piver, W.T. Metallic elements in fossil fuel combustion products: amounts and form of emissions. *Environmental Health Perspectives*, **47**, 1983, 201–225, <http://www.ehponline.org/members/1983/047/47017.PDF>.

Emissions at any moment are small. However, the United States burns a billion tons of coal each year; China burns more than that. Thus, even small emissions of metal pollutants build up over time, especially near combustion sources. Petroleum combustion to a lesser extent emits metal pollutants. ▪ Air Except for mercury, metal emissions are particulates or attached to particles. ▪ Water and land Within days or weeks the particulates settle onto land or water (Table 15.1). ▪ Combustion ash Coal-burning plants produce immense quantities of ash. Because the organic portion of coal has burned away, metals in ash are concentrated. A portion of both fly ash and bottom ash find use in making Portland cement and asphalt concrete aggregate.⁸ Disposing of the rest of the ash is a problem. Much is stored in lagoons, but remains potentially usable. It is important to keep it wet as dry ash can blow away. If unprotected, rainwater can leach metals from the ash. ▪ Catastrophic failure of an ash pond⁹ An earthen dam pond at a TVA coal-fired power plant held decades' accumulation of coal ash on the banks of the Emory River in Harriman Tennessee; the Emory flows into two other rivers, which are a drinking water source for many municipalities. On December 22, 2008, after heavy rains, the dam "failed catastrophically" and a billion gallons (3.8 million liters) of coal ash sludge and water flooded out, covering 300 acres (121 hectares). Homes were also destroyed or partially so by the sludge. Elevated levels of lead and thallium, and very high levels of arsenic were found in water samples taken near the site of the spill. An environmental advocacy group had further professional tests performed; these showed concentrations of eight metals above drinking water standards. There was concern for fish and other aquatic life directly exposed to elevated metal concentrations. Environmentalists and, to some extent, the EPA already believed that coal ash should be regulated as hazardous waste; this tremendous spill has brought that issue to the fore again.

Other sources

▪ Municipal and industrial wastewater treatment plants are point sources of metal pollutants to water. ▪ Paved roads and construction sites are among the sources from which metal particulates can be blown with the wind or runoff with rainwater. ▪ Metal-containing wastes disposed on land are a source of pollution. ▪ Some fertilizers, pesticides, sewage sludge, and animal wastes applied to soil have higher metal concentrations than those found naturally.

Natural sources

These include volcanoes, forest fires, and sea salt sprays. Although significant, it is human activities that are increasing the environmental load of metals.

⁸ (1) Coal fly ash. *Turner-Fairbank Highway Research Center*, <http://www.tfhrcc.gov/hnr20/recycle/waste/cfa51.htm>. (2) Coal bottom ash/boiler slag. *Turner-Fairbank Highway Research Center*, <http://www.tfhrcc.gov/hnr20/recycle/waste/cbabs1.htm>.

⁹ Dewan, S. At plant in coal ash spill, toxic deposits. *New York Times*, December 29, 2008, <http://www.nytimes.com/2008/12/30/us/30sludge.html>.

Box 15.2

Ancient mining

Most metal mining occurred in the twentieth century. However, humanity is fortunate that the ancient Greeks and Romans didn't mine and smelt as much ore as their twentieth century counterparts. The ancient Romans smelted metal ores over open fires with emissions so noxious that authors of the day complained of them. Lead and copper pollution from thousands of years ago is still detectable around the world today, recorded in buried layers of ice, and in bogs and sediment. In the sixteenth century, large furnaces with tall stacks were developed to process ores. These still badly polluted their surroundings, but were an improvement over ancient methods. Without careful controls, modern mining, smelting, and refining can still pollute badly.

Where metal pollution can present problems

- Fresh water bodies Because fresh-water organisms evolved with low metal levels, higher concentrations can be problematic. Moreover, many lakes have small volumes or few outlets to dilute or displace polluting metals.
- Marine waters Metal levels in marine waters are naturally higher than in fresh. Nonetheless, ever-growing coastal populations have led to increasing marine pollution as runoff and rivers carry pollutants to the sea from ever-more developed land.
- Acid rain In acidified lakes, bacteria convert elemental mercury to the highly toxic methylmercury more efficiently. ▪ Metals are more soluble in acid soils. Aluminum is a prominent example; it can be washed out by rain, and run off into nearby water bodies.
- Cities Older cities had more metal-processing facilities than rural areas leaving some city soils highly polluted.
- Agricultural soils Some European agricultural soils, even in Western Europe, where pollution is better controlled are above or close to the *maximum loading rate* for some metals. Above that rate, the soil is not fit to grow crops. Some agricultural villages in Eastern Europe are deserted due to metal contamination. In Japan, metal contamination has made nearly 10% of rice paddy land unusable. The cost to remediate metal-contaminated soil is high. Much cannot be cleaned up at all.
- Hazardous waste sites Lead, cadmium, mercury, and arsenic are four of the ten most common pollutants found at US hazardous waste sites.

Human exposure

Human exposure to metal pollutants occurs in various ways. ▪ Fish consumption is the major route of exposure to mercury. ▪ Shellfish, if eaten frequently, can be a major route of exposure to cadmium, but for smokers, tobacco is the major route of exposure. ▪ For most

Box 15.3**A healthy diet can reduce risk**

A diet emphasizing fruits, vegetables, and grains provides many benefits including a lowered susceptibility to toxic substances such as metals as well as lessened susceptibility to infections. A varied diet contains a variety of metals including, but not limited to, nutrient metals. Some metals oppose the biological effects of others. ▪ Dietary calcium and iron provide some protection against ingested lead by inhibiting lead absorption from the gut. ▪ Zinc antagonizes some toxic effects of cadmium. ▪ Selenium provides some protection against toxic effects of mercury, cadmium, and silver. A diet high in calcium, iron, and fiber is associated with lower blood levels of cadmium. ▪ In the arsenic poisonings described in Chapter 10, people with good nutrition were less likely to develop skin lesions from drinking water with high arsenic levels. ▪ Such examples demonstrate the need for a varied diet. However, a healthy diet is often not available to the poor. Remember also, that too high a dose of any metal can be toxic. In fact, selenium – a nutrient when taken in proper amounts – has been poisoning wildlife for years in the western United States.

of us, food is the highest source of arsenic exposure, although much of that arsenic can be natural. But recall the many millions of individuals in Asian countries exposed to high arsenic levels in contaminated well water. For them, drinking water is the most significant source of arsenic. Adverse health and environmental effects are specific to the metal involved.

Treating diseases with metals

As with other chemicals, metal toxicity depends upon the dose absorbed into the body, nutritional status, and many other factors. Long before antibiotics existed, arsenic was used to treat syphilis, and patients were sometimes poisoned. ▪ Metals still have medicinal uses. Bismuth, as in Pepto Bismol, treats some stomach problems. Gold is sometimes used to treat rheumatoid arthritis, lithium for manic-depressive illness, and zinc is found in some drugs. ▪ More dangerous situations arise when the hazardous metals, lead, mercury, cadmium, and arsenic are used in “folk remedies.” Some Caribbean religions such as Santeria see mercury as a substance attracting good and repelling evil, and use it in medicine. Poisoning cases have been reported among US immigrants who brought metal remedies with them. A well-balanced diet can help protect against ingested pollutants including metals (Box 15.3).

Reducing metal risk

Many countries have laws to control metal emissions, but not all enforce them well. US law controls point source metal discharges to water. Air emissions are controlled under the 1990

Box 15.4

Fouling ocean-going vessels

Tin is not very toxic. Indeed, elemental tin has often been the inner layer in metal food cans, coming in direct contact with food. But *organotin* chemicals are toxic. Algae, barnacles, slime, fungi, diatoms, and crustaceans attach themselves to the hulls of ocean-going vessels, slowing speed, decreasing maneuverability, and increasing fuel use. In the 1970s antifouling paints with organotin additives (especially *tributyltin*, TBT) were introduced. Hulls became much cleaner. Unfortunately, water leaches TBT from the paint into surrounding waters. ▪ Persistence Released near the water's surface TBT persists only a few days. Microbes can degrade TBT to the less toxic dibutyltin and monobutyltin. However, degradation is slower for TBT in sediments. In cold-water sediments, its half-life is over 2 years. Harbors and marinas are often the spots most polluted with TBT. Bioaccumulation TBT bioaccumulates in fat. Toxicity TBT is exceptionally toxic. Depending on dose and conditions TBT causes high rates of death among mussel larvae, can thicken oyster shells, and causes snail imposex (female snails have a penis). TBT can be toxic to crustaceans at concentrations of less than 1 µg/l. ▪ Reducing risk Some countries had already banned or restricted TBTs. Then, in 2001 the 159 member states of the International Maritime Organization voted to restrict persistent organotin additives in paint, and to ban them in 2008. The delay was to allow time to find less environmentally harmful substitute biocides.

Questions 15.1

1. Why would TBT near the water's surface break down more quickly than that which is buried in sediments?
2. Why was it possible to ban tributyl tin but not to ban methylmercury – what is the difference?

Clean Air Act Amendments. EPA regulations greatly reduce lead, cadmium, and mercury emissions from municipal solid waste and medical waste incinerators. A joint Canadian–US effort is working to prevent further metal buildup in the Great Lakes. Modern technology such as used in a new smelter-refinery complex in Utah, among the cleanest of the world's smelters, can help lower metal pollution.¹⁰ Pollution prevention efforts have resulted in lowered metal pollution in many cases as when the printing industry replaced hazardous metal pigments with soy-based ones, or when hazardous metals in paper and plastic packaging were restricted.

¹⁰ Rio Tinto: reclaiming the environment from a century of mining. *Kennecott Utah Copper*, 2008, http://www.kennecott.com/library/media/papers/pdf/Final_August_Remediation_Report.pdf.

SECTION II

Three PBT metals¹¹

The US EPA ranks metals as among the agents posing the greatest hazard to humans. Four metals, lead, mercury, cadmium, and arsenic are among the 10 most common pollutants found at US hazardous waste sites. All four metals with the exception of arsenic are characterized as PBTs. Lead, mercury, and cadmium are also included among 31 chemicals that EPA considers of high priority.¹²

Lead¹³ and lead products

Lead has wonderful properties. Ductile and easy to work with, humans have used lead for thousands of years. The greatest quantity was used in the twentieth century. ▪ It is widely used in plumbing¹⁴ and soldering. Added to paint, lead protects both indoor and outside surfaces. In gas, tetraethyl lead is an excellent antiknock agent. Lead print was used in printing newspapers, magazines, and books. ▪ Considering its emission sources (below) it is not surprising that lead became ubiquitous in the environment. The lead concentration in recently formed Antarctic ice is four times greater than in ice formed prior to the industrial age. Its concentration in recent coral shells is 15 times greater than in shells deposited a century ago. In household dusts lead's concentration can be 500 times greater than the background level in the Earth's crust.

Sources of lead

Lead emissions Assuming that you live in a country that no longer adds lead to its gasoline, the largest lead-emitting sources to air¹⁵ are coal-burning power plants and incinerators, and also mining and smelting. The most concentrated emissions are near lead smelters. Facilities manufacturing lead-acid batteries may also be high emitters. Natural emissions These are volcanoes, airborne soil particles, sea spray, and forest fires. Lead already in the environment *The lead already in the environment* due to human actions often represents the most serious exposure.

¹¹ Action on heavy metals among key GC decisions. *UNEP*, February 25, 2005, <http://www.unep.org/Documents.Multilingual/Default.asp?DocumentID=424&ArticleID=4740&l=en>.

¹² Priority chemicals chemical name and summary fact sheet. *US EPA*, January 12, 2009, <http://www.epa.gov/epawaste/hazard/wastemin/priority.htm>.

¹³ Lead and cadmium working group, Geneva, *UNEP*, September 18–22, 2006, 6–12, http://www.chem.unep.ch/pb_and_cd/WG/Docs/K0653416%20-%20Lead%20Cadmium%20Report.pdf.

¹⁴ The word plumbing comes from the Latin word for lead, plumbum. The Romans used lead to make water pipes and to create urban water systems: it doesn't rust, is easy-to-work-with, and readily available; it seemed ideal for plumbing.

¹⁵ Lead in air. *US EPA*, October 16, 2008, <http://epa.gov/air/lead/>.

Movement

Lead is released into air as particles and after days or weeks settles or is rained out; progressively less is found with increasing distance from the source. Remember the heavy winter haze that pilots flying in the Arctic saw in the 1950s? Among the haze's components was lead, all carried by wind currents that were traced back to Europe and the Asian part of Russia. Another example of lead transport was the finding of lead in the soil of Kauai, Hawaii; this lead was transported from both Asia and North America.

Sources of lead exposure

Children Most at risk of lead poisoning are small children, who live in improperly maintained older houses containing leaded paint.¹⁶ They inhale the dust that forms as peeling leaded paint crumbles and becomes airborne. Exposure may come too from lead-contaminated soil around older homes where exterior leaded paint flakes off into the soil. Tracked indoors, the soil may enter household dust. Lead is also ingested: toddlers may suck on sweet-tasting leaded paint on windowsills. Moreover, poor children often have less than optimal calcium and iron in their diet; this leads to more absorption of the ingested lead. ▪ Old housing is more likely to have lead solder in the water pipes, so drinking water can contribute to exposure. For people living in lead-free or lead-safe homes *food* is the highest source of exposure. Workplace exposure Wealthy countries control lead exposure in the workplace. Jobs that involve working with lead have moved to countries with poor protection. Moreover, less-developed countries often have small "cottage industries." Without controls on fume emissions, these recycle lead-acid batteries, or add lead glazing to pottery. Toxic effects suffered by workers include high blood pressure and kidney failure. Children are employed in some of these cottage industries.

Toxic effects¹⁷

The ancients knew that lead was toxic, and forced slaves to do the lead mining. Thousands of years later lead still presents major hazards. Children Childhood lead poisoning was described as the most consequential environmental health problem in the United States. Lead's effect on the nervous system of the developing fetus and small child is of most concern. The potential for damage starts long before pregnancy. The mother may have been exposed to lead as a child and, because the body treats lead much as it does calcium, lead that she ingested would have bioaccumulated in her bones and teeth. About 90% of a person's lead intake is eventually stored in the skeleton. Lead levels in modern human skeletons and teeth are hundreds of times greater than those found in pre – industrial age skeletons. During pregnancy, when the mother's bones release calcium to the blood to meet the needs of her fetus, lead is released too. And along with calcium, lead too passes through the placenta exposing the fetus. ▪ Very low doses of lead may not obviously harm the fetus or small child.

¹⁶ Lead in paint, dust and soil. *US EPA*, November 6, 2008, <http://www.epa.gov/lead/>.

¹⁷ ToxFAQs™ for Lead. *ATSDR*, October 5, 2007, <http://www.atsdr.cdc.gov/tfacts13.html>.

However, it can have subtle effects on the nervous system, detected as lowered intelligence quotients (IQ). The average deficit may be only a few points, but one author noted, “On a societal basis, the aggregate loss of cognitive acuity due to lead exposure can be enormous.” And for children who would have had a low IQ anyway, a further lowering could shift them into a severe deficit range. For children with higher exposure to lead and higher than average body burdens, lead is associated with increased distractibility, aggressiveness, and delinquency.¹⁸ In addition to lead’s toxicity to the developing nervous system, lead may cause kidney cancer. Mice exposed to lead in utero developed kidney cancer later in their lives.

- Adults Adults are not as sensitive as children, but do suffer toxic effects from lead exposure. Chronic workplace exposure increases the likelihood of high blood pressure; can damage the nervous system and kidneys; and sometimes lead to anemia and infertility. In one disturbing study, Johns Hopkins University researchers followed 535 individuals who had worked with lead an average of 8 years. They went unexposed in the subsequent 16 years. Thereafter they were compared to a control group of 118 unexposed individuals living in the same neighborhood. Lead-exposed workers still showed clear deficits in memory and learning abilities, as compared to controls. Researchers said it was as if lead exposure had aged the workers’ brains by 5 years.¹⁹

Reducing lead’s risk

Because lead was used in dozens of useful products, it was difficult to back off, but step-by-step industrialized countries banned lead from plumbing, paint, gasoline, print, and many smaller uses. These removal efforts represent pollution prevention (P²).

- Removing lead from gasoline Until the mid-1970s, motor vehicle exhaust was a major source of lead to the US environment. Such dispersively emitted lead was the major source of exposure. After banning lead from gasoline (a phase out that began in 1976), air emissions fell more than 90%, and blood levels in US children fell concurrently. A level of 10 µg/100 ml of blood is the threshold of concern. By the mid-1990s, lead levels in the blood of most children in the critical age range of 1–5 years, was down to 4–6 µg/100 ml. Only 4.3% tested above 10 µg/100 ml. The P² measure of banning lead from gasoline is given most credit for lowering body burdens of lead although, in some locales reducing lead emissions from incinerators is also considered to have been a factor. Many developing countries have also prohibited adding lead to gasoline (although some still use leaded gasoline in 2008). China, where 65% of children had blood lead levels greater than 10 µg/100 ml has banned lead additions to gasoline.
- Other P² measures Over the years, improved control of incinerator emissions limited emissions of lead and other metals into air; recent US EPA regulations are reducing emissions even more significantly. In the late 1970s adding lead to paint used for home purposes was banned, as was the use of lead solder for drinking water pipes and lead in drinking water fountains. Lead solder to seal food and soft drink cans was banned. In the

¹⁸ (1) Bellinger, D. C. Lead. *Pediatrics*, **113**(4), April, 2004, 1016–1022, <http://pediatrics.aappublications.org/cgi/content/full/113/4/S1/1016>. (2) What makes a failing school? *Arizona School Board Association*, 2009, <http://www.azsba.org/static/index.cfm?contentID=152>.

¹⁹ Lead exposure at work can be lifelong problem. *UPI*, October 27, 2000, <http://www.applesforhealth.com/HealthyBusiness/leadjob2.html>.

printing industry soy ink replaced lead print. Even the soft lead foil used to seal wine bottles was banned. Air standard Recall that lead is one of the six criteria air pollutants (Chapter 5). As such it has a health-based standard for ambient air that is periodically updated as more information emerges. Most recently EPA tightened the standard by 10-fold, from $1.5 \mu\text{g}/\text{m}^3$ to $0.15 \mu\text{g}/\text{m}^3$ (measured as total suspended particles).²⁰ Remaining uses of lead Lead's major remaining use in the United States and globally is in lead-acid automobile batteries. There is no substitute for the lead in these batteries and globally 78% of lead is used for this purpose. Moreover, as the number of cars increases so do the number of lead batteries. Many US states do require removing batteries before municipal waste is incinerated. ▪ Lead is still added to gasoline in some countries, but this now represents less than 1% of lead's use. It is also used for lead sheets, ammunition, alloys, and cable sheathing.

Questions 15.2

1. How does lead in gasoline represent a greater risk than its use in lead-acid batteries?
2. (a) Consider the four life-cycle stages of a lead-acid battery. Which could result in the greatest lead *emissions* to the environment? Explain. (b) Which stage might result in the highest *exposure*?
3. An epidemiological study has shown that individuals with high workplace exposure to lead have more than a three-fold increased risk of Alzheimer's disease. What else would you want to know before you decided the link between lead and Alzheimer's was real?

Reducing the risk of lead already in the environment

Lead is a metal and is persistent. It is also pervasive. Many roadsides still have high lead levels in soil. Lead paint remains in place for many years and is found in virtually any US house built before 1980. Older houses have more. If the walls painted with lead paint are covered with wallpaper or wall board, they can be regarded as *lead safe*. However, it is harder to remove the risk to small children of dust and crumbled paint from surfaces such as window sills; it does help to daily wash these surfaces, and regularly mop up dust. (Using a vacuum cleaner can just disperse part of the leaded dust into the household's air.) Away from home, day care centers are regulated to assure provision of a lead-safe environment. Some municipalities test the blood from high-risk small children, such as those living in deteriorated older homes, for lead. Lead in water pipes also remains in place for many years, so the US EPA requires municipalities to maintain drinking water at a pH alkaline enough to limit the leaching of lead from old pipes. Individuals living in homes with lead solder in the water pipes can protect themselves by allowing water from each faucet to run for a half-minute every morning to wash out lead leached overnight into the standing water. If water pipes contain lead, it is also important not to use hot water for cooking because hot water leaches more lead from pipes than cold water. ▪ Despite impressive declines in environmental

²⁰ Fact sheet: final revisions to the NAAQS for lead. US EPA, October 15, 2008, <http://www.epa.gov/air/lead/pdfs/20081015pbfactsheet.pdf>.

contamination with lead, issues remain. Even the 4–6 µg/100 ml now found in most US children is hundreds of times greater than the estimated 0.016 µg/100 ml of prehistoric people. And blood levels are still high in many African–American children because they are more likely to live in old substandard inner-city housing. This puts them at risk of adverse effects on behavior and mental abilities. In the United States, if a child’s blood level is only slightly above 10, the recommended follow-up is to find and reduce sources of lead exposure. Levels greater than 10 elicit more aggressive attempts to find the source of lead exposure, and eliminate it. Medical intervention has been used to remove lead from children’s bodies although it is considered of questionable value.

Reducing lead’s risk in Mexico

In Mexico a phase out of lead in gasoline began in 1992. But lead-glazed pottery is still made and used. Investigators found that children in Tijuana, a city on the Mexico–US border, had blood-lead levels twice the average of US children. Moreover, unlike US children, the levels did not decrease with age, and sometimes increased. This was partially attributed to the use of lead-glazed pottery. Investigators doing the study provided information to parents of those children whose lead levels they had measured; they showed them how to identify sources of lead and minimize its risk. Children of parents so educated were later tested again. Their blood lead levels had dropped. Investigators concluded that parental education could partially protect children. However, limited resources prevented more aggressive forms of intervention that could have lowered blood levels further. In countries still using leaded gasoline, motor vehicle exhaust remains a major source of exposure, but an increasing number of countries have banned leaded gasoline.

Some lead is natural

It is vital to reduce human exposure to lead as much as possible. But remember that lead, like other metals, is a natural element. We cannot totally eliminate it. And alternatives can pose problems too. In gasoline, lead was added as an antiknock agent. After lead was banned, it was replaced by benzene – a human carcinogen. The amount of benzene in gasoline has also been substantially reduced. Worldwide, most of the lead in use is in lead-acid batteries.²¹ Lead use in consumer electronics is also slowly growing.

Mercury²²

You have probably heard of “quicksilver,” seen mercury in thermometers, and know it is a liquid metal. Or, you may have read of the “Mad Hatter” in Lewis Carroll’s *Alice in*

²¹ Lead and cadmium working group, Geneva, *UNEP*, September 2006, 18–22, http://www.chem.unep.ch/pb_and_cd/WG/Docs/K0653416%20-%20Lead%20Cadmium%20Report.pdf.

²² (1) Mercury programme, *UNEP*, September, 2002, <http://www.chem.unep.ch/mercury/default.htm>. (2) Mercury information. *US EPA*, October 24, 2008, www.epa.gov/mercury/about.htm. (3) Mercury quick finder. *US EPA*, December 11, 2008, <http://www.epa.gov/mercury/>.

Table 15.2 Global mercury demand (tonnes)*

Processes using mercury	Year 2000	Year 2005
Small-scale gold mining	650	1000
Making vinyl chloride monomer	—	700
Chlor-alkali plants	797	618
Products containing mercury		
Batteries	1081	400
Dental amalgam	272	270
Measuring & control devices	166	150
Electrical & electronic	154	140
Lighting	91	120
Other uses	175	120

Information from European Commission

<http://ec.europa.eu/environment/chemicals/mercury/pdf/conf/doa.pdf>

* 1 metric tonne is equivalent to 1.1 tons

Wonderland. In Carroll's time, hatters were exposed to mercury vapor as part of the felting process, and often suffered damaged nervous systems as a result. Mercury is mined from a mercury-containing ore called cinnabar.

Products,²³ processes and end of life

- Common *products* containing mercury are seen in Table 15.2. By 2005, the only batteries containing mercury were rechargeable- and button batteries. ▪ Mercury use in dental amalgam was second only to batteries in 2005. ▪ About 3% of mercury is used in fluorescent lights, which receive negative attention because of this. Although the mercury does not escape unless the bulb is broken careful recycling is required. Smaller amounts of mercury are used in mercury thermometers and other mercury measuring devices such as thermostats and blood pressure cuffs; and electrical devices such as switches, and electronic products.
- Three *processes* commonly use mercury; small-scale (artisanal) gold mining; production of vinyl chloride monomer; and chlor-alkali production – electrolyzing sodium chloride to make chlorine and sodium hydroxide). Again see Table 15.2.
- End-of-life In developed countries, mercury-containing products such as batteries may be incinerated at the end of their lives; if so, emission standards for mercury must be met. For landfilled products containing mercury, investigation revealed that the air above landfills contains mercury including significant amounts of methylmercury, so landfills have bacteria that convert mercury to methylmercury.

²³ Agarwal, R. Mercury working group, heavy metals meeting, Budapest, September 23, 2006, http://www.who.int/ifcs/documents/forums/forum5/hm_agarwal.pdf. See: Global mercury demand by use, 2005.

Mercury sources

- A recent UNEP report²⁴ estimates global air emissions of mercury of about 5700 tons/year (5200 tonnes),²⁵ of which human activity accounts for about 2130 tons (1930 tonnes). Natural sources (out gassing from the ocean and other surface waters, rocks and soil, and volcanic eruptions) are about 1765 tons (1600 tonnes). Re-emissions are about 1875 tons (1700 tonnes). Re-emissions (or “recycling” of mercury) arise as follows. Over the years as happened during mining operations in the western United States, thousands of tons of mercury were emitted to the atmosphere. This mercury once mobilized, continues to move: it is taken up by soil, plants, and sediments. From there it can once again escape to the atmosphere – it is re-emitted – and continue cycling through the environment. It is estimated that the total amount of mercury in the environment is two to four times greater than in pre-industrial times.
- The largest American source of mercury emissions is coal-burning power plants. In the United States the 600 largest coal-burning power plants emit about 48 tons (44 tonnes) mercury a year, which is close to 40% of the United States total. Altogether US anthropogenic mercury emissions are about 3% of the global total.^{26,27} Globally, power plants are also the largest source of mercury emissions, about 1500 tons (1360 tonnes) a year. About two-thirds are from Asia, especially China and India. Another important global source is mining, both artisanal and industrial. Artisanal gold mining is small-scale mining by artisans and generates about 18% of global emissions; UNEP estimates that 10–15 million people work, largely unprotected in artisanal gold mining and produce 20–30% of the world’s gold (Figure 15.3. Mercury mining itself contributes much less to world emissions, about 1%. Cement production contributes about 10% of global mercury emissions.

Mercury can move far from its emission point

Much of the mercury emitted by fossil-fuel burning facilities is elemental mercury vapor, which can remain airborne for 6–18 months, and travel long distances including globally. Eventually atmospheric reactions result in its transformation into mercury compounds such as mercuric oxide, which can then rain out or slowly fall out. ■ An illustration of transport from distant

²⁴ (1) The global atmospheric mercury assessment: sources, emissions and transport. *UNEP Chemicals Branch*, December, 2008, http://www.chem.unep.ch/mercury/Atmospheric_Emissions/UNEP%20SUMMARY%20REPORT%20-%20CORRECTED%20May09%20%20final%20for%20WEB%202008.pdf. (2) Clean air mercury rule, basic information. *US EPA*, February 26, 2008, <http://www.epa.gov/camr/basic.htm> and another mercury report (3) Pavlish, J. H. Global mercury emissions. *EERC Technology*, August 11, 2006, <http://www.undeerc.org/catm/pdf/PavlishMercury2006SpecialSessionSlides.pdf>.

²⁵ Each of these numerical figures is the mid-point of a high and low estimate of the range given for emissions in each case

²⁶ Mercury emissions, the global context. *US EPA*, October 24, 2008, http://www.epa.gov/mercury/control_emissions/global.htm.

²⁷ Other mercury emission sources are industrial boilers (considered separately from power plant boilers), which contribute about 10% of the US total. Hazardous-waste incinerators emit about 5%, and chlorine production is about 5%. Tightly regulated municipal solid waste and medical waste incinerators currently release very little. Combustion in US residences emits a few tons.



Figure 15.3 Two artisanal miners in Sudan. Credit: Marcello Veiga and Patrick Schein, UNIDO Global Mercury Project and University of British Columbia Norman B. Keevil Institute of Mining Engineering

sources was seen when scientists analyzed the sediments of isolated lakes in Minnesota, a US state. By analyzing successively deeper sediment layers, and comparing them to more recent layers, they found that mercury concentrations had tripled over 150 years. Because these lakes were far from industrial activity, and there were no known natural phenomena to explain the increase, the mercury had to have arrived in the lakes by air transport from other locales. ■ Depending on how wind currents move, some regions end up with more mercury than others. Consider the northeastern US states and Canada's Maritime Provinces, where fish suffer from excess mercury carried on wind currents from western states.

One story with a favorable ending occurred in Florida's Everglades. There, mercury in largemouth bass was often higher than 1.5 ppm making the fish unsafe to eat. Investigation revealed the mercury did not arrive from streams feeding into the Everglades. Rather it was traced to air emissions of Florida incinerators. After cutting incinerator emissions 99%, mercury in fish also fell. However, this was a fortunate instance. If the mercury had accumulated for many years in the sediment, it could continue moving into the food web even if emissions were cut, and it could take many years to see decreased mercury levels in living creatures. ■ Another problem is the difficulty in identifying the source of the mercury. This is true because mercury travels so extensively and can also arise from natural sources. That is beginning to change: coal from different parts of the world contains different mercury *isotopes* (see Chapter 19). In the future we may be able to trace to its origin the mercury arriving in a lake.²⁸

²⁸ Renner, R. Mercury isotopes may put the finger on coal. *Environmental Science & Technology*, **42** (22), November 15, 2008, 8177.

Table 15.3 Mercury biomagnification in fish and animals

Mercury (mainly elemental mercury vapor) is emitted to air from human and natural sources
↓
Mercury is transported by the wind. Eventually, elemental mercury is oxidized to mercury compounds, which are particles and so can wash out with rain, or fall out by gravity*
↓
If deposited into water** mercury binds to sediment. Bacteria transform a portion to methylmercury. Algae and other phytoplankton take up methylmercury.
↓
Invertebrate animals eat the mercury-containing phytoplankton. Small fish eat the invertebrate animals. Larger fish eat the smaller. Larger fish accumulate successively more mercury. Birds, animals, and humans eat the contaminated fish.

* Elemental mercury may remain in the atmosphere for as long as two years.

** Mercury compounds also fall on soil and vegetation, but conversion to the very toxic methylmercury requires the airless environment of sediment, rice paddy, or the interior of a landfill.

Mercury in sediments

An unfortunate twist worsens mercury's damage when it comes into a water body. There it attaches to sediments where certain bacteria convert it to an organometallic chemical, *methylmercury*, a chemical much more toxic when ingested than elemental mercury. Making matters worse, methylmercury powerfully biomagnifies in the food web, sometimes a million-fold or more compared to its water concentration: Single-celled algae concentrate the methylmercury. Tiny animals (zooplankton such as daphnia) eat the algae. Fish eat the daphnia. Larger fish eat smaller ones. At each step, methylmercury concentrates further (See Table 15.3). Some game fish have methylmercury concentrations 200 000 times greater than the surrounding water. Fish-eating birds and mammals can accumulate still higher levels. This has led to most US states posting freshwater lake advisories warning pregnant women, women of childbearing age, and small children not to eat the fish, or to eat only limited amounts of certain fish. (Figure 15.4) About 95% of the average person's mercury exposure comes from eating contaminated fish. ■ Although some chemical levels have fallen in the blood of the Inuit in Canada, mercury has not decreased.²⁹

Exposure and toxic effects of mercury³⁰

- **Prenatal exposure** As with lead, the greatest concern about mercury is its toxicity to the nervous system. Again, like lead, the fetus and small child bear the greatest risk. The

²⁹ Mercury: Toxic chemical levels finally dropping in Arctic animals, new study shows. *The Canadian Press*, July 14, 2008, <http://www.panna.org/files/CanadianPressArcticToxicsDrop20080714.pdf>.

³⁰ Medical management guidelines for mercury. *ATSDR*, September 24, 2007, <http://www.atsdr.cdc.gov/MHMI/mmg46.html>.

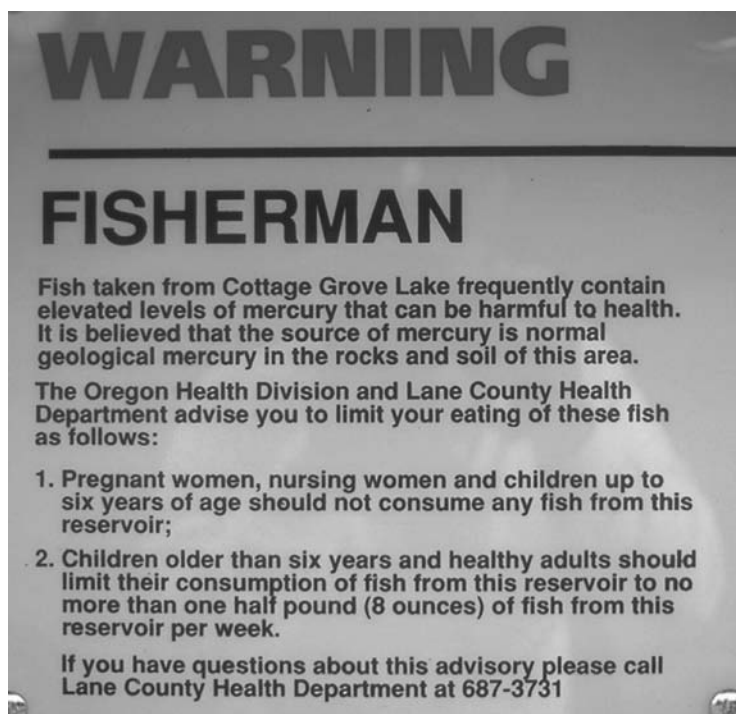


Figure 15.4

Mercury advisory warning posted at a lake. Credit: USGS

developing embryo is up to 10 times more sensitive to mercury than adults. In 2000, the US National Research Council (NRC) reported that 60 000 US babies born each year are at risk of slowed development such as delayed walking and talking because of prenatal methylmercury exposure. Most maternal exposure results from eating contaminated fish.

- Workplace exposure Excepting some dental workers, workplace exposures are generally well controlled in developed countries. However, facilities making mercury-measuring devices are now located in countries where workers often lack basic protection. Chronic inhalation of elemental mercury vapor over weeks, months, or years leads to poor coordination and strange sensations in fingers, toes, and lips. Hearing and eyesight can be impaired, and a “Mad Hatter” tremor occurs; severe poisoning can lead to blindness. High levels of exposure to mercury vapor can result in adverse effects within hours, deafness, kidney damage, irreversible brain damage, even death.
- Wildlife exposure Northeastern US states and Canada’s Eastern Maritime provinces have “hot spots” resulting from wind currents carrying mercury to the northeast from coal-burning power plants and incinerators in Midwestern states. Think about birds that eat large quantities of fish such as loons and eagles. In Maine, a far northeastern US state, loons have some of the highest levels of mercury ever recorded, up to 35 ppm. Captive

Box 15.5

A mercury poisoning disaster

Beginning in the 1930s and continuing until the late 1960s, Tokyo's Chisso Corporation routinely discharged elemental mercury into Japan's Minamata Bay. There, bacteria converted some to methylmercury, which built up in the food web (Figure 16.3). Methylmercury levels in Bay fish ranged from 9–24 ppm although some were as high as 40 ppm. Unknowing people ate the fish, and as many as 200 000 were poisoned. Hundreds died. Thousands suffered chronic disease. Chronic, sometimes severe and debilitating nervous system damage was seen. So were miscarriages, and deformed fetuses. Victims charged authorities with knowing about the pollution and its risks, but failing to stop them or inform the public. The poisonings resulted in a bitter lawsuit against Chisso that continued for nearly 30 years. In 1996, 3171 victims finally settled. However, one elderly and still ill embittered group, refused to settle until the government officially apologized to them. • The tragedy at Minamata was later eclipsed by other industrial tragedies such as the Bhopal explosion (Chapter 1) and the Exxon Valdez oil spill (Chapter 9). But a World Bank report emphasized Minamata as a watershed event that brought increased international attention to industrial pollution. After Minamata was publicized, many developing countries set up environmental agencies to control pollution, and many of these countries have made progress. Mercury guidelines Fish in Minamata Bay had mercury levels as high as 40 ppm. Compare these to US Food and Drug Administration (FDA) guidelines for eating fish.

Fish with less than 0.5 ppm mercury are considered safe for consumption in any amount.

At 1 ppm, people are advised to limit fish consumption. A level of 1 ppm is 10 times lower than the amount shown to produce toxic effects in adults in the Minamata Bay poisoning.

Above 1.5 ppm, people are advised not to eat the fish at all.

In 1991, the FDA reported that mercury in most American fish ranged from 0.01 to 0.5 ppm. Exceptions were larger or older ocean fish, shark, and swordfish, which naturally bioaccumulate mercury to 3 ppm or more. In 2002, both the US FDA and the UK Food Standards Agency issued alerts advising pregnant women, women who may become pregnant, infants, and children under 16 not to eat shark, swordfish, and marlin because of high mercury levels. These are marine species. • Since 1991, 37 US states have issued health advisories on mercury in fish. Usually state standards are stricter than those of the US FDA. Recommendations from the US EPA and State and Canadian Province agencies for freshwater fish advise those who eat large quantities of fish, such as some Native Americans to pay special attention to advisories. In 1995, mercury contamination accounted for about two-thirds of all fish advisories issued in the United States. Other contaminants on which advisories are still sometimes posted include dioxins and PCBs.

birds with levels of mercury as high as those found in wild loons reproduce poorly, as do eagles that have high levels of mercury in their feathers. It is feared that such birds have poorer physical dexterity and may have more difficulty catching fish or avoiding predators. Wild animals that eat contaminated fish are also at risk.

Reducing mercury's risk

- EPA regulations Mercury emissions³¹ from municipal waste combustors were reduced about 90% between 1990 and 2005. Emissions from medical waste incinerators fell 95% between 1990 and 1998. Hazardous waste incinerators, industrial boilers, and facilities using the mercury-cell process to make chlorine also reduced emissions.³² ■ Overall, mercury deposits on land and water has fallen considerably: analysis of peat cores in the state of Minnesota indicate that mercury deposition reached a peak in 1960 and subsequently began falling. By the 1980s deposition was less than half of the 1950s.
- Regulations of power plants Despite such progress, the EPA did not control the biggest source of mercury emissions to the US atmosphere, coal-burning power plants. EPA's rule Finally, in 2005, the agency issued a rule to cap and reduce mercury emissions from the nation's 1100 power plants.³³ The EPA stated that, even without using technologies specific to reducing mercury emissions that the technologies applied to reduce sulfur dioxide and nitrogen oxides emissions were simultaneously recovering about a third of the mercury released during coal combustion. So the EPA proposed to regulate mercury emissions as part of a multi-pollutant strategy in which sulfur dioxide and nitrogen oxides emissions were also further controlled. The rule was to create a cap-and-trade program to allow utilities to swap rights to emit mercury (as is done with sulfur dioxide emissions). The result would be that plants emitting 48 tons (43.5 tonnes) of mercury a year would emit 38 tons (34.5 tonnes) in 2010 and 15 tons (13.6 tonnes) in 2018, a 70% drop. Suing the EPA Seventeen states plus environmental organizations sued the EPA saying that it was required to set strict limits on mercury emissions under requirements of the Clean Air Act (CAA) as an hazardous air pollutant. They stated that "maximum achievable control technology" could cut mercury emissions by 90% in 3 years. A US Court of Appeals agreed, and ruled that EPA had violated the CAA. It further noted that the EPA itself, in 2000, had concluded that coal-fired power plants are sources of hazardous air pollutants and their mercury emissions should be regulated under the CAA.³⁴ EPA appeals The EPA appealed to the US Supreme Court in 2008 for permission to implement its mercury-control program.³⁵ While this case moves forward, individual states can choose whether to set stricter controls on mercury emissions.
- Reducing workplace exposure Workers in less-developed countries often remain unprotected from mercury exposure. Visitors to China describe toxic reactions among unprotected workers as routine. Workers are simply allowed some time off work to partially recover.

³¹ What else is EPA doing to reduce mercury emissions? *US EPA*, January 3, 2008, http://publicaccess.custhelp.com/cgi-bin/publicaccess.cfg/php/enduser/std_adp.php?p_faaid=1834&p_created=1106164694.

³² Mercury emission control R&D. *US DOE*, January 18, 2006, http://www.fossil.energy.gov/programs/power_systems/pollutioncontrols/overview_mercurycontrols.html.

³³ Controlling power plant emissions of mercury. *US EPA*, October 24, 2008, http://www.epa.gov/mercury/control_emissions/index.htm.

³⁴ Baltimore, C. EPA must rewrite utility mercury rule: U.S. federal court. *Reuters*, Feb 8, 2008, <http://www.reuters.com/article/environmentNews/idUSN0847678520080208?sp=true>.

³⁵ Cicero, R. EPA asks Supreme Court to review mercury emissions case. *Andrews Publications*, October 24, 2008, http://news.findlaw.com/andrews/en/haz/20081024/20081024_epa.html.

- Reducing or eliminating mercury-containing products³⁶ Mercury use in the United States fell sharply between 1980 and 2001, from 2453 tons (2225 tonnes) to 300 tons (271 tonnes). A major reason for this decline is that mercury use in disposable batteries fell almost 85% over this time; only rechargeable batteries and button batteries still contain mercury. See Table 15.2. The EPA cancelled fungicide registrations for the use of mercury in paint after a child's death resulting from mercury emissions into indoor air.³⁷ Many chlor-alkali manufacturing plants have closed or are closing in the United States and Europe. ▪ Although mercury is used in fluorescent lights in smaller amounts than previous years, the use of mercury in lighting nonetheless (Table 15.2) went up because more lights are being produced. A goal of the EPA's voluntary Green Lights program is to eliminate mercury use in lighting and, in the interim, recycle all spent fluorescent tubes. Some states regulate mercury-containing fluorescent lights as hazardous waste. ▪ See Table 15.2 for reductions in mercury use just between 2000 and 2005. ▪ Some US states are also diligent in eliminating mercury-containing products, even fever thermometers and other measuring and control devices. The group, "Health Care without Harm" is successfully working with hospitals to phase out the use of mercury-containing products including blood pressure cuffs, thermometers and lab chemicals. Another program, "Mad as a Hatter" aims to eliminate mercury from research facilities under the control of the National Institutes of Health.
- International The UN is urging countries to speed up their phase outs of mercury for all processes that now use it.³⁸ A number of less-developed countries rely on mercury for artisanal gold mining. Experts believe that there are reasonable alternatives for virtually all industrial processes and mercury-containing products. There is broad international agreement to phase out mercury use including the EU. However, some governments oppose a legally binding treaty to impose firm target dates. The United States opposed it until the Obama Administration took office; it now promotes a treaty.³⁹

Box 15.6

A dental quandary

Some human exposure results from minute amounts of mercury vapor emitted within the mouth by amalgams used to fill dental cavities.⁴⁰ Some contain 50% mercury. Critics of mercury amalgams – used for more than 150 years to fill cavities – claim they are linked to multiple sclerosis, arthritis, mental disorders, and other diseases. People with amalgam fillings do have higher mercury concentrations in their blood than people who don't. However, a 1994

³⁶ Doa, M. J. Addressing reduction of demand and supply of mercury. International Mercury Conference, Brussels, 2006, <http://ec.europa.eu/environment/chemicals/mercury/pdf/conf/doa.pdf>.

³⁷ Until the early 1990s, mercury was also used as a fungicide for seeds, and golf course greens.

³⁸ (1) Global agreement on mercury pollution focus of international meeting, *UNEP*, November 12, 2007, <http://www.unep.org/Documents.Multilingual/Default.asp?DocumentID=521&ArticleID=5702&l=en>. (2) Wallis, D. UN wants global action on mercury threat. *Reuters*, November 12, 2007, <http://uk.reuters.com/article/environmentNews/idUKL1265692120071112?sp=true>.

³⁹ Maliti, T. US calls for treaty on mercury reduction. *San Francisco Chronicle*, February 16, 2009, <http://www.sfgate.com/cgi-bin/article.cgi?f=/n/a/2009/02/16/international/i074829S39.DTL>.

⁴⁰ Questions and answers on dental amalgam. *Food and Drug Administration*, June 3, 2008, <http://www.fda.gov/cdrh/consumer/amalgams.html>.

article in a dentistry journal reported that although dentists have a much higher body burden of mercury than the average American, they have no higher incidence of any disease. Also, a study of elderly nuns in Java showed no association between long-term amalgams in teeth, and lowered reasoning ability. Three-quarters of US dentists continue to use silver-mercury amalgams, but the fillings remain controversial. Because other, albeit somewhat more costly options exist – gold and composite materials – some dentists no longer use mercury amalgams. The position of the US Public Health Service is that amalgam use should not be regulated unless it is linked to illness. Rarely, individuals have an amalgam allergy with symptoms similar to a skin allergy. However, Norway, Sweden, and Denmark have banned dental mercury use as of 2008 because of the precautionary principle and the belief that composites are now strong enough to be good replacements for the amalgam.⁴¹

Questions 15.3

1. In the United States, several federal agencies evaluated psychological and motor tests done on the babies and small children of island-dwelling peoples who eat large amounts of fish contaminated with methylmercury. Using this evaluation the US EPA set guidelines about four times more stringent than the US FDA standard. The guidelines are used by regulators who make decisions ranging from fish consumption advisories to air emissions standards. The EPA was criticized for being so strict relative to the FDA, but the EPA reminded critics that its charge is to protect the most sensitive population, in this case women of child-bearing age and small children. A US NRC report supported EPA's conclusion. It concluded that 60 000 US babies a year are at risk of slowed development because of prenatal methylmercury exposure. The FDA made the counterpoint that, if the EPA's guideline stood, it would prevent sales of swordfish, shark, and most tuna. The FDA asks: How can we protect people without scaring them away from a food providing a good source of protein, polyunsaturated fatty acids, and antioxidants, and without needlessly hurting the fishing industry? (a) With which agency do you tend to agree and why? (b) What do you see as a possible way to resolve the issue?
2. The NRC report estimated that 60 000 US babies a year are at risk of slowed development such as delayed walking and talking after prenatal exposure to methylmercury. Does this mean that 60 000 babies will be born each year with these adverse effects? Explain.
3. The lowest methylmercury concentration in human blood associated with any observed toxic effect in adults is 200 ppb. The average mercury concentration in American blood is about 8 ppb. (a) Do you believe that 8 ppb is a comfortable margin of safety for adults? Explain using, if you can the factor-10 concept from Chapter 4. (b) Would your answer be the same if women of childbearing age had an average of 25 ppb methylmercury in their blood? Explain.
4. Assume you ingested elemental mercury in an amount equivalent to that in a thermometer. (a) What would happen to the ingested mercury? (b) Does your answer explain why

⁴¹ Dental mercury use banned in Norway, Sweden, and Denmark because composites are adequate replacements. *Reuters*, Jan 3, 2008, <http://www.orthomolecular.org/resources/omns/v04n24.shtml>.

ingested elemental mercury is much less toxic than methylmercury. (c) What if the mercury in a thermometer was broken in a small bathroom and not cleaned up – would the mercury then pose somewhat greater risk? Explain.

5. Older larger fish such as sharks and swordfish have higher mercury concentrations than younger or smaller fish. Why?
6. Unlike organic PBTs (which concentrate in fat) mercury concentrates in fish muscle. Remember the techniques you could use to remove PCBs or dioxins from fish that you have purchased – could you use the same techniques to remove mercury? Why?
7. In 1996, the US Department of Defense (DOD) proposed selling its mercury stockpile, then 60% of the world's supply, on the open market. After much protest, the DOD dropped its proposal. (a) What would be your reaction to such a sale and why? (b) In Brazil, mercury used in gold mining resulted in the release of about 170 tons (154 tonnes) of mercury into the environment between 1989 and 2004. Brazil imports mercury from other countries. Had the DOD sale gone through, part could have been sold to Brazil. Does knowing this affect your viewpoint on selling mercury abroad? (c) Most nations that sell mercury to Brazil restrict the use of mercury within their own borders. Does this raise ethical concerns? Explain.

Cadmium^{42,43}

Cadmium is not mined as such. Rather cadmium is found in zinc ores and recovered during the smelting and refining of zinc. Whereas lead has been mined for at least 4000 years, cadmium was not even discovered until 1817, and has been heavily mined only since the mid-1940s. Environmental cadmium levels are lower than those of lead and people ordinarily have lower exposure. *But* cadmium levels in the environment have been increasing, and exposure is hundreds of times greater than in pre-industrial times.

Cadmium uses, sources, and movement

- Because cadmium has good corrosion resistance it has value for a number of uses. It is used in electroplating on iron and steel; in alloys with lead, copper, and tin; as a stabilizer for PVC plastic; and in ceramics, enamels, and pigments. Some of these uses have decreased in recent years. The largest use by far in the United States and globally, is in NiCad (nickel-cadmium) rechargeable batteries. In 2004, this represented 82% of all cadmium used. In the United States, NiCad batteries are a major source of cadmium in municipal solid waste.
- Sources Cadmium is released into the air during the smelting and refining of the metals zinc, lead, and copper. However, the largest source of cadmium is fossil fuel burning, especially of coal. Municipal solid-waste and other incinerators can emit cadmium too.

⁴² Lead and cadmium working group, Geneva, *UNEP*, 18–22 September 2006, 13–18, http://www.chem.unep.ch/pb_and_cd/WG/Docs/K0653416%20-%20Lead%20Cadmium%20Report.pdf.

⁴³ Cadmium, *US EPA*, <http://www.epa.gov/epawaste/hazard/wastemin/minimize/factshts/cadmium.pdf>.

- Because cadmium is found naturally in soils, rocks (coal too) and mineral fertilizers, it ends up as an impurity in such products as phosphate fertilizers, detergents and refined petroleum products. Polyphosphate fertilizers and sewage sludge contribute to cadmium buildup in soils.
- Movement Like lead, cadmium is released as a particulate and thus has a limited atmospheric life, days to weeks before settling out. However, within that time a portion reaches remote locales including the Arctic. The Arctic presence has been demonstrated by Arctic ice cores: cadmium deposition in Greenland in the 1960s and 1970s was eight-fold greater than in pre-industrial times. Fortunately, recent information indicates that cadmium levels have steadily declined since then.

Routes of exposure

- Food More than 90% of the average non-smoker's exposure to cadmium is from food. Shellfish concentrate cadmium, and can be a major exposure for those who eat scallops and oysters. Fish concentrate less. Because liver and kidney concentrate this metal, hunters in some locales are advised not to eat moose or bear liver or kidney.
 - Cadmium also is taken up in some crops, especially irrigated rice. Vegetarians and others consuming high levels of cereals and vegetables may have higher exposure. High soil levels are a special concern because plants take up cadmium more readily than other metals.
- Tobacco products Because tobacco plants accumulate cadmium so well, smoking one pack of cigarettes each day can double exposure. Smokers absorb more than 90% of inhaled cadmium. Conversely only about 5% of the cadmium ingested in food is absorbed. Inhalation is also the greatest route of exposure among those with occupational exposure and those living near industrial sources. Recall once again the value of good nutrition: a balanced diet can reduce the amount of cadmium absorbed into the body from food and drink.

Toxic effects⁴⁴

- The kidney is a critical target organ for cadmium, and it bioaccumulates in that organ; storage increases with age. Kidney damage is the most common chronic effect among those who suffered high occupational exposure; it may also contribute to kidney stones. Cadmium is stored in the liver too. It takes 10–30 years to eliminate half of the cadmium from kidney and liver.
 - In individuals occupationally exposed to airborne cadmium, lungs are the primary target organ, and severe lung damage can result. More generally, as one ages cadmium levels in kidney, liver, and other tissues increase. Among middle-aged or older individuals *not* occupationally exposed, cases have been observed in which cadmium became concentrated to levels almost as high as those known to affect kidney function.

⁴⁴ ToxFAQs™ for cadmium. ATSDR, September, 2008, <http://www.atsdr.cdc.gov/tfacts5.html>.

- Cadmium affects calcium metabolism too. Chronic exposure accentuates bone damage including osteoporosis. Recall from Questions 3.1 a cadmium poisoning event, which occurred among poor elderly Japanese women, whose diet was largely limited to rice grown in cadmium-contaminated rice paddies.⁴⁵ They experienced *itai itai* (pain, pain) disease, characterized by kidney damage and brittle painful bones (Questions 3.1).
- Cadmium is a known human carcinogen (via inhalation, but not ingestion). In 2006, the journal, *Lancet Oncology*, reported results of a study of individuals living near zinc smelters. Professor Jan Staessen of the University of Leuven and colleagues studied 521 people living close to zinc smelters in northeastern Belgium and compared them to 473 people living further away. Cadmium exposures were directly evaluated by measuring levels of cadmium in urine over a four-year period (1985–1989). For 17 years thereafter, until 2004, they looked for cancer diagnoses, both lung cancer and other cancers in these populations, correlating cancer cases to urine levels of cadmium. Results indicated that a doubling of urinary cadmium was associated with a 30% increased risk of all cancers and a 70% increased risk of lung cancers. The increased risk of lung cancer was comparable to that from smoking.⁴⁶

Reducing risk

- Environmental cadmium Society controls cadmium in several ways. In the United States, an enforceable standard limits exposure to cadmium through drinking water. Because cadmium is a hazardous air pollutant, its air emissions are controlled by Best Available Technology. As with lead and mercury, recent EPA regulations are greatly reducing cadmium emissions from municipal solid waste and medical waste incinerators. *But* for cadmium, as for lead, power plant emissions have not been controlled. Overall, although more data are needed, it appears that anthropogenic cadmium emissions have decreased about half between 1990 and 2003 in developed countries.
- Products containing cadmium Cadmium is no longer used in disposable batteries. However, large amounts are used in NiCad rechargeable batteries and, as with one-time use batteries, rechargeable batteries end up discarded and become a major source of cadmium in solid waste. The amount continues to grow.

Reducing risk in Australia

Although cadmium concentrations in Australian soils were still low, they had been increasing over the years, perhaps as a result of phosphate fertilizer. This raised concern. In 2002, the Australian government decided to reverse this trend, and maintain the “clean and green” image of their exported agricultural products.⁴⁷ ■ It tightened permissible levels of cadmium

⁴⁵ Kjellstrom T. 1986. Itai-itai disease. In: *Cadmium and Health: A Toxicological and Epidemiological Appraisal. Vol II. Effects and Response*, Friberg, L., Elinder, C. G., Kjellstrom, T. and Nordberg G. (eds.). Boca Raton, FL: CRC Press, 257–290.

⁴⁶ Osterweil, N. Cadmium exposure increases cancer risk. *MedPage Today*, January 16, 2006, <http://www.medpagetoday.com/PublicHealthPolicy/EnvironmentalHealth/2491>.

⁴⁷ Australia cadmium minimisation strategy. CSIRO Land and Water, February 7, 2008, <http://www.cadmium-management.org.au/about.html>.

in foods such as chocolate, peanuts, mollusks, and organ meats. To meet these new food standards, the government had to minimize cadmium additions to soils. This was done by lowering permissible amounts entering the soil from manures, sewage sludge and fertilizers. The fertilizer industry significantly decreased the cadmium in its products by using rock phosphate, which has less cadmium than polyphosphate. The government also developed guidelines for livestock, vegetables, other crops, water, and soil.⁴⁸

Arsenic⁴⁹

A metal – or a metalloid in the case of arsenic – need not be a PBT for it to cause severe harm. In Chapter 10 you learned of the toxicity of arsenic and that its contamination of drinking water⁵⁰ is becoming “the key environmental health problem of the twenty-first century.” It is sickening millions in Asia, “the largest mass poisoning of a population in history.”

Uses and sources

Uses

- Until recently, most industrially-used arsenic went to making *chromated copper arsenate* (CCA), a wood preservative used in “pressure-treated” lumber since the 1940s. ▪ CCA in playground and homes In earlier years, playground equipment was metal, but was replaced by wood. To lengthen its life, about 98% of wood destined for outdoor use in the United States was impregnated with CCA. CCA is regulated as a pesticide as it prevents mold, insects and other creatures from feeding on the wood.⁵¹ However, there were concerns with CCA-treated wood when used around homes or in playgrounds:⁵² unless properly sealed and maintained to remain sealed, arsenic comes in contact with children’s hands and, through hand-to-mouth activity they may ingest it. Arsenic can leach from CCA wood and contaminate playground soil, sometimes with risky levels of arsenic. ▪ Disposal CCA-treated wood structures may endure for decades, but at the end of their usefulness, disposal is a problem. If mulched, metals can leach out. If burned, emissions must be carefully controlled. If landfilled, arsenic leaching from the wood must be captured. So, the EPA worked with pesticide manufacturers to voluntarily phase out

⁴⁸ Final Report on cadmium minimisation. *National Cadmium Management Committee*, 2000–2006, April 2007, <http://www.cadmium-management.org.au/publications.html>.

⁴⁹ Public access, frequent questions: Where can I find information on arsenic? December 1, 2008, http://publicaccess.custhelp.com/cgi-bin/publicaccess.cfg/php/enduser/std_adp.php?p_faaid=2123&p_created=1126044551&p_topview=1.

⁵⁰ Arsenic as a primary drinking water contaminant: see table, <http://www.epa.gov/OGWDW/contaminants/index.html>.

⁵¹ Pesticides, chromated copper arsenate. *US EPA*, November, 2008, <http://www.epa.gov/oppad001/reregistration/cca/>.

⁵² Beder, S. Arsenic and old wood. *Sydney Morning Herald*, July 15, 2003, <http://www.ewg.org/node/15559>.

CCA-treated wood products used around homes and children's play areas.⁵³

- Alternatives On December 31, 2003, CCA wood was banned for residential use, with certain exceptions. One of the arsenic-free alternatives⁵⁴ developed is borate-treated wood.⁵⁵ Other countries including Sweden, Germany, Vietnam, and Indonesia have also restricted or banned CCA-treated wood.
- Industry CCA wood continues to be used in industrial settings – utility poles, dock pilings, etc.
- The arsenic used in CCA is inorganic, more risky than organic arsenic. Organoarsenic compounds are primarily used as pesticides, but not as broadly as was the case historically.⁵⁶
 - Arsenic compounds are added to chicken feed to promote growth, and kill parasites.⁵⁷ It provides pigmentation in chicken meat. In 2007, it was used in 70% of broiler chickens in the United States. In the chicken's body organic arsenic is converted into the more hazardous inorganic arsenic, almost all of which is excreted into chicken litter; the litter is often used to fertilize farm fields.⁵⁸ The EU banned arsenic from chicken feed in 1999; its use has been voluntarily discontinued by some American companies.
- Arsenic also has many uses in paints, dyes, metals, drugs, soaps, and semi-conductors. A darker use, as most people know, was arsenic use for many hundreds of years as an instrument of murder. That seldom happens now because arsenic is easily detected by forensic scientists.

Delving deeper

1. Steel use dwarfs that of all other metals combined. It is used in producing motor vehicles, construction and appliances. The steel in cars is already highly recycled in the United States; in fact, 71% of all steel produced in 2003 in the United States was from scrap with only 29% produced from virgin ore. What are the barriers to recycling other steel-containing items, appliances, and constructions? How could barriers be overcome?
2. Feeding arsenic to chickens Those supporting the addition of arsenic to chicken feed say the level subsequently found in the meat is too low to harm humans. Explain why this statement is or is not consistent with the fact that it can change the pigmentation of chicken meat. What is the most likely reason that chicken producers still use arsenic? Based on your examination of this question, do you believe that the practice should be allowed? Explain. You will need to do some research to answer these questions.

⁵³ Public access, frequent questions: What is being done about wood treated with CCA? December 1, 2008, http://publicaccess.custhelp.com/cgi-bin/publicaccess.cfg/php/enduser/std_adp.php?p_faaid=325&p_created=1090509617.

⁵⁴ Alternatives to CCA. *US EPA*, May 5, 2008, <http://www.epa.gov/oppad001/reregistration/cca/alternativestocca.htm>.

⁵⁵ Borates, an alternative to CCA. *US EPA*, April 7, 2008, <http://www.epa.gov/oppad001/reregistration/cca/borates.htm>.

⁵⁶ Before modern pesticides emerged, arsenic was a common weedkiller and rat poison. It was stored in homes and outbuildings where old containers can still be found. In a recent incident in the US state of Maine, arsenic from an old container was somehow added to coffee drunk by a group of people. One died and others were seriously poisoned.

⁵⁷ Hileman, B. Arsenic in chicken production. *Chemical & Engineering News*, **85**(15), April 9, 2007, 34–35.

⁵⁸ Hopey, D. Chicken feed may present arsenic danger. *Pittsburgh Post-Gazette*, March 08, 2007, <http://www.post-gazette.com/pg/07067/767756-34.stm>.

Sources

- Anthropogenic sources of arsenic include mining and dust emissions from metal smelting, especially of copper and lead ores, which often contain arsenic. It is this dust, when captured that is the source of arsenic used in CCA-treated wood. ■ Coal burning is a source of arsenic. Some coals such as those in some parts of China have high arsenic levels.
- Natural sources are volcanic eruptions and forest fires. Arsenic occurs naturally in rocks and soil. Some soils, such as those in the western United States have relatively high levels. A few natural mineral springs and other waters contain very high arsenic levels.

Sources of exposure and toxicity

- Sources of exposure Unless you live in an area with arsenic-contaminated drinking water as is common in Bangladesh and some other Asian countries, *food* is your biggest exposure. This is true because arsenic is naturally present in soil and taken up into plants. Arsenic in rice is likely to be a problem in some parts of the world: Bangladesh often irrigates rice with water from arsenic-contaminated wells.⁵⁹ Arsenic is present in seafood at levels higher than in land-grown foods; however, arsenic toxicity varies depending upon its chemical form, and much of the arsenic in seafood does not seem to be bioavailable.
- Toxicity⁶⁰ Arsenic toxicity is described in Section I of Chapter 10.

Questions 15.4

1. Recall that mercury in fish continue to accumulate as the fish age. How does that fact relate to what happens to humans with long-term exposure to cadmium?
2. (a) What is the relationship between the emissions of metals to the environment and coal burning? (b) Several radioactive elements (metals) are also released during coal burning, more than from nuclear power plants. What is your reaction to this?
3. Individuals in industrialized countries have a cadmium intake between 10–50 µg/day. EPA recommends as an upper limit 70 µg/day. (a) Think back to risk assessment in Chapter 4. Do you believe that 10–50 µg provides a comfortable margin of safety? Explain. (b) What else could society do to limit cadmium emissions or exposure? (c) Are there ways that you can lower your cadmium exposure?
4. Seafood contains higher levels of metals such as mercury, cadmium and arsenic than do freshwater fish. Does the composition of seawater versus freshwater explain this? Explain.

⁵⁹ Lubick, N. Rice paddies map arsenic problem. *Environmental Science & Technology*, **41**(17), September 1, 2007, 5928. The soil absorbs arsenic from the contaminated water, and the rice takes it up from the soil. This adds another source of arsenic exposure to an already very serious problem with arsenic-contaminated drinking water.

⁶⁰ What are arsenic's health effects? ToxFAQs™ for arsenic. *ATSDR*, August, 2007, <http://www.atsdr.cdc.gov/toxfacts2.html>.

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“Good soil is not just dirt. It is a hive of life, much of it either microscopic or even disgusting to urban eyes because urbanites don’t understand the need for the growth and decay of slimy things to sustain life. Good farmers are not just people who dig in the dirt. They are the stewards of healthy soil.”

George B. Pyle, Land Institute, Salina, Kansas

Pesticide use is both controversial and prevalent. Many individuals believe pesticides are necessary to destroy the enemies of human agriculture and health. Others believe we can use *organic farming* to accomplish these ends without synthetic pesticides. Another group believes pesticides are needed, but recognizes their limitations, and use *integrated pest management* to minimize pesticide use. There is no simple answer, but we do need answers. Consider this challenge from the authors of an article called, Can green chemistry promote sustainable agriculture? “Human population is increasing. Demand for food is rising . . . Environmental impacts are worsening. Taken together, few issues reflect the difficulties of sustainable development more than the problem of controlling pests and increasing food production while protecting the environment and conserving natural resources.” Section I of this chapter overviews what pesticides are, why we use them and who uses them. Section II looks at pesticides as pollutants, where exposure occurs, their impacts on non-target species and pesticide resistance. Section III examines how we can reduce the risk of pesticides by regulation, by changing the nature of pesticides, and by changing farming methods. It compares integrated pest management and organic farming to conventional agriculture. Section IV looks at some of the problems posed by pesticide use in less-developed countries and at their attempts to reduce pesticide use.

SECTION I

Background on pollutants of concern: pesticides

What are pesticides?¹

Pesticides are agents used to destroy pests. Under certain circumstances almost any living creature can be a pest. The goals of pesticide use are to increase the production of food and

¹ (1) What is a pesticide? *US EPA*, February 3, 2009, <http://www.epa.gov/pesticides/about/>. (2) Pesticides, A-Z index, *US EPA* December 17, 2008, <http://www.epa.gov/pesticides/a-z/index.htm>. (3) Pesticides, frequent questions. *US EPA*, August 26, 2008, http://pesticides.custhelp.com/cgi-bin/pesticides.cfg/php/enduser/std_alp.php.

Table 16.1 Some categories of pesticides

Pesticide ^a	Pest killed
Insecticides	Insects
Larvicides	Insect larvae
Fungicides	Fungi growing on plants (or animals)
Herbicides	Plants (weeds)
Fumigants	All life forms
Disinfectants	Microorganisms outside body

^a There are also pesticides specific to mites, algae, birds, snails, slugs and other mollusks, nematodes, fish, and other organisms.

fiber and to promote public health; they are also used for aesthetic reasons. A pesticide that kills insects is an *insecticide*. Some typical pesticide categories are seen in Table 16.1. Among the pests attacking agricultural crops are insects, weeds, rodents, birds, and disease-causing organisms, including fungi and bacteria. Developed societies with abundant food supplies don't ordinarily think of the possibility of totally losing a food crop. But consider the devastation of potato crops by a fungal infection that occurred in nineteenth-century Ireland. The resulting famine drove millions to immigrate to the United States, and resulted in the death of another million remaining behind. Similar fungal infections still occur in potatoes today, but are controlled using pesticides. Pest infestations have afflicted agriculture for as long as humans have farmed. For even longer periods, pests, including fleas, lice, mosquitoes, flies, roundworms, rats, and mice, have threatened human health.

For thousands of years, people have sought means to rid their crops of pests, the insects eating them, the weeds crowding them out, or the fungi making them uneatable. People began using the chemical element, *sulfur* as a pesticide thousands of years ago; some organic gardeners still do. Extracts of chrysanthemum flowers containing *pyrethrum* have been applied for nearly as long. Tobacco extracts containing *nicotine* have been used for hundreds of years. ■ In the late 1800s, inorganic chemical pesticides containing arsenic, mercury, lead, and copper came into widespread use. An elderly man wrote a letter to a periodical in 1989 describing his grandmother's 1920s gardening chemicals. In addition to occasionally using the highly toxic gas hydrogen cyanide as a fumigant, she used Paris green (copper arsenate), lead arsenate, and nicotine sulfate to control garden pests. Given the widespread use of metal pesticides in the first half of the twentieth century, it was not surprising that the first household hazardous waste roundup that Massachusetts carried out in the 1980s, recovered 3 tons (2.7 tonnes) of arsenic chemicals that had lain around sheds and barns for many years.

Early pesticides were only partially effective. So, when the seemingly miraculous synthetic insecticide *dichlorodiphenyltrichloroethane* (DDT) was introduced in 1942, farmers and the public health community embraced it ² (Figure 16.1). DDT was lethal to the many insects infesting crops and the mosquitoes and flies that spread disease, and other insects, such as body lice. The person discovering its insecticidal activity received the 1948 Nobel

² History of pesticide use, DDT. *Oregon State University*, January 28, 2007, <http://oregonstate.edu/~muirp/pesthist.htm>.

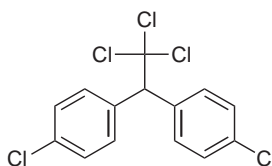


Figure 16.1

The structure of DDT (dichloro-diphenyl-trichloroethane)



Figure 16.2

Tribute to Rachel Carson on the occasion of her 100th birthday. Credit: US Fish and Wildlife Service, 2007, <http://www.fws.gov/rachelcarson/>

Prize in medicine. Many other synthetic chemical pesticides were quickly developed and widely used. Even in the 1940s, the ability of some pests to develop resistance to pesticides was observed. Still, most remained effective and resistance caused little concern. DDT and similar organochlorine pesticides showed low acute toxicity to humans, and little was absorbed through the skin.³ Possible chronic toxicity was little considered. The result was wide and often indiscriminate pesticide use. It was not until the early 1960s that Rachel Carson's famous book *Silent Spring* forced Americans to see the darker face of DDT and other pesticides (Figure 16.2).

³ Toxicological profile, DDT, DDE and DDE. *ATSDR*, September, 2002, <http://www.atsdr.cdc.gov/toxprofiles/tp35.html#bookmark07>.

Types of pesticides⁴

In addition to the types of organisms that pesticides are targeted toward (Table 16.1), another way to look at a pesticide is, how specific is it on the basis of what it kills? ▪ A *selective* or *narrow-spectrum* pesticide is specific to a limited group of organisms, often affecting a step of metabolism common to just those organisms. Consider an herbicide that interacts only with a specific plant enzyme; a major advantage is that it is less likely to harm animals, birds, or humans. Or a growth regulator, designed to keep juvenile insects from maturing, is not very toxic to animals and humans. A pheromone is also very narrow, and may be specific to one species. ▪ But consider the many perceived needs for pesticides. Agricultural crops alone are affected by 80 000 plant diseases, 30 000 weeds, and 10 000 insect pests. So, except for more important pests, they cannot be dealt with selectively.

- *Broad-spectrum* pesticides are non-specific, they can kill many organisms. DDT was a broad-spectrum insecticide – it killed on a basis common to all insects, the insect nervous system.
- *Fumigants* are a group of *gaseous* broad spectrum pesticides able to kill a great many species. Fumigate refers to using smoke or fumes to kill pest species. Fumigants are designed to kill the pests that infest grain stored in an elevator or greenhouse, for example. Fumigants are also used to sterilize soil or seeds. They are gases that can penetrate an enclosed space to do the job required of them. Humans are often at major risk from fumigants, which must be used with great care.⁵ Hydrogen cyanide is an example of a fumigant; it works by inhibiting respiration at the cellular level in mammals. Another is methyl bromide, which depresses the central nervous system.
- *Disinfectants*, used to kill disease-carrying microorganisms found *outside* the body, are regulated as pesticides.⁶ Most are nonselective: when used to wash a surface, the disinfectant destroys all microbes there, not just pathogens. Disinfectants have been used since 1867, when Lister began using phenol to disinfect operating rooms in France. Chemicals related to phenol, such as those found in *Lysol*, are still widely used. Other disinfectants commonly used in the home and industry contain chlorine compounds such as sodium hypochlorite (common household bleach).⁷ For certain purposes, disinfection is carried out by heat or ionizing radiation rather than by a chemical.

⁴ Pesticides, A-Z index. *US EPA*, , March 20, 2009. <http://www.epa.gov/pesticides/a-z/index.htm>.

⁵ Fumigants. *National Pesticide Information Center*, http://npic.orst.edu/RMPP/rmpp_ch16.pdf.

⁶ (1) Selected EPA-registered disinfectants. *US EPA*, June 30, 2008, <http://www.epa.gov/oppad001/chemregindex.htm>
 (2) Disinfectants (what they are and how they work). *US EPA*, <http://www.epa.gov/opp00001/safety/healthcare/handbook/Chap19.pdf>.

⁷ Antibiotics also have some external uses, e.g., on skin. However, antibiotics are typically taken *internally* to kill pathogenic microorganisms. Antibiotics are not considered pesticides. They are regulated by the US FDA not the EPA.

Table 16.2 Alternatives to synthetic pesticides

Alternative	Definition	Examples
Natural	An extract prepared from a living organism	An extract of chrysanthemum, tobacco, or the neem tree
Botanical	An ingredient purified from a natural extract	Pyrethrum purified from chrysanthemum extract or nicotine from tobacco extract
Biological ^a	A living agent that acts as a pesticide (e.g., a microorganism, insect, or fish)	An explosion in the rabbit population in Australia was controlled by releasing a microbe, which infected and killed them
Microbial ^b	A biological agent, that is a microorganism (bacterium, virus, fungus, or protozoan)	The Bt virus or baculovirus, either of which can act as a pesticide
Bioengineered organism ^b	A living organism with genes – taken from another organism – inserted into its DNA. The genes allow it to make a substance (in this case, a pesticide) that it previously could not	A plant with the Bt gene inserted into its DNA allowing it to produce a pesticide that repels insects A plant given genes to produce a product that makes it resistant to herbicides

^a These are not extracts or chemicals, but living organisms.

^b In a *biological* the living organism itself is the pesticide. In a *bioengineered organism*, a living organism has had its DNA modified so that it produces a pesticide or other protective chemical.

Box 16.1**Biopesticides**

The US EPA distinguishes three classes of *biopesticides*, pesticides derived from natural sources.

- (1) Some biopesticides are biochemicals, i.e., chemicals produced within living organisms,⁸ and then extracted from those organisms (plants, animals, or bacteria).⁹ Sometimes the extract itself may be used or a specific biochemical may be isolated from the extract. A *botanical* pesticide¹⁰ is a biochemical purified from a plant extract. See Table 16.2. ■ Four insecticides available in the United States are biochemicals derived from the neem tree, grown in India.¹¹ These have limited uses because, when exposed to sunlight, they quickly degrade. Still they have meaningful uses. ■ Pyrethrum, purified from chrysanthemums is a botanical pesticide. Because natural pyrethrums have limited uses, more effective synthetic pyrethrins have been developed and synthesized by humans: from this example,

⁸ What are biopesticides? *US EPA*, October 15, 2008, <http://www.epa.gov/pesticides/biopesticides/whatarebio-pesticides.htm>.

⁹ Biologicals and insecticides of biological origin. *US EPA*, <http://www.epa.gov/pesticides/safety/healthcare/handbook/Chap07.pdf>.

¹⁰ Natural insecticides. *Yardener*, 2003–2008, <http://yardener.com/?search=natural+insecticides>

¹¹ Neem oil insecticides. *LivingWithBugs.com*, http://www.livingwithbugs.com/neem_oil.html.

you can see that a botanical pesticide may be closely related to a synthetic pesticide.

- Even more closely related is a chemical, e.g., a pheromone produced by an insect to influence the behavior of another insect. Pheromones are produced naturally in such tiny quantities that it may not be possible to extract enough from insects to be practical. However, once the structure of the pheromone is known, the exact same chemical can be synthesized. So the question can be asked: is it natural or is it synthetic? In fact the US EPA has a committee that ponders such questions when registering a biochemical pesticide.

- (2) Another category of biopesticide is a microbial pesticide¹², i.e., it is a living microorganism, but is applied just as a chemical pesticide. The best known microbial is the bacterium *Bacillus thuringiensis* (Bt) used to control caterpillars, beetles, and flies. Microbial insecticides such as Bt and baculoviruses are narrow spectrum pesticides, thus lessening the threat to non-target species. Bt pesticides are favored by organic farmers. But, like other pesticides, a microbial must be shown not to threaten humans, animals, or the environment. Also, although pesticides specific to one pest are environmentally desirable, they may be less profitable to the company that manufactures them because each is applicable to few species.

- (3) *Bioengineered microorganisms* are still microbes (often the Bt microbes just referred to), but with modified DNA. It has become a genetically engineered organism (GEO) with foreign DNA inserted into its genetic material. This gives the GEO organism the ability to make a new chemical, such as a pesticide that it could not previously produce.¹³ The reasons for developing GEOs include increasing crop yield, crop nutritional value, reducing the need for pesticides, or providing disease resistance. A long-term goal is to develop GEOs with abilities such as being able to grow in salty soil or dry soils. A number of GEO crops are already widely planted in the United States and around much of the world.
 - Some GEOs have *Plant-Incorporated-Protectants* (PIPs) within their DNA, i.e., they have been given a fragment of DNA that, when translated within the organism produces a pesticide. For example, a gene can be taken from a pesticidal Bt microbe and that gene introduced into a plant's genetic material. Thereafter the plant and its progeny can produce the same pesticide as did the Bt microbe. PIPs are becoming widely used but, at the same time, are rejected by those very much concerned about GEOs. A major concern is the possibility that the plant's modified DNA may escape into the broader environment and have unexpected, possibly adverse, impacts.

Why are pesticides used?

As you read the reasons for pesticide use, distinguish between what pesticides *allow* us to do, versus whether what they allow is always necessary.

- Pesticides make it possible to grow crops at times of year where they could not otherwise grow because pests would make it impossible. Fruits and vegetables are found at the market year round not only because they can be transported long distances from warmer

¹² Weinzierl, R., Henn, T., Koehler, P. G. and Tucker, C. L. Microbial insecticides. *University of Florida Cooperative Extension*, 2008, <http://edis.ifas.ufl.edu/IN081>.

¹³ GEOs are also called transgenic organisms or genetically-modified (GM) organisms.

climates, but also because pesticides make longer growing seasons possible. Without fungicides, for example, certain crops could not grow under climatic conditions when fungi proliferate. Many believe that the health advantages of fresh fruit and vegetable available year round and their lowered cost make up for any health risk that pesticides pose.

- Pesticides make it possible to grow crops in ecologically inappropriate regions where they could not otherwise be reliably grown, at least on a commercial scale. In such locales, greater quantities of pesticides are often required for successful crops. Cotton grows well in some sections of Texas with little or no pesticide. However, in the humid southeastern US states, cotton requires many pesticide applications. Strawberries would not grow there without pesticides. Growing such crops in more appropriate regions may not be easy or even possible for established farmers as, for instance, when a farmer has already established a fruit orchard in a region requiring high pesticide use. If we grew crops only in ecologically appropriate locales, it would mean lower yields of some crops. It also means that some foods would be available only seasonally.
- Public health uses of pesticides allow the killing of disease-carrying organisms, mosquitoes, flies, ticks, and rats. Another health-related reason is reducing growth of fungi on crops, those which produce toxic chemicals. Recall the highly-toxic aflatoxins (Box 3.2)
- Pesticides make it possible to store food products for long periods. After harvest, grain is fumigated to kill insects and other infesting organisms, which could otherwise multiply during storage, destroying grain or making it inedible. For similar reasons, crops are fumigated before being transported long distances to market.
- Pesticides are often used for aesthetic reasons. People growing up in an age of pesticides expect perfect fruits and vegetables. Many blemishes on fruit and vegetables caused by insects do not harm the produce, but people won't buy blemished fruit – even fruits such as oranges, which are peeled anyway. Or, although caterpillars on broccoli can be washed away, people wouldn't buy broccoli with caterpillars. Half a century ago, a worm in an apple was something to pare from it, not a reason to throw it away. Golfing greens are kept looking perfect using pesticides although historically golf was played on imperfect greens.
- Pesticides make monocultures possible allowing large tracts of land to be devoted season after season to only one crop such as wheat, cotton, soybeans, or corn. Without pesticides, the pests that prey on a crop would build up to a point the crop could no longer be grown at that location. In fact, monocultures were not possible until the 1940s when effective and inexpensive pesticides became available. Moreover, monoculture crops are farmed using heavy machinery leading to soil compaction. Soil quality is further degraded because unlike manure or compost neither pesticides nor synthetic fertilizers provide organic material to the soil. Lack of organic matter makes the soil inhospitable to the worms and microorganisms needed for good soil fertility. Fields planted in row-crop monocultures are also prone to soil erosion and runoff of fertilizer and pesticides. Monocultures – by definition – do not support biodiversity. University of Maine entomologist Dr. Randall Alford spoke of entering cotton fields as a student in the Southern United States and being struck by the stillness, the awareness that he and the cotton plants were probably the only living creatures there because intensive pesticide application had, for a time, destroyed all other life. At one point, when he entered a field not posted as

having been recently treated with organophosphate pesticide, he became very ill with sweating, trembling, and tunnel vision.

Who uses pesticides?

Perhaps a more pertinent question would be who does not use pesticides? Few people don't.

- Farmers are the largest users employing them to control pests on their crops. The herbicides, which they use account for half of the volume of pesticide used in the United States. Lower amounts of insecticides and fungicides are used, and on significantly fewer acres.
- Public-health officials control rats, insects, or other pests in the community that carry disease or present other dangers.
- Foresters kill invasions of insects or other pests.
- Utility owners keep rights-of-way clear using pesticides.
- Golf course owners maintain weed-free greens using pesticides.
- Businesses maintain their premises free of insects, mold, and other pests.
- Industrial enterprises control mold and algae that would otherwise grow in their process tanks.
- Homeowners kill hornets in a nest too close to the home, unwanted dandelions, garden slugs, insects, house flies, cockroaches, ants, moths, rodents, fleas on a pet, or mildew.

Questions 16.1

- 1 (a) For what purposes do you believe that it is acceptable to use a pesticide in your home, yard, or garden? (b) Are there uses of pesticides that you would consider trivial? What are these?
- 2 Recall and describe, if you can, a TV advertisement for pesticides.
- 3 To willingly buy discolored or less-attractive fruits and vegetables, you may have to overcome certain preconceived notions. What types of blemished produce would you avoid buying?
- 4 By the year 2000, humans used 5 billion pounds (~2.3 billion kg) yearly of pesticides worldwide. In the United States that figure was 1.2 billion pounds (0.5 billion kg).¹⁴ Despite this, an estimated third of crops are lost to pests (insects, weeds, and plant diseases), a figure similar to the losses in 1945. Does this mean that pesticides are ineffective? Or does it mean that humans harvest no more crops now than in 1940? Explain.

SECTION II

Sources of pesticide pollution

Pesticide movement

Herbicides and insecticides are applied over large areas of agricultural fields and forests. Farmers may apply them a dozen or more times during a growing season. Less than half of

¹⁴ Fishel, F. M. Pesticide use trends in the US: global consumption. *University of Florida, EDIS*, 2008, <http://edis.ifas.ufl.edu/PI180>.

the applied pesticide actually reaches the insect, weed, or other pest. The rest settles onto soil, vegetation, land, and water close to the point of application. Smaller amounts, swept up into the atmosphere can travel many miles, and be found far from the areas in which they are applied. The polychlorinated pesticides (POPs) detected in wilderness lakes in the northern United States or Canada are not used there, but are blown north from Mexico or other Latin American countries. Because a POP is persistent, its level can build up even in areas far from where it was applied (Box 1.3). In cold areas, once contamination occurs, it may persist indefinitely, especially in locales where low temperature and lack of intense sunlight prevent it from degrading. ■ Pesticides also move through surface water, groundwater, and soil. They runoff from lands to which they have been applied as well as percolating through soil to contaminate groundwater.

Where pesticides are detected

Considering their movements in the environment, it is not surprising that pesticides are detected in many places. Surface and ground waters Pesticides applied to farms and other areas are often found in water bodies into which they have run off (See Chapter 9). Pesticides also run off from municipal streets and grounds, areas sprayed by utilities, golf course greens, and homeowners' yards and gardens. They are detected in streams and other surface waters and groundwater in the United States and other industrialized countries.¹⁵ Pesticides are especially prevalent in waters of areas where they are used heavily, e.g., the US Midwest. A 10-year study in the Mississippi River basin detected more than 40 pesticides in surface and ground water. Pesticides were also detected in 80% of the fish of the rivers and streams studied. The most heavily used herbicide in the United States, atrazine (used especially on corn), was found in 95% of the samples. ■ In some places, atrazine has been found at levels above 1 ppb in rainwater. In localized areas, atrazine in surface water exceeds the EPA's Maximum Contaminant Level for drinking water. Several European countries have banned atrazine. The US EPA is still reviewing its risk.¹⁶

Human and animal exposure

- Air Pesticides pose the greatest risk to those who actually work with and apply them. Pesticides also concern individuals living near areas being sprayed.
- Groundwater The organochlorine pesticides with their low water solubility cling to soil particles, and are less likely to contaminate groundwater. However, water-soluble organophosphate pesticides can seep down to groundwater. An EPA study found that 10% of American community drinking water wells and 4% of rural wells contained detectable – not

¹⁵ (1) Pesticides in the nation's streams and ground water, 1992–2001. *USGS*, February 15, 2007, <http://pubs.usgs.gov/circ/2005/1291/>. (2) Pesticides in ground water. *USGS*, November 17, 2008, <http://ga.water.usgs.gov/edu/pesticidesgw.html>.

¹⁶ Atrazine updates. *US EPA*, November 24, 2008, http://www.epa.gov/pesticides/reregistration/atrazine/atrazine_update.htm.

necessarily significant – amounts of at least one pesticide.¹⁷ Groundwater contamination presents special concerns because even pesticides, short-lived in surface water may degrade very slowly in groundwater. Moreover private well owners are not required to test their water for pesticides or other contaminants.

- Municipal water Recall that municipal drinking water (whatever its source) is tested for many pollutants, including a number of pesticides. The water must be treated if a contaminant is found above its Maximum Contaminant Level (Chapter 10). Thus, significant human exposure is less likely to occur through municipal drinking water systems.
- Consumer exposure to pesticide residues on food Legally, a specific pesticide can be applied only to certain crops. For each pesticide and each crop on which it is used, the EPA places a legal limit on the residue that can remain after harvest. This so-called *tolerance*¹⁸ must present a “reasonable certainty of no harm.” The crop cannot be legally harvested until a specified number of days after the last application to allow time for the pesticide to decay to a level below its set tolerance. The length of time varies with each pesticide and crop.¹⁹
 - Tolerances Before a new pesticide can be marketed it must go through a lengthy and expensive registration process. Its chemistry is studied and it undergoes many acute and chronic toxicity tests as well as studies of its potential effects on wildlife and environment. The process can take nine or more years, and few pesticide candidates make it through to approval. In 1996, the US Congress passed the Food Quality Protection Act (FQPA) under which the EPA had to *reassess all previous tolerances*. And for foods commonly eaten by children, the EPA had to take a new step in setting tolerances: lacking strong scientific evidence to do contrary, it must use safety factors 10 times more strict than for adults.²⁰ The EPA also must consider the cumulative effect of all exposures to pesticides food, water and other sources (Box 4.3). And the EPA must assess whether a pesticide is a likely endocrine disrupter.
 - Monitoring Only a small percentage of fresh produce can be checked by the US Food and Drug Administration (FDA) for pesticide residues. Most of the more than 40 fruits and vegetables on the market go un-examined. Other factors are more reassuring. One is that, when produce is tested only a tiny percentage shows residues above tolerance levels, and much is well below. Another reassurance is that the produce samples tested by the FDA are raw, unpeeled, unwashed, and fresh from the field. This is an important point because such produce represents a worst case picture of pesticide residue levels. Pesticides continue to degrade after the produce has been picked, goes to market, and up to the time the food is eaten. Peeling or removing outer leaves removes more residues and cooking the food

¹⁷ National pesticide survey. *Global Change National Directory*, NASA, February 27, 2008, http://gcmd.nasa.gov/records/GCMD_EPA0129.html.

¹⁸ Pesticide tolerances. *US EPA*, December 18, 2008, <http://www.epa.gov/pesticides/regulating/tolerances.htm>.

¹⁹ There are cases in which farmers inadvertently, or deliberately mishandle a pesticide by applying it to a crop for which it was not registered or harvesting it too soon after application. In one notorious case in 1985, aldicarb – one of the most toxic pesticides in use – was illegally applied to watermelons in several US western states and Canada’s British Columbia. More than 1000 people became ill after eating the melons. Fortunately, such incidents are rare.

²⁰ Children, on a per pound basis sometime eat seven times more apples, bananas, grapes, pears, and carrots than adults. Efforts are being made to reduce children’s pesticide exposure on foods, and in other settings too, especially schools. Erickson, B. Schools urged to reduce pesticide use. *Chemical & Engineering News*, **87**(02), January 12, 2009, 31.

degrades yet more. ▪ Imports It is less reassuring that most food imports remain unchecked. It may be impossible to do pesticide analyses on more than a tiny proportion of imported foods.

Many people remain concerned about pesticide residues on food. Partially in response to that, the sale of organic produce is growing. In North American and European countries and Japan, the sale of produce grown without synthetic pesticides continues to grow by 20% or more a year. This happens although organic produce is more expensive.

Toxic effects

There are many ways that a given insecticide, herbicide or other pesticide can exert its killing effects. Box 16.2 describes some of these with the emphasis on insecticides.

Box 16.2

How insecticides are toxic

There are many pesticides and many ways that they exert toxic effects. The emphasis below is comparing families of insecticides that are especially toxic to the nervous system.

Polychlorinated insecticides

DDT is the best known organochlorine pesticide (Figure 16.1). DDT acts on nerve membranes to prevent normal conduction of nervous impulses. Lindane, aldrin, and heptachlor are other polychlorinated insecticides that are also POPs and widely used. Most of these have been banned, or their use greatly restricted because of environmental persistence, ability to bioaccumulate in fat, and damage to animal populations. Direct sunlight can destroy them and oxygen can help, but they are often trapped in sediments. Until it was banned in 1972, after over 30 years of use, DDT accumulated in many locations, including the Great Lakes region of the United States. Given time polychlorinated chemicals do break down, and, 20 years after banning DDT, its environmental levels had dramatically declined in the Great Lakes area, as had its level in fish, blood, breast milk, and tissues of humans eating the fish. Nonetheless, DDT remains detectable and will be for years to come. See Figure 16.3 for an illustration of DDT's biomagnification in the food web. ▪ Another defining characteristic of organochlorine pesticides is their high solubility in lipid materials, including animal fat. The opposite side of this is that they have low water solubility, and cling to soil particles; thus, little is lost to rainwater runoff. However, recall (Chapter 1) the ability of polychlorinated chemicals to reach the Arctic. Once there, extreme cold prevents their degradation.

Organophosphate insecticides

These came into wide use during the period that POP insecticides were being banned. Organophosphates are also toxic to the nervous system. In their case, they inhibit the action of the enzyme that breaks down acetylcholine. As this neurotransmitter builds up, nerves fire

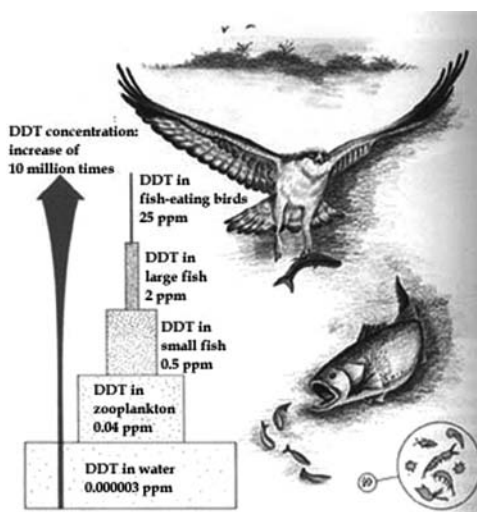


Figure 16.3

Biomagnification of DDT in the food web. Credit: US Fish & Wildlife Service

uncontrollably. Organophosphates are more, sometimes much more, acutely toxic than organochlorine pesticides. Whereas DDT, for example, has an LD_{50} of 113 mg/kg in rats, the LD_{50} of the organophosphate insecticide *parathion* is 30 times lower – 3.6 mg/kg in male rats. Some organophosphate pesticides – again consider *parathion* – are absorbed across the skin, which greatly increases the danger to pesticide applicators. Most acute poisonings in humans are caused by organophosphate pesticides. In fact, organophosphates are chemical relatives of the exceedingly toxic organophosphate nerve gases. More positively, organophosphates have short lives in the environment and, not being fat soluble don't bioaccumulate to high levels in fat. However, this implies increased water solubility; thus, after application to a field, they can runoff in rainwater readily or percolate into groundwater.

Carbamate insecticides

Most carbamates are less acutely toxic than organophosphate pesticides although a few are exceptionally toxic. They exert toxicity in a manner similar to organophosphates, but their effects don't last as long. Like the organophosphates, they are short-lived in the environment. Because of their lower toxicity, they are often found in products used by homeowners but are less useful to farmers.

How to expose insects to insecticides

No matter how an insecticide ultimately kills, the insect must first be exposed to it. Recall, from Chapter 3, ingestion, inhalation and dermal contact. *Rotenone*, a botanical insecticide (Table 16.2), is a stomach and contact poison: a stomach poison is one ingested as the insect eats treated leaves; a contact poison exerts its effect after an insect comes into contact with it externally. Fumigants are gases, or can become gases, so the insect breathes it in. There are

many other ways that an insecticide can be described on the basis of how they impact insects.²¹

Herbicides

Because the metabolism of plants is, in many ways, different than that of insects, other means have been developed to kill weeds. Herbicides fall into groups based on their chemistry and how they kill. As illustrations, they may interfere with plant metabolism to inhibit the action of particular enzymes, cause abnormal growth, or impact the function of plant cell membranes.

Impacts on non-target species

In locales where pesticides are being applied, birds, animals, and insects are often exposed. The adverse impacts seen depend upon the specific pesticide used. With high pesticide exposure as when a large amount of pesticide runs off into a water body, toxic effects can be acute (as in fish kills). However, chronic impacts, e.g., damage to the immune system of wildlife or to wildlife reproduction, take longer to observe. As you read the information below, remember that a given pesticide can often be toxic to a number of species, not just the ones mentioned, and exhibit toxicity in a number of ways.

- Pollinating insects are of great importance to successful crops. Yet, in California, an estimated 11% of honeybee colonies are lost each year to pesticide exposure. Responsible applicators are careful to minimize the exposure of desirable insects by carefully choosing the pesticides used, not applying them during blossoming, and spraying when pollinating insects are absent (early morning or evening). Another precaution is to use ground, not aerial spraying to lessen the pesticide drift that could harm nearby colonies.²²
 - However, in 2006, a mass die off of honey bees began in the United States, *colony collapse disorder*.²³ Up to 90% of hives were lost in places. The cause is not clear, pathogens, artificial diets, stress, or pesticides. Some cite pesticides as the cause, but no consensus has emerged.
- Some years ago the Cornell Laboratory of Ornithology estimated that 67 million birds died each year just on US farmland from pesticide poisoning.²⁴ A great many bird deaths also reportedly result from homeowners' pesticide misuse; homeowners use on average three times more pesticide per amount of land than farmers.
 - Birds can die from direct

²¹ Koehler, P. G. and Belmont, R. A. What are pesticides? Introduction. *US EPA*, <http://schoolipm.ifas.ufl.edu/newtechp1.htm> (briefly describes how various categories of pesticides exert their toxic effects).

²² Riedl, H., Johansen, E., Brewer, L. and Barbour, J. How to reduce bee poisoning from pesticides. *Pacific Northwest Extension*, November, 2006, <http://extension.oregonstate.edu/catalog/pdf/pnw/pnw591.pdf>.

²³ Pesticide issues in the works: honey bee colony collapse disorder. *US EPA*, October, 2008, <http://www.epa.gov/pesticides/about/intheworks/honeybee.htm>.

²⁴ (1) Frequently asked questions on pesticides and birds. *American Bird Conservancy*, 2007, <http://www.abcbirds.org/abcprograms/policy/pesticides/faq.html>. (2) Phillips, T. Pesticides and birds. *Birdscope*, 2001. Cornell Laboratory of Ornithology, <http://www.birds.cornell.edu/Publications/Birdscope/Summer2001/pesticides.html>.

pesticide exposure or from eating pesticide-treated seeds, foliage, insects, or poisoned prey. Pesticides can also make birds more susceptible to predators, or have chronic effects. ▪ On the US East Coast, as many as 2 million bird deaths in one incident were associated with *carbofuran*, an insecticide also extremely toxic to humans. When applied in granular form, birds mistake it for dietary grit, eat it, and die. In a tragic incident on the Argentine Pampas, nearly 6000 migrating Swainson's hawks died from exposure to the pesticide *monocrotophos* which the Argentine government later banned. The US EPA has now banned, restricted use, or begun the phase out of several particularly toxic pesticides, diazinon, chlorpyrifos, monocrotophos, and carbofuran²⁵. But, bird *poisonings continue to occur*.

- **Fish** die by hundreds, thousands, or in some cases millions along with other aquatic species. Deaths are attributed to pesticide runoff or pesticide drift settling onto water. Pesticides may also cause acute illness or death in fish and other aquatic creatures. In lower concentrations, many present chronic health risks, including cancer. Fish kills continue to be reported.
- **Amphibians** An alarming trend is the disappearance or much reduced populations world-wide of frogs and other amphibians. Amphibians have thin skins making them especially vulnerable to outside agents. Some see the loss of amphibians as the "canary in the mine" reminding humans that we too are at peril. Many factors appear to be implicated in amphibian decline –loss of habitat is a major factor – but organophosphate-pesticide exposure may also be important. ▪ A significant study: University of Pittsburgh researcher, Rick Relyea, in a 9-year study examined impacts of individual pesticides as compared to mixtures of ten pesticides (herbicides and insecticides) on the tadpoles of leopard frogs and gray tree frogs.²⁶ He tested pesticides at concentrations far below those that EPA calculates as harmful to humans, but toxicity in frogs may be very different (Chapter 3), and the impact of mixtures different than toxicants tested one by one. Relyea found that insecticide mixtures were especially lethal to tadpoles. And such low concentration mixtures can be found in natural settings not just in the laboratory. One insecticide he examined, endosulfan, was about 1000-times more lethal than the other pesticides studied.

Humans – chronic effects

In developed countries with the exceptions of persons directly working with pesticides or living close to sites that are sprayed, most concerns relate to possible chronic effects of exposure to pesticides at low doses. Major concerns are possible cancer or damage to the developing fetus or small child. In less-developed countries cases of acute toxic effects from pesticides are very common.

²⁵ Erickson, B. E. Manufacturer drops carbofuran uses. *Chemical & Engineering News*, **87**(1), January 5, 2009, 18.

²⁶ Low concentrations of pesticides can become toxic mixture for amphibians. *Science Daily*, November 18, 2008, <http://www.sciencedaily.com/releases/2008/11/081111183041.htm>.

Questions 16.2

- 1 Velpar (hexazinone) is an herbicide used on Maine's blueberry barrens. In 1995, after 10 years of use, Velpar was detected in groundwater at an average concentration of 5 ppb in locales where it was used. The drinking water of one school had less than 2 ppb, but school board members decided to install a filter to remove it. Some individuals want to forbid blueberry growers to continue using Velpar. (a) The EPA's health-based limit for this herbicide is 210 ppb. Knowing this, would you be concerned about 2 ppb in water that you yourself drink? (b) Would you be concerned if the 2 ppb were in water drunk by your child? Why? (c) Do you believe that pesticides that migrate into groundwater should be banned, or restrictions placed on their use? Explain. (d) Assume that current levels of Velpar do not concern you. Would you nonetheless support continued groundwater monitoring? Why?
- 2 Long-term use of Velpar or other herbicides leads to loss of organic material from soil. (a) Why does the soil lose organic material? (b) Why is loss of organic matter a concern?

Effects of pesticides on the pests themselves

Secondary pests and pest resurgence

The pest that a farmer wants to kill, called the *primary pest* may sometimes be holding down the population of a potential pest, the *secondary pest*. Killing the primary pest may free the secondary pest of its enemy, allowing it to undergo population growth, until it becomes a pest itself. ▪ Or, pesticides may kill the natural predators of the primary pest. Then, when primary pest survivors reproduce their population rebounds because their predator is gone or reduced. This is *pest resurgence*.

Pest resistance

Resistance is a major pesticide-use problem. When a pesticide is used on a population of insects, plants, or other pests, one or more individuals may have a genetic mutation permitting them to tolerate the pesticide. When these resistant individuals reproduce, they pass resistance genes to their offspring. Over time, the resistant population increases until most individuals are resistant to the pesticide. Often, when resistance is observed, the response is to apply larger quantities of pesticide. This allows the pest to express resistance to the higher doses too. Or, if the applicator switches to a different pesticide, resistance develops to it as well. Because some pest species reproduce very quickly and in huge numbers, resistance sometimes develops rapidly. There are cases of insect resistance appearing in as little as 5-years.²⁷

²⁷ Part of the problem may be that crop breeders over the years based their work on selecting crop offspring that had enhanced yields. They ignored or were unaware of resistance genes that help plants naturally fight off pests, and many resistance genes were lost during the process of selecting for traits giving enhanced yields. Curiously, genetic engineering is used now to introduce genes, albeit from a different species, to help resist pests.

Hundreds of insects, mites, weeds, and plant diseases have become resistant to one or more pesticides. The numbers of resistant pests continue growing and some weeds already resist all known herbicides. One entomologist said, “We’re about a half step ahead of the insects, and only a little more than that for weeds and plant diseases.” Insects have inhabited Earth for several hundred million years, plants and microbes for much longer still. They have adapted to ever-changing sometimes dramatically different circumstances. Human-made chemicals are but one more challenge. Consider the *Anopheles* mosquito that carries the malaria parasite. Worldwide 2.4 billion people live in locales where they could contract malaria, which now causes about 3 million deaths a year. DDT and other pesticides once killed *Anopheles* mosquitoes easily, and the possibility seemed real that malaria could be wiped out. Now, mosquitoes are increasingly resistant. And in some places the incidence of malaria is higher than before pesticides were introduced. However, spraying a home’s walls with a DDT solution can still keep mosquitoes from entering. ▪ The process of pests developing resistance to pesticides is entirely analogous to microorganisms developing resistance to antibiotic drugs. In the case of antibiotics, this situation has become so serious that physicians now refer to a post-antibiotic age. For pesticides too, as increasing numbers of pest species become resistant, many agricultural scientists worry whether effective and relatively safe new pesticides can be developed fast enough to cope with them.

SECTION III

Reducing the risk of pesticides

There are many approaches to reducing pesticide use. One piece of advice from Rachel Carson was: “Spray as little as you possibly can, rather than, ‘Spray to the limit of your capacity.’”

Reducing risk through regulation²⁸

The US law regulating pesticides is the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) administered by the EPA.²⁹ The EPA must ensure that a pesticide will not pose unreasonable adverse effects on human health and the environment. The Fish & Wildlife Service works with the EPA to prevent and minimize the pesticide impacts on fish, wildlife, and plants. In 2008, the EPA started a Pesticide Registration Review Program with which it plans to re-evaluate effects of all pesticides on threatened or endangered species. But, although FIFRA mandates no “unreasonable adverse effects” it also mandates that pesticide risks be balanced with their benefits. ▪ FIFRA covers the *active* ingredients in pesticide

²⁸ Pesticide topics. *US EPA*, November 15, 2007, <http://www.epa.gov/oecaagct/pesticide.html>.

²⁹ About EPA’s pesticide program. *US EPA*, April, 2007, <http://www.epa.gov/pesticides/about/aboutus.htm>.

preparations, i.e., the ingredients actually killing the pest. The EPA does not regulate the inert ingredients, although these are often the bulk of the product. However, if the inert ingredient is a highly toxic substance, it must be identified.³⁰ The purpose of inert ingredients is to make the active ingredient soluble, to stabilize it, or allow it to be applied in a specific way.

Controlling a pest with the pest's own chemicals

One major example of a *pheromone* is a chemical produced by female insects to attract males. In the world of pesticides, a pheromone is used to attract males into a trap. Another example of using an insect's own chemicals is *growth regulators*, chemicals that control stages of insects' life cycle. The regulator is sprayed on a crop infested with that insect's larvae, where it interferes with larval development into adults. ▪ Notice that the chemist's handiwork is necessary to obtain pheromones or growth regulators. A pheromone or growth regulator must first be identified for what it is, purified from insects and its structure elucidated. Then, because such tiny amounts of these chemicals are produced naturally by the insects, the chemicals are synthesized to provide quantities large enough to be useful – they are synthetic chemicals, but the information used to make them comes from living organisms.

Green chemistry

Two major goals of “green chemistry” are to develop chemicals that are less toxic or to make chemicals in less toxic ways, preferably both. The pheromones and growth regulators just mentioned are examples of green chemistry; they are toxic only to the insects whose lives they disrupt. In recent years, chemical companies have emphasized the development of pesticides less toxic to non-target species and to the environment, and pesticides working at much lower concentrations. ▪ See Table 16.3 for desirable traits in a pesticide. Some examples follow. ▪ An herbicide applied at only teaspoons per acre (about 8 g) affects one plant enzyme, and has very low toxicity to humans and animals. Compare this to about 2 pounds per acre (2.2 kg per hectare) for older herbicides. ▪ An insecticide (also applied in tiny quantities) affects one insect enzyme, and shows low toxicity to non-target species. ▪ An herbicide used on corn and soybeans has an LD₅₀ in rats of 500 mg /kg body weight, i.e., only slightly toxic (Table 3.4). The herbicide is also not a teratogen or carcinogen, breaks down quickly in the environment, and does not threaten groundwater. ▪ US Department of Agriculture scientists developed a crop protectant. This simple product called *Surround*³¹ is made of processed kaolin (clay). Sprayed onto plants it forms a film barrier that inhibits many insect species and mites from feeding on the plants while also reducing sun damage and heat stress. It also has low toxicity. *Surround* is not considered a pesticide and didn't need to go through the usual EPA registration process.

³⁰ Inert or other ingredients. *US EPA*, December, 2000, <http://npic.orst.edu/factsheets/inerts.pdf>.

³¹ Surround at home crop protectant. *Gardens Alive*, 2009, http://www.gardensalive.com/product.asp_Q_pn_E_8072.

Table 16.3 Desirable characteristics in a pesticide

Only a small amount is needed to kill targeted pests
 Low toxicity to non-target species
 Specific to one or a few pests
 A lifetime just long enough to kill target pests (does not persist)
 Degrades into benign products
 Does not bioaccumulate
 Does not runoff with water from application site
 Pests are slow to develop resistance to it

Note: Ideally a pesticide would have all these characteristics. In practice, certain characteristics are incompatible. For example, it is desirable that a pesticide not migrate from its application site. However, the reason it may not migrate is that it binds tightly to the soil and is not soluble in water – characteristics associated with the undesirable traits of environmental persistence and bioaccumulation.

Recall from above that new pesticides can take 9 years or longer to be reviewed and approval from the EPA. However, the 1996 FQPA discussed above allows the EPA to expedite review when the chemicals involved are biopesticides or reduced-risk synthetic pesticides. This is a stimulus to the development of “greener” pesticides.

Reducing pesticide risks by changing farmers' ways

There are three ways of farming, each with a different approach to pesticides. (1) *Conventional farmers* use synthetic pesticides and commonly use them according to a predetermined calendar schedule rather than on the basis of a known need for pesticide. There are often frequent applications. (2) *Organic farmers* use no synthetic pesticides at all. (3) The approach of farmers using *integrated pest management (IPM)* is to *manage not eliminate* pests. This means managing *when* pesticides are used, the *amount* used, and the *toxicity* of the pesticides used.

Organic farming³²

Organic farmers or gardeners don't use synthetic pesticides or synthetic fertilizers. ■ They use “natural” pesticides, such as low-toxicity Bt (*Bacillus thuringiensis*) a microbial insecticide, or occasionally, a copper fungicide. They definitely do not use and don't approve the use of genetically engineered Bt. Even these pesticides are used in limited amounts to avoid developing pest resistance. They prefer to control pests by intercropping, crop rotation and

³² Organic farming. NCAT, August 26, 2008, <http://attra.ncat.org/organic.html>.

other methods described below. ▪ They don't use synthetic fertilizers either. Nor do they use sewage sludge because it often has extraneous components. They *do* use manure and compost as fertilizers or grow legumes in rotation with regular crops; the legumes provide nitrogen nutrients to the soil and also condition the soil by providing organic matter.

Integrated pest management (IPM)³³

IPM farmers do use synthetic pesticides, but the major tenet is to *manage pests, not eradicate them*. IPM farmers assess their fields and identify what pests are present. They check for signs that a pest is reaching a stage where it could cause significant damage. Only then is pesticide applied – there is no predetermined spraying schedule. Depending on the particular crop and the circumstances under which it is grown IPM can reduce pesticide use 50–70%. Critics say that, sometimes pest populations inflict damage too rapidly for an inspection regime to work. Other tactics that IPM farmers may use follow. ▪ Choose, whenever possible, pesticides with low toxicity to humans and other organisms. ▪ Apply the pesticide in the lowest quantity that can do the job.

Techniques used by organic farmers and many IPM farmers

Change how farming and gardening is done to reduce pesticide use.

- Grow crops in ecologically appropriate regions, locales that require the least pesticide for a successful crop. This can much reduce pesticide use.
- Control weeds mechanically, not with herbicides when possible, i.e., use hand tools or farm machinery to destroy them. This reduces herbicide use but requires more energy use, human or machinery.
- Use crop rotation, i.e., vary the crops grown on a piece of land, season to season or year to year. This controls pests that cannot long survive without a specific crop present. Corn illustrates the value of rotation. Corn root-worm survives over the winter, living to damage or destroy corn if it is replanted in the same place again. In crop rotation, corn is planted one year and soybeans the next greatly reducing the amount of pesticide needed. Rotation has another advantage if legumes are included; they replenish soil organic nitrogen and organic matter so, when the alternate crop is grown, less pesticide and less fertilizer are needed. (Conventional farmers typically grow large tracts of monoculture corn, cotton, wheat, or other crops, and would find rotation impracticable or expensive.)
- Intercropping, growing more than one crop on the land at the same time also lowers pesticide dependence. (Conventional farmers would find intercropping too labor intensive.)
- Eliminate pest-breeding places by destroying crop residues after harvest. This does not leave pests a place to overwinter.

³³ (1) Integrated pest management (IPM), How to manage pests. *University of California IPM online*, 2008, <http://www.ipm.ucdavis.edu/>. (2) Matthews, G. Integrated pest management. *Scitopics*, November 7, 2008, http://www.scitopics.com/Integrated_Pest_Management.html. (3) IPM. *US Fish & Wildlife Service*, September 24, 2008, <http://www.fws.gov/contaminants/Issues/IPM.cfm>

- When possible, plant a crop in a season that minimizes its exposure to destructive pests.
- Use biological control (biocontrol), i.e., use a natural enemy of the pest (a pest of the pest). This can be a parasitic insect that preys on the pest, or a microorganism that causes a disease in the pest. Well-known examples of insect predators are praying mantises and ladybugs. Ladybugs are reared in large numbers and released to infested areas, where they temporarily, reduce insect populations. Biocontrol does not fully replace pesticides. For example, introduced parasites partially control the alfalfa weevil, but some pesticide is still needed. In another instance of biocontrol, large numbers of a pest's eggs are hatched, raised to adulthood, sterilized and released. The sterilized pests mate with normal insects, but with no offspring are produced, there are fewer pests. ▪ A part of biocontrol involves ensuring that enough habitat exists to allow a pest's natural enemies to grow. ▪ Sometimes an *exotic* enemy is, after careful consideration imported from a distant location (Box 16.3).

Box 16.3

Importing biocontrol agents

▪ In nineteenth century California, the *cottony-cushion scale* threatened the California citrus industry. This pest was an insect that had been introduced from Australia. Australian entomologists identified two enemies of the scale and, in the 1880s, took them to California. Within a few months the scale was brought under control and, over the years has remained so. ▪ Nearly a hundred years later, cassava plant roots (a basic food for millions in Africa) became infested by the *cassava mealybug*, an insect that grows entirely on cassava. In heavily infested fields, farmers could lose 80% of their crop. Detective work revealed that the mealybug was not African, but South American, the same continent from which cassava came. Subsequently, a wasp, *Epidinocarsis lopezi*, a natural enemy of the mealybug, was identified in South America. After careful study, the wasp was introduced into African cassava fields. Once it was clear that the wasp effectively killed mealybugs, researchers bred it in large numbers and distributed it over the large region of Africa affected by the mealybug.

There is a major concern with importing exotics. Introducing an exotic insect – from another region or country – may allow the exotic to become a pest itself as it may have no enemies in its new setting. This is why the South American wasp was carefully studied before it was introduced into Africa to control the mealybug. However, an insect that preys on other insects has a fortunate characteristic. It usually preys only on those species with which it evolved. Because it attacks only the pest it was introduced to control, the concern associated with introducing an exotic species is reduced.

The Californian and African examples given here are not isolated instances. In more than 160 countries, about 560 biological control agents have been introduced to combat nearly 300 target insect pests with substantial or complete success. Professor L. E. Ehler of the University of California at Davis points out that this remedy does not have the toxic side effects of chemical pesticides and is often permanent and economical. Not just insects, but weeds and other pests can be biologically controlled. As with insects, many weeds infesting US crops are exotics. To control an exotic weed, researchers go to its place of origin to find an insect or pathogenic microorganism that can control it. A critical caveat in all these efforts is that the biocontrol agent be very carefully studied to minimize the chance that it will itself become a pest.

For either IPM or organic farming to work well farmers and gardeners must be educated to understand the crops they grow, the pests that infest them, and how climatic conditions affect crops and pests. They must also take the time and effort to use their knowledge to find less-toxic pesticides (or non-pesticide alternatives).

Which mode of agriculture is sustainable?

Critics of organic agriculture hold that on a given land area, food yields cannot match those of pesticide- and fertilizer-aided agriculture. In recent years there may be a shift toward the belief that organic agriculture can work,³⁴ especially in less-developed nations. In industrialized societies where a great deal of fertilizer and other inputs are added to ensure maximum possible yields, an equivalent yield with organic agriculture may be less feasible. ▪ On the other hand, many do not believe that high-input agriculture – input of energy, pesticides, fertilizers, water, and expensive machinery, and the impact of these on soil – is sustainable. ▪ Some see IPM as an intermediate path that may be sustainable. ▪ Some are strong proponents of transgenic plants (GEOs) believing they are necessary to produce enough food for the growing human population, and that they may have much to offer the less-developed world. One of several criticisms of GEOs is that they will encourage monoculture crops and the problems associated with monoculture. ▪ Whichever approach demonstrates the greatest compatibility with the environment must, in the long run, win out because sustainable agriculture is, by definition, necessary.

Questions 16.3

- 1 As a consumer of food, would you rather buy food from conventional farmers or organic and IPM farmers? Why?
- 2 (a) If you could eliminate *one* use of pesticides, what would it be, and what would be the consequences of eliminating this use? (b) Could this use reasonably be eliminated? Explain.
- 3 Do you believe the increased high-input food production seen over the past 50 years is sustainable over the long term? Explain.

³⁴ (1) Meeting the food security challenge through organic agriculture. FAO Newsroom 3, May 2007. <http://www.fao.org/newsroom/en/news/2007/1000550/index.html> (2) Halweil, B. Can Organic Farming Feed Us All? *World Watch*, 19(3), May/June, 2006, 18–24 (Also, <http://www.worldwatch.org/node/3918> interview with Halweil) (3) Cummings, C.H. Ripe for Change: Agriculture's Tipping Point. *World Watch*, 19(4), July/August 2006, 38 (4) Cooney, C.M. Sustainable agriculture delivers the crops. *World Prout Assembly*, February 17, 2006. http://www.worldproutassembly.org/archives/2006/02/sustainable_agr_1.html.

Questions 16.4

- 1 Growing crops such as cotton, fruit, or other produce in ecologically “inappropriate” regions means using much more pesticide. However, growing them only in ecologically appropriate regions could mean a lower crop yield. (a) Is this an important reason to grow crops in ecologically inappropriate regions? Explain. (b) How important is it to you personally that a given fruit or vegetable be available year round?
- 2 A product not available year around in your own state or country could be grown in an ecologically appropriate region elsewhere, and shipped to where you live. (a) What are the environmental consequences of transporting agricultural or other goods long distances to market? (b) How would you begin to do a comparison of the environmental consequences of shipping a good as opposed to growing a crop in an ecologically inappropriate region? (c) If you were able to choose which crops to import long distances, which would be most important to you? Explain.
- 3 (a) Some believe that conventional high-input agriculture is not sustainable – why? (b) Can IPM be sustainable? Explain.

SECTION IV

Pesticide use in less-developed countries

Improper use of pesticides

Pesticide users in less-developed countries often suffer much greater exposure than individuals in developed countries. The World Health Organization (WHO) estimates that 3 million people a year suffer severe poisoning from improperly used pesticides,³⁵ and that 300 000 die.³⁶ In one case of gross negligence 24 children in a Peruvian village died after drinking milk into which a woman had mixed parathion to kill a stray dog. Less-developed countries use 25% of the world’s pesticides, but suffer 99% of the deaths. There is occupational exposure and also a significant number of suicides using pesticides. Moreover, salesmen are often willing to sell banned pesticides made by unscrupulous manufacturers. Plantation owners may not provide workers with personal protection or the education needed to safely use pesticides. Many small farmers are ignorant about the products they buy and how to use them safely. And even carefully prepared labels are useless for farmers who cannot read.

Many millions of children work or live in agricultural settings in Africa, Asia, and Latin America, and are often exposed to pesticides. Recall the Yaqui Indian children (Box 3.5).

³⁵ Reducing pesticide risks through building capacity of African regulators. *WAHSA*, 2008, <http://web.uct.ac.za/depts/oehru/dox/capacity.pdf>.

³⁶ Konradsen, F. Acute pesticide poisoning: a global health problem. *Danish Medical Bulletin*, **54**(1), February 2007, 58–9, http://www.danmedbul.dk/DMB_2007/0107/0107-artikler/DMB3886.htm.

▪ In one Cambodian study, more than half the farmers interviewed allowed their children to spray pesticide. Although the children often suffered from “excess tiredness, dizziness, headache, and pale skin after spraying,” the parents did not link the symptoms to pesticide use. ▪ In China, with its limited land and high population, many farmers use excess quantities of pesticides and fertilizer to push up crop yield.³⁷ Farmers’ health can be impacted directly and indirectly through runoff of pesticides into water used for drinking. A market study in Hebei Province found more than half the vegetables sampled exceeded China’s maximum allowed pesticide residue levels. Another study estimated that about half of fruits and vegetables have pesticide residues exceeding China’s standards for certain pesticides.

Dangerous pesticides

In 2002, the UN reported that the use of especially poisonous organophosphates was continuing to grow. The Food and Agriculture Organization (FAO) Director stated that “In many developing countries conditions do not allow small farmers to use highly toxic pesticides safely, and the result is continued damage to the health of farmers and poisoning of the environment.” The Rotterdam Convention was the response to these concerns; it became legally binding in 2004.³⁸ ▪ Recall from Chapter 14 the *Basel Convention* (to control imports of hazardous waste into developing countries). The *Rotterdam Convention on Pesticides and Hazardous Chemicals* serves a similar role, in this case to control imports of 22 hazardous pesticides plus a number of industrial chemicals. A country is provided with information on chemicals including pesticides that it is considering importing, and can exclude those it cannot manage. However, if it gives its *prior informed consent* to import a pesticide, the Convention assures that the imports will have good labeling and provide technical support. It ensures too that exporters who send the chemicals comply with requirements. ▪ Another program (not treaty), the *International Code of Conduct on the Distribution and Use of Pesticides* is administered under the auspices of the FAO.³⁹ Its aim is to reduce the widespread risks that pesticides pose in the developing world. It provides a framework for judicious use of pesticides, especially until countries have established their own effective regulatory infrastructures.

Obsolete pesticides

The UN FAO estimated in 2002 that 551 000 tons (500 000 tonnes) of unused-outdated pesticides and pesticide wastes still exist in developing countries, including old POPs such as DDT as well as dangerous organophosphates such as parathion and monocrotophos, see Figure 16.4. About 132 000 tons (120 000 tonnes) are in Africa. Even well stored pesticides eventually leak. Others, stored unprotected and in the open threaten human health and the

³⁷ Yang, Y. Pesticides and environmental health trends in China. *China Environment Forum*, February 28, 2007, http://www.wilsoncenter.org/topics/docs/pesticides_feb28.pdf.

³⁸ Rotterdam Convention enters into force. FAO, February 24, 2004, <http://www.fao.org/newsroom/en/news/2004/37667/index.html>.

³⁹ International Code of Conduct on the Distribution and Use of Pesticides, revised. *FAO Council*, 2005, <ftp://ftp.fao.org/docrep/fao/009/a0220e/a0220e00.pdf>.



Figure 16.4

Poorly stored obsolete pesticides in an African country. Credit: World Bank Group, 2009

environment. As containers corrode, pesticides leak into the soil, evaporate into the air, and run off into local waters. Because Africa has no hazardous waste destruction facilities, the pesticides must be shipped abroad for destruction at high cost, which Africans cannot pay.

▪ For all these reasons, obsolete pesticides were not being destroyed. A multinational effort, the Africa Stockpiles Programme was begun⁴⁰ with the aim of ridding Africa of obsolete pesticides and contaminated waste. It also promotes prevention measures and capacity building for the future. Costs will be a quarter billion dollars.

Reducing pesticide use

Many have concluded that it is almost impossible to safely use pesticides in impoverished locales. Thus, the UN FAO supports IPM and organic farming to minimize pesticide use. ▪ In 1986, Indonesia's President Suharto banned the use of 57 pesticides used on rice. One reason was that growth of the brown plant hopper (BPH), one of the worst enemies of the rice crop was actually enhanced by pesticide use; rice yields in fields using pesticides were lower than yields in fields managed by IPM. This happened because heavy pesticide applications killed off many of the natural predators of the BPH such as dragonflies, wasps, and spiders. Many amphibians and other non-target species were killed too. Three planting seasons later, the FAO reported that pesticide use had declined 90% and rice yields had risen 11%.⁴¹ ▪ Since then the FAO, using "Farmer Field Schools," has trained about a million farmers in the principles of IPM⁴². Training includes rice ecology, how pesticides

⁴⁰ Stockpiles of obsolete pesticides in Africa higher than expected. FAO, September 18, 2002, <http://www.fao.org/english/newsroom/news/2002/9109-en.html> (this partnership has 13 donors: many countries plus the Global Environment Facility, World Bank, and CropLife International). (2) Cleaning-up Obsolete Pesticides Across Africa: Stockpiles Programme shows the way. *World Bank*, September 11, 2007, <http://web.worldbank.org/WBSITE/EXTERNAL/NEWS/0,,print:Y~isCURL:Y~contentMDK:21468541~menuPK:34457~pagePK:34370~piPK:34424~theSitePK:4607,00.html>. (3) Manufacturing and agriculture: making products makes waste. *UNEP*, 2009, <http://www.grida.no/publications/vg/waste/page/2860.aspx>.

⁴¹ Hendriadi, A. and Alihamsyah, T. Sustainable agriculture development in Indonesia. *UNAPCAEM*, November 23, 2007, <http://www.unapcaem.org/Activities%20Files/A0711/01id.pdf>.

⁴² Feder, G., Murgai, R. and Quizon, J. B. Sending farmers back to school: the impact of Farmer Field Schools in Indonesia. Review of Agricultural Economics, February, 2003, are.berkeley.edu/courses/envres_seminar/s2003/FFSImpact.doc.

affect ecosystems, and how to recognize pests and when they reach significant levels. FAO now has training projects in more than 40 countries for a variety of crops. Pesticide use is absolutely minimized. An FAO Coordinator noted that “countries across the Asia region are now at a crossroads where they must choose between a future of farmer-based, sustainable agriculture, or a return to the input-led systems fostered by the Green Revolution in decades past.” ▪ In Latin America, the Inter-American Development Bank loaned the Nicaraguan government money to train 14 000 farmers in IPM and soil conservation techniques including contour plowing, ditching, and terracing.

Many farmers are losing knowledge of farming techniques indigenous to their cultures. Former UN Environment Program Director Klaus Töpfer stated, “Enshrined in their cultures and customs are secrets of how to manage habitats and the land in environmentally friendly, sustainable ways.” For an illustration of how this works, see Andean potato peasants are “seed bankers.”⁴³ ▪ In another case, the African country of Ethiopia, after years of drought and soil degradation was suffering famine and malnutrition. Government agents encouraged farmers to use synthetic pesticides and fertilizers to improve crop yields. But farmers had difficulty with pesticides, which led to human and animal poisonings. The organization Save the Children began training Ethiopian farmers on how to use traditional methods and IPM. Farmers learned to recognize pests and beneficial insects, and how to enhance populations of beneficial creatures. They did not automatically use synthetic pesticides. Instead, when possible, they used local alternatives to pesticides, various plant extracts and even fermented cow’s urine. Participating farmers significantly reduced pesticide use.⁴⁴ ▪ One of the objections to organic farming and IPM is that they require more human labor. However, labor is plentiful in many less-developed countries as is the desire to own and care for their own land. An important benefit for farmers is that they learn to trust their own judgment, rather than automatically depending on pesticides.

Delving deeper

Read the article “Greening the Farm.”⁴⁵ Then do the following. (1) Using the raising of Christmas trees as an example show how pesticide use has been decreasing in the United States and the positive impacts being seen as a result. (2) Again using Christmas trees, show how IPM has been helpful in reducing pesticide use. (3) Now do the same for organic farming techniques.

⁴³ Benzing, A. Andean potato peasants are “seed bankers.” *ILEIA Newsletter*, December, 1989, http://www.leisa.info/index.php?url=getblob.php&o_id=69084&a_id=211&a_seq=1.

⁴⁴ Ademe, M. S. Progress in farmer field school, IPM in Ethiopia’s lowlands. *PAN*, March, 2003, <http://www.pan-uk.org/pestnews/Issue/pn59/pn59p15.htm>.

⁴⁵ Ritter, S. K. Greening the farm. *Chemical & Engineering News*, **87**(07), February 16, 2009, 13–20, <http://pubs.acs.org/cen/coverstory/87/8707cover.html>.

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“Seeing things differently is the first step toward doing things differently.”

Anon.

Thirty years ago, the US EPA, working with Harvard University was studying the sources of various environmental pollutants. They made what was then a startling observation: regardless of the community studied – its location, whether rural or urban, lightly or highly industrialized, and regardless of sex, age, smoking habits, and occupation – indoor air pollution was the major source of exposure to many air pollutants. This is perhaps not surprising: Most people spend 90% or more of their time indoors, indoor sources emit many of the same pollutants as outdoors sources, and dilution with outdoor air may be slow to occur. In the following years, the Advisory Board of the US EPA ranked indoor air pollution as a priority environmental health risk.

▪ Section I of this chapter reviews specific contaminants that impact indoor air quality: combustion pollutants (including tobacco smoke), volatile organic chemicals (VOCs), radon and biological pollutants. It also examines health impacts of combustion particulates on people in less-developed countries. Section II delves into hazardous household products and household hazardous waste, and describes two old hazards that remain with us, asbestos and lead paint.

SECTION I

Indoor air pollution¹

Contaminants affecting indoor air quality spring from many sources (Table 17.1²). To fully understand Figure 17.1, go to URL in footnote ³ and, one-by-one click each room shown.

- Combustion appliances⁴ including wood stoves and fireplaces, gas stoves, and kerosene heaters emit particulates and several criteria air pollutants (Chapter 5).

¹ (1) The inside story, a guide to indoor air quality (CPSC Document #450). *US CPSC and US EPA*, no date, <http://www.cpsc.gov/cpscpub/pubs/450.html#Look6>. (2) Indoor air quality. *US EPA*, January 5, 2009, <http://www.epa.gov/iaq/>. (3) EPA's report on the environment: indoor air. *US EPA*, March 26, 2009, <http://oaspub.epa.gov/hd/home#11>.

² (1) Indoor air quality, subject index. *US EPA*, November 25, 2008, <http://www.epa.gov/iaq/atozindex.html>. (2) Air pollution and your home. *American Lung Association*, 1995–2009, http://www.alaw.org/air_Quality/indoor_air_Quality/air_pollution_in_your_home.html.

³ Remodeling your home? Have you considered indoor air quality. *US EPA*, August 26, 2008, <http://www.epa.gov/iaq/homes/hip-front.html>.

⁴ What you should know about combustion appliances and indoor air pollution (Doc. #452). *Consumer Product Safety Commission*, no date, <http://www.cpsc.gov/CPSC/PUBS/452.html>.

Table 17.1 Indoor air pollutants

Sources	Pollutants released
Household products	
- Paints, stains, thinners, strippers, polishes, cleansers, solvents, air fresheners	VOCs such as formaldehyde, benzene, toluene, xylene, and hexane. Many other VOCs are also possible, depending on the products used. Some also emit particulates.
- Cosmetics, perfumes, and colognes	
- Hobby supplies (paints, glues, metals, wood, glass, others)	
- Propellants in aerosol sprays	
- Pesticides + their solvents	
Household furnishings	
- Drapes, upholstered furniture, pressed-wood in cabinets, walls, sub-flooring	<u>New furnishings</u> Formaldehyde and other VOCs
- Carpets, shelving, other surfaces, “dust catchers” (Also see biological hazards)	<u>Older furnishings</u> Dust, biological pollutants
- Carpets, furnishings, bedding	Dust mites and dust
Dust and dirt getting into the home	Can carry pesticide residues, metals, and biological pollutants.
Combustion sources	Without good controls, these can release carbon monoxide, nitrogen oxides, sulfur dioxide, particulates (sometimes formaldehyde, benzene, other VOCs).
- Oil or gas furnace, unvented kerosene or gas stoves, wood stoves, fireplaces	
- Gas water heater or clothing dryer	
- Environmental tobacco smoke (ETS)	ETS emits these & many others too
Biological hazards	
- Moist areas (basement, bathroom, etc.)	Mold VOCs, bacteria, bacterial toxins, viruses If not clean can emit all of the above
- Humidifiers and dehumidifiers	
- Pets, intruding rodents and insects	Animal dander, dried saliva, urine Pollen and dust
- Outdoor air	
Hazards old and new	
- Old paint	Lead
- Old insulation(furnace pipes, old tiles)	Asbestos
- Construction materials, wood paneling	VOCs including formaldehyde
- New carpets, padding, adhesives	VOCs
- Painting, stripping old paint, etc.	VOCs
VOCs including formaldehyde	
Basement floor (cracks, sump openings)	Radon
Household water	
- Municipal chlorinated drinking water	Chloroform and other VOCs
- Well water	Radon, sometimes VOCs

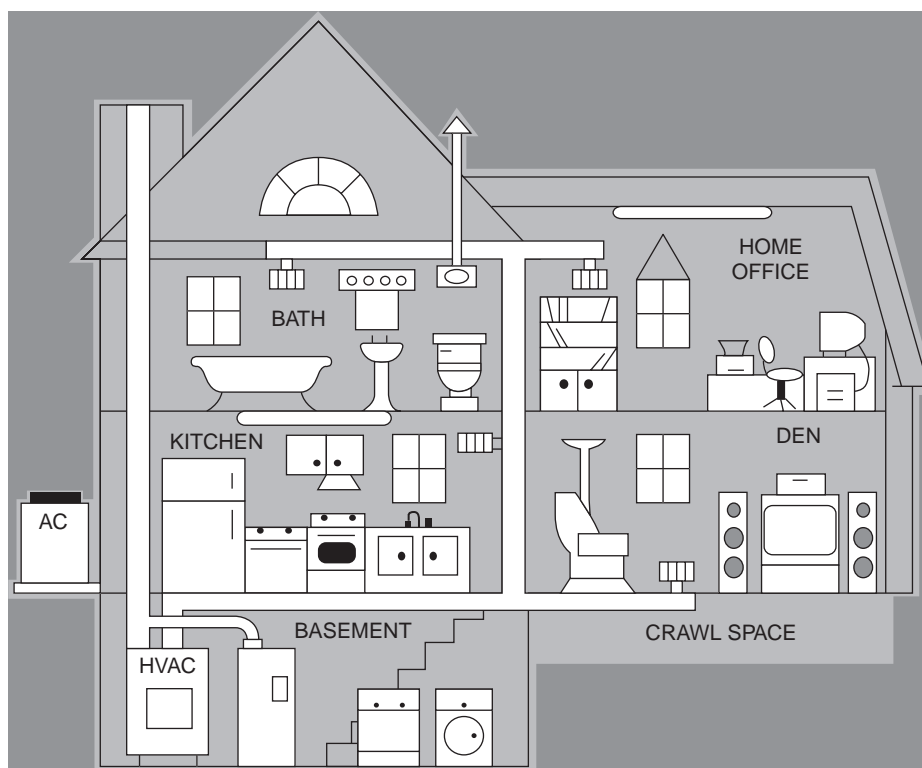


Figure 17.1 Sources of indoor air pollution. Credit: US EPA [Click on individual rooms at <http://www.epa.gov/iaq/homes/hip-front.html>]

- VOCs arise from construction materials (particle board is one) and consumer products including cleansers, polishes, paints, moth balls, glue, new rugs, furniture, drapes, rugs, clothing, and hobby materials. Chlorinated water emits VOCs too.
- Biological contaminants grow in moist areas in homes and become airborne.
- Radon, a natural radioactive gas seeps up from rocks and soil under homes into indoor air. It also enters air from well water pumped into the home (Table 17.1).
- Older homes may have flaking lead paint or asbestos. Some may have more biological contaminants resulting from persistent wet places or old rugs.

Health effects of indoor air pollutants⁵

Health effects may be negligible or major depending on the pollutant, its concentration, how exposure occurs and length of exposure. Acute effects can result from high levels of a pollutant. Chronic effects may result from lower ongoing exposure. Examples:

⁵ Indoor air quality resources (questions and answers). *US EPA*, November 25, 2008, <http://www.epa.gov/iaq/iaqinfo.html>.

- Irritation of eyes, nose, and throat can result from formaldehyde or nitrogen oxides.
- Allergies or infections can result from exposure to airborne microorganisms.
- Flu-like symptoms or headaches can result from low level exposure to carbon monoxide (CO); high CO levels can be deadly.

What are some adverse effects that can result from household exposures?

- Temporary reactions can arise many ways: ▪ A college student fainted while using a spray cleaner in a small unventilated bathroom. ▪ A student reported coughing and choking after using an aerosol spray near his face. ▪ An individual sneezes and tears up when walking through a store aisle lined with VOC-emitting products. ▪ Another temporary, but severe reaction occurred in a woman temporarily paralyzed after vigorously applying flea spray inside her home without adequate ventilation.
- Chronic, sometimes life-threatening, effects also occur. ▪ A woman, whose hobby was refinishing furniture, developed liver cirrhosis after using paint stripper in a closed room over several winter months. ▪ Over a four-month period, a man stripped lead paint from the interior of his old house without any protection. He developed an ongoing fever and other symptoms. Investigation revealed a blood lead level of 116 µg/100 ml, the highest ever seen in the US state of Maine.

Many reactions are not serious and quickly over. Or, as in the case of the persons overexposed to flea killer, paint stripper, and leaded paint, reactions were severe. Some people live miserable lives due to a syndrome called Multiple Chemical Sensitivity. These individuals are hyper-sensitive to VOC odors. Others are equally miserable from the emissions of molds growing in the home.

Reducing indoor air pollution⁶

Precautionary steps to protect one's home against harmful emissions follow.

- Products Become aware of products emitting VOCs or other pollutants. Unless their use is necessary, consider eliminating them, i.e., practice source reduction (P²).
- Mold⁷ One major P² step is to assure that your home does not develop long-lasting wet spots. These promote mold growth, which release VOCs and spores that promote and aggravate allergies. Occasionally, reactions to mold toxins are deadly. Mold grows in moist basements, but no place is immune. In bathrooms and other often-moist places, install fans and vent them to the outside.
- Ventilation⁸ Because you cannot eliminate every source likely to affect indoor air quality, your home needs good ventilation. Make sure your stove has an exhaust fan vented to the outside. In a modern tight home, install an air-to-air heat exchanger to provide ventilation

⁶ Links to a number of useful sites: A list of indoor air quality (IAQ) and IAQ-related resources. *Hygenair*, 2001, <http://www.hygenaire.com/Indoor%20Air%20Quality%20Publications.htm>.

⁷ (1) Mold resources. *US EPA*, September 18, 2008, <http://www.epa.gov/mold/moldresources.html>. (2) Mold. *CDC*, <http://www.cdc.gov/mold/faqs.htm>. (3) Mold, questions and answers. *US CDC*, November, 2004, <http://www.cdc.gov/mold/pdfs/stachy.pdf>.

⁸ Ventilation and indoor air quality. *Alliance for healthy homes*, http://www.afhh.org/dah/dah_ventilation.htm.

with minimum heat loss. Someone coined a phrase to emphasize the need for both energy conservation and good ventilation: “Seal tight, ventilate right.” Electronic air cleaners and high efficiency particulate air (HEPA) filters work by trapping dust, fibers, pollens, skin flakes, and pet dander. But filters do not trap VOCs. Filters also need to be regularly changed.

- Other steps are noted below for specific groups of indoor air pollutants.

Combustion pollutants

Almost all homes use combustion appliances such as furnaces, stoves, fireplaces, gas-burning appliances, or kerosene heaters, and many homes have smokers. In less-developed countries, cooking and heating fires may be built inside the home with little ventilation.

Combustion pollutants and sources

- Carbon monoxide⁹ In enclosed spaces CO causes hundreds of deaths in the United States each year. Lower levels of this colorless odorless gas can lead to headaches, dizziness, nausea, and flu-like symptoms. The US Consumer Product Safety Commission (CPSC) recommends that households install CO detectors that will sound an alarm if CO reaches unsafe levels. To largely eliminate CO emissions, combustion appliances need good maintenance. This is true of all types of stoves and furnaces and of fireplaces, and chimneys, and their connections. Kerosene heaters should be vented outdoors. Also vent stove hoods to the outside and install appliances according to the manufacturer’s instructions. Don’t leave a fire smoldering in a fireplace; if a fire is still burning, close it off from the room (Figure 17.2).
- Nitrogen oxides¹⁰ Efficient burning is typically desirable except that a very hot flame promotes reactions between atmospheric nitrogen and oxygen to produce NO_x. These can irritate eyes, nose, and throat, increase asthma attacks and susceptibility to infection. NO_x sometimes reach significant levels in homes with a gas stove or dryer or a kerosene heater.
- Particulates Wood-burning stoves and fireplaces are a major source of particulates to indoor air. This is true anywhere, but much more so in the homes of hundreds of millions of the world’s impoverished people who burn biomass such as wood indoors. There concentrations are often so high that millions of deaths a year are attributed to them.

Other sources of combustion pollutants¹¹

- Environmental Tobacco Smoke (ETS) When present ETS poses serious environmental health risks. Burning tobacco emits particulates and hundreds of chemicals, including

⁹ Carbon monoxide, questions and answers (#466CPSD). *Consumer Product Safety Commission*, September, 2008, <http://www.cpsc.gov/CPSCPUB/PUBS/466.html>.

¹⁰ ToxFAQ™ for nitrogen oxides. *ATSDR*, April, 2002, <http://www.atsdr.cdc.gov/tfacts175.html>.

¹¹ Diseases A-Z. *American Lung Association*, 2008, <http://www.lungusa.org/diseases/>.

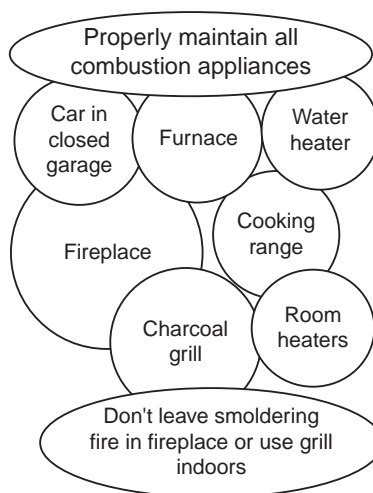


Figure 17.2

Sources of and potential sources of carbon monoxide

CO, benzene, formaldehyde, cadmium, lead, arsenic, even tiny amounts of dioxins. Especially in enclosed spaces, levels of combustion products build up. Children living in homes with smokers often develop respiratory problems or such problems may worsen. Smokers also run the risk of lung cancer, and severe pulmonary and heart disease. The association of ETS with heart diseases results from the CO in smoke. Inhaled CO deprives the body, including the heart of oxygen. A cigarette left smoldering produces more CO than one being smoked.

- **Wood-burning stoves and fireplaces** Fires are lovely, but they emit VOCs, CO, and NO_x, and can be large sources of particulates including PAHs. Many are very-fine particulates, which can be breathed deeply into the lungs. Particulates contribute to or cause respiratory diseases, and sometimes, infections. They can irritate the eyes, nose, and throat. Very efficient, but costly stoves and fireplaces exist, which greatly reduce emissions.
- **Garages** Homes with garages attached to or under them, expose occupants to combustion products from the exhausts of automobiles, lawnmowers, and other internal combustion engines. In addition to CO, much of the benzene in indoor air is traced to attached garages. Car exhaust, stoves, and furnaces also emit formaldehyde.

Volatile organic chemicals (VOCs)

VOC sources are almost ubiquitous

- Many building materials, furnishings, and often new clothing emit VOCs.
- Paints, stains, paint thinners and strippers, varnishes, and turpentine emit VOCs. *When paint is in use*, it is the major emitter of VOCs in indoor air. This was a greater problem when oil-based paints were often used indoors, but water-based paints are now more common.

- Pesticides, if not volatile themselves, can volatilize when discharged in aerosol sprays. Certain solid pesticides such as naphthalene in moth balls also slowly volatilize.
- Floor and furniture polishes and some waxes emit VOCs, as do many home cleaning products, and many personal care products such as nail polish, nail polish removers, and hair sprays. Home products containing chemicals from petroleum emit VOCs.
- Art and craft materials, glues, paints, etc. emit VOCs. Hobbies that generate pollutants, sometimes in significant amounts include model building, photography, ceramics, painting, jewelry making, metal- and stained-glass working, and pottery making. Some of these activities generate metal fumes too. Woodworking generates enough VOCs and particulates that some individuals are forced to give up this activity. See Box 17.1.
- Aerosol sprays emit VOCs and tiny particulates. Hand-pump sprays are a lesser problem.

Box 17.1**Some pollutants are difficult to avoid**

We can avoid many VOCs and hazardous chemicals by shunning products that contain them, but some are too prevalent to totally avoid. As you read about the chemicals below, recall that “the dose makes the poison,” and that exposures are often low. However, if a product is thoughtlessly used, air concentrations can rapidly increase as happened with the girl who vigorously sprayed a cleanser into the air of a tiny closed bathroom. And, some people are exceptionally sensitive. A third consideration is that we are typically exposed to mixtures of chemicals, not just one; this makes it hard to assess the impact.

- *Polycyclic aromatic hydrocarbons (PAHs)*¹² are a family of more than a hundred chemicals. See Box 5.7. They occur naturally in petroleum, but our major exposure to PAHs is from combustion: they are products of incomplete combustion. Soot from wood stoves and fireplaces contain PAHs. Kerosene stoves can be sources too. Smokers can produce large amounts. One PAH, benzo[*a*]pyrene (BaP) is a potent carcinogen; other PAHs are mutagens. With combustion so prevalent, we cannot totally avoid these contaminants in our air, food, and water. Even browned foods and toast contain tiny quantities, and charbroiled foods have larger amounts. PAHs are common contaminants in carpets. Two US EPA researchers pointed out that some urban infants are exposed to BaP the equivalent of smoking three cigarettes a day.
- *Formaldehyde*¹³ This small and volatile molecule, HCHO, can react with other chemicals, linking them into useful polymers. It is an exceptionally useful chemical used in and emitted by dozens of products including construction materials, resins and glues in pressed wood products (particleboard, fiberboard, and hardwood plywood), and sealants in floors and cabinets and other furniture. Drapes, wall coverings, and permanent-press clothing often also emit formaldehyde. Many cosmetics emit tiny amounts. Because of its high reactivity, HCHO also functions as a fungicide in latex paints and wallpaper. Unfortunately, the same property that makes formaldehyde so useful allows it to irritate the moist membranes in our

¹² ToxFAQs™ for polycyclic aromatic hydrocarbons (PAHs). ATSDR, October 11, 2007, <http://www.atsdr.cdc.gov/tfacts69.html>.

¹³ ToxFAQs for formaldehyde. ATSDR, June, 1999, <http://www.atsdr.cdc.gov/tfacts111.html>.

respiratory tract and eyes. Some individuals react severely. Fatigue and nausea are among possible symptoms. Others develop an allergy and become sensitive to even tiny amounts of formaldehyde.¹⁴ For especially sensitive individuals, formaldehyde home monitors are available. • When formaldehyde reacts to form polymers it becomes an integral part of the product. The problem arises because a portion of the formaldehyde did not react and become part of the polymer. This escapes into air. Some products, plywood, particleboard (found in cabinets and other furniture) and sub-flooring can continue emitting HCHO for months after installation, or for weeks for plastic-laminate counters. New carpets are no longer a HCHO source. When possible, do remodeling and install new furnishings in the summer when windows can be open. Wash wrinkle-resistant clothing before wearing them. Clean permanent-press drapes before installation or at least install them with plenty of ventilation. (A new method to make wrinkle-free fabrics without formaldehyde was recently reported. This is an example of “green chemistry,” of design for the environment.) Formaldehyde emissions from many building products have been reduced in recent years. Ask for low-formaldehyde emitters when you buy building products.

- *Benzene*¹⁵ occurs naturally in petroleum. As with formaldehyde, benzene is almost ubiquitous. Vapor traps protect us from benzene and other VOCs as we pump gasoline, but benzene is in motor-vehicle exhausts too. Benzene was added to gasoline as an anti-knock agent years ago to replace lead. However, because of benzene’s toxicity, the amount in gasoline was lowered. At levels once found in certain occupational settings benzene was associated with leukemia and aplastic anemia. Smokers are exposed to benzene too, but at considerably lower levels than industrial workers once were. Non-smokers are exposed to lower levels still. Still, benzene in indoor air may be three times higher than outdoors. It is found in small amounts in fumes evaporating from glues, paints, furniture wax, detergents, nail polish, and remover. Wood-burning stoves and fireplaces are sources. Garages attached to homes allow gasoline fumes to seep inside. Stored paints, incompletely sealed, and stored products containing gasoline are sources too. Although benzene levels in homes are typically small, regulatory agencies treat exposure to a cancer-causing substance at any level greater than zero as posing some risk. But tiny amounts of benzene are naturally present in water and in foods such as nuts, fruit, vegetables, and dairy products.
- *Tetrachloroethylene*¹⁶ (perchloroethylene) or PERC is another ongoing, albeit small exposure for individuals wearing dry-cleaned clothing. At high doses it is a carcinogen in experimental animals. Among humans, drycleaners have the highest exposures. People living in buildings with dry-cleaning facilities can have quite high exposures too. Wearing dry-cleaned clothing or entering closets containing them involves some exposure. Compared to earlier years, less PERC remains in dry-cleaned clothing. Reduce it further by airing dry-cleaned clothing before wearing. Some dry-cleaners are using alternative cleaners, and PERC use is expected to decrease.

¹⁴ We don’t develop allergies to molecules as tiny as formaldehyde, but formaldehyde reacts with proteins in the body. The formaldehyde-linked proteins can lead to allergic reactions. At high levels (not found in homes), formaldehyde causes nasal cancer in rodents. Even formaldehyde levels in our homes present a hypothetical risk of cancer.

¹⁵ ToxFAQsTM for benzene. *ATSDR*, August, 2007, <http://www.atsdr.cdc.gov/tfacts3.html>.

¹⁶ ToxFAQsTM for tetrachloroethylene. *ATSDR*, September, 1997, <http://www.atsdr.cdc.gov/tfacts18.html>.

- *Paradichlorobenzene*¹⁷ is added to stored clothing and other fabrics to repel moths. It is also found in some toilet disinfectants, deodorizers, and air “fresheners.” Like the chemicals mentioned above it too is an animal carcinogen at high doses. Almost all exposure to paradichlorobenzene occurs indoors. Of 1000 Americans selected at random, more than 95% had detectable levels in their urine or blood. ▪ Depending on the brand of air freshener, other ingredients are present too such as camphor, alcohol, or the lemony-smelling limonene. As the University of California *Wellness Letter* points out, “a product label may say “natural, but natural doesn’t necessarily mean you want it in your home.” Disperse unwanted odors by increasing home ventilation, or sprinkling baking soda in areas needing odor control.
- *Other indoor pollutants* The chemicals discussed here are among well studied indoor contaminants. Currently, phthalates, commonly used as plasticizers in consumer products are among the chemicals being more carefully examined as indoor air pollutants. Because phthalates are not chemically bound to the matrix of a product, they volatilize into air and house dust. They have been found in home air at levels as much as 10-fold higher than PAHs. House dust could be a large source of phthalate exposure to children. Finding detectable amounts of phthalates in indoor air does not necessarily indicate a problem. The concern is that so many substances are found, which raises the topic of chemical mixtures.

Does the impact of a mixture differ from that of a lone chemical?

In one study scientists studied people’s reactions to VOCs in the air they were breathing. They started testing one chemical at a time. They looked for the concentration of each chemical that caused objectively measurable amounts of eye or nasal irritation. Subsequently, they tested the chemicals again, but in mixtures. With mixtures, irritations were more likely to occur. More investigations are needed because it is to mixtures that we are most often exposed. ▪ But notice that the concentrations studied were high enough to actually cause irritation. In homes, contaminant concentrations are likely lower or much lower. Still, the conclusion holds that it is prudent to be aware of VOCs: don’t use more than necessary, and use them with care. See Chapter 3.

Advice

Don’t try to remember each product that emits VOCs. Instead, remember that almost any consumer product *can* do so, and can pose a risk. Routinely read labels and follow instructions. If *danger* or *poison* is on the label, consider an alternative.

¹⁷ (1) IRIS Toxicological review and summary documents for 1,4-dichlorobenzene. *US EPA*, January 17, 2009, <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=155906>. (2) Moth balls (naphthalene and paradichlorobenzene). *NPIC*, no date, <http://npic.orst.edu/hottopic/mothball/health.html>. (3) Health effects document for naphthalene. *US EPA*, February, 2003, http://www.epa.gov/safewater/ccl/pdfs/reg_determine1/support_cc1_naphthalene_healtheffects.pdf.

Health effects of VOCs¹⁸

Some among many potential effects of VOCs were noted above.

Recommendations for reducing VOC emissions

- *Avoid* unneeded products.
- Maintain *good ventilation*.
- Read *labels*, not just for products known to be hazardous such as pesticides, but also of cleaning products, polishes and cosmetics.
- Use the *minimum amount* of a VOC-emitting product that will do the job.
- Ask for products with low VOC emissions such as low-formaldehyde emitting wood products.

EPA cannot regulate VOC-emitting products, but actively studies them, and works with manufacturers to make changes that would produce products with lower VOC emissions. Increasingly, paints have lower VOCs. As a means to pressure manufacturers to develop more such products, it is helpful for consumers to ask for them even if they are not now available. However, recall that consumers want products that do just as good a job as a high-emitting product.

Moisture

Chronic moisture is an enemy of human health, and also of the structural integrity of a house. Wetness supports mold and bacteria growth. Molds emit the bioaerosols and spores (which are particulates), and also emit VOCs detected as a moldy smell. Some mold aerosols contain highly-toxic *mycotoxins*. Mold emissions are at best only a nuisance, but at worst can cause or aggravate respiratory diseases and allergies, or result in infections. Mold infestations are often detected as a well-known “moldy” smell. If enough mold grows, it can be seen as well.¹⁹

Moisture Sources and Remediation

- Damp attics and basements When a cold wall exposed to moisture hits the dew point, moisture settles onto it, and it becomes a place for mold growth. A place that is warm as well as moist is especially attractive to microorganism growth. A device sold at hardware stores can measure indoor humidity.

¹⁸ Diseases A-Z. *American Lung Association*, 2008, <http://www.lungusa.org/diseases/>.

¹⁹ An estimated 25% of the world's biomass is in the fungal kingdom. This includes molds and other members of their family such as mildew. Outdoors, molds play the vital role of degrading organic matter. It is indoor growth that presents problems. Avoiding mold growth inside homes is worth the effort.

- Water-damaged areas of a house and water-damaged household items (carpets, furniture, papers, books) are all attractive to mold growth.
- Other sources include humidifiers, air conditioners, ventilation systems, and refrigerator drip pans. These all need to be maintained properly.
- Plants in the home can be healthful, but, kept too moist, they breed microbial growth. Changing plant soils frequently can minimize mold growth.

Recommended humidity levels are 30%–50% although some argue that anything over 30% encourages growth of undesired organisms. However, especially in summer, humidity may naturally be higher. ▀ Recommended actions: when indoor air is too dry in the winter or in desert homes, health specialists may recommend drinking more water rather than installing a humidifier. If you use a humidifier, choose one generating steam, not cold mist. If using a cold-mist, humidifier, use deionized water to avoid the mineral particulates that tap water can generate. Regularly clean humidifiers and dehumidifiers. Make sure that wet places do not persist in the home. ▀ Diluted bleach can be used to clean bathrooms contaminated with mold, but damaged furnishings often cannot easily be cleaned, and may need to be discarded. ▀ As with indoor VOCs, always maintain good ventilation. A particulate-trapping air purifier can remove mold spores.

Biological pollutants

The molds just described are biological contaminants and produce air-borne contaminants such as spores. However, the word biological goes beyond microbes. Biological pollutants include pollens, animal dander, dust mites and their feces, cockroaches and their feces, cat saliva, rodent urine, i.e., a great many biological substances can become contaminants of indoor air. Almost any of these can cause or enhance allergies. Airborne microbes need not be dead to cause reactions. Bits of dead cockroaches or plants can also be allergenic. About 15% of people are allergic to dust mite feces. Dust mite and cockroach exposure is associated with an increased likelihood of asthma. Some microbes cause infectious diseases.

Sources and remediation

- Sources of molds were discussed above. Other sources of biological contaminants are carpets, mattresses, and other bedding, which often harbor dust mites. Pollens are contaminants originating outdoors that enter the home with outside air or carried in on pets. Animal dander and cat saliva obviously come from pets; after they dry, the particles can also become airborne. Cockroaches find their way inside especially in warm regions. Their body parts and feces can enter a home's dust.
- Prevention and remediation strategies include maintaining a home without food particles that attract cockroaches. Seal cracks that allow entry to cockroaches, ants, and other insects. Maintain clean carpets or even eliminate carpets; use wood flooring or washable

throw rugs instead. Allergic people must sometimes avoid pets. There are ways for sensitive individuals to allergy-proof a home; the internet, libraries and bookstores, and physicians are sources of information.

Dust and dirt

A US EPA study provided the interesting information that – like the Peanuts cartoon character *Pig-Pen* – each of us moves about in a cloud of tiny particles. These are released from clothing, carpets, furniture, and other items, stirred up as we move around or when cooking. Almost any contaminant capable of becoming airborne – molds, bacteria, pesticide residues, leaded dust, or anything tracked in with dirt on shoes – can become associated with dust particles. These also deposit onto carpets and furniture. Carpets can be almost impossible to keep completely clean. Vacuuming carpets or sweeping wood floors gives rise to airborne dust. To lessen dust, damp mop the floor before sweeping. Plants, artificial flowers, and dried arrangements are truly dust catchers. Get in the habit of leaving shoes in the entry way.

Radon²⁰

Radon (radon-222 or ^{222}Rn), is a natural radioactive gas found outdoors and indoors. Its ultimate source is *uranium* (uranium-238 or ^{238}U),²¹ which is naturally found in soil and rocks throughout the world. ^{238}U goes through a series of decay reactions to form ^{222}Rn (Figure 17.3). As a gas, radon makes its way to the surface as it is formed or into underground water where part dissolves. If radon surfaces outside, it dissipates into the atmosphere. However, if it surfaces beneath a house or other building, it seeps through openings into indoor air. There, unless ventilation is very good, its concentration builds up especially when it surfaces in basements. Radon in schools can be a concern. Trailers do not contact the earth and don't have radon. Radon levels in outdoor air range from 0.1–0.4 pCi/l (pCi picocurie, a unit of radioactivity). An average home has over 1 pCi/l in its air, and even 1 pCi/l is equivalent to about 50 chest X-rays a year. In the United States, the *action level* is 4 pCi/l: if a home's radon level is 4 pCi/l or higher, EPA recommends taking action to lower it.²² An estimated 6–8 million American homes have more than 4 pCi/l. Canada's action level is 20 pCi/l. Action levels for the UK and Germany are between 3 and 10 pCi/l. See Boxes 17.2 and 17.3.

²⁰ A citizen's guide to radon. *US EPA*, September 9, 2008, <http://www.epa.gov/radon/pubs/citguide.html>.

²¹ Radon also results from the radioactive decay of thorium, found naturally in rock, soil, and water. Thorium decays by a path that is different than that of uranium.

²² This does not mean that radon levels below 4 pCi/l are safe. As is the case for carcinogenic chemicals, any exposure to ionizing radiation greater than zero may pose some risk. Thus, even small amounts of radon may pose a small risk.

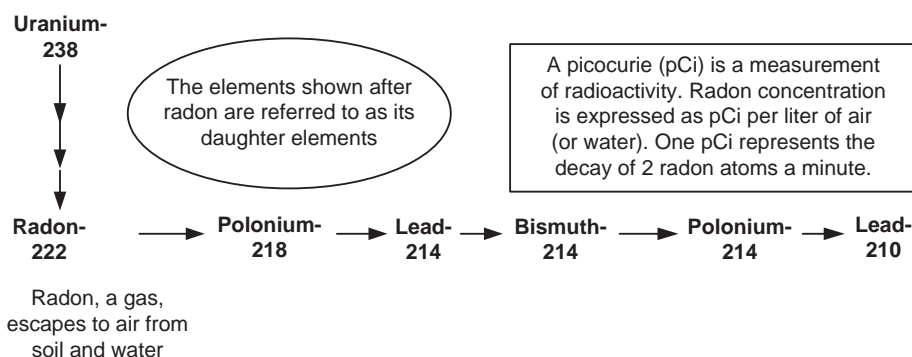


Figure 17.3

Decay of Radon-222

Box 17.2

Sources of exposure to ionizing radiation²³

Natural sources About 82% of the average American's exposure to ionizing radiation is from natural sources (Figure 17.4).

- Radon is responsible for about 55% of total exposure. The actual percentage varies among individuals depending upon the radon level in the surrounding environment.
- Within our own bodies are radioisotopes that provide another 11% of exposure, especially ¹⁴C (*carbon-14*) and ⁴⁰K (*potassium-40*), which find their way into air we breathe and the water and food we ingest. An estimated 1 in every 10 000 potassium atoms in our bodies is radioactive.
- Terrestrial sources, rocks and soils, provide another 8%. Uranium-238 is the largest terrestrial source. *Thorium-232* and *potassium-40* contribute lesser amounts.
- Another 8% is from cosmic rays (electrons, protons, gamma rays, and X-rays entering the Earth's atmosphere from space²⁴). About 300 cosmic rays per second pass through a person living at sea level. This doubles at a 6000 ft (1829 m) elevation; aircraft crews and passengers experience higher still.

Even homes with average radon levels engender interesting comparisons. Because of radon, the average nuclear plant worker goes home to higher levels of radioactivity than experienced at work. Indeed, radon first received major attention in 1984 when engineer Stanley Watras, set off an alarm at a nuclear power plant in Pennsylvania – he was radioactive. Investigation revealed the source was his home, which had 4400 pCi/l radon in his cellar, 3200 in the living room and 1800 pCi/l in the bedrooms – thousands of times greater than an

²³ Sources of ionizing radiation. *National Safety Council*, March 25, 2002, <http://www.nsc.org/resources/issues/rad/ionize.aspx>.

²⁴ Cosmic rays react with elements in the Earth's atmosphere to form ¹⁴C and ³H. ¹⁴C and ³H settle to earth and find their way into plants and animals. ¹⁴C dating is often used to determine the age of once-living plants and animals.

average home. Nonetheless, it was possible to remediate the home and the Watras family moved back into it.²⁵

Anthropogenic sources represent 18–19% of total exposure.

- About 15% comes from medical diagnostic procedures, especially X-rays (chest and dental exams and mammograms).
- Another 3% arises from building materials and consumer products including color TVs and smoke detectors.
- The other 1% results from occupational exposure, nuclear fallout, and nuclear power.

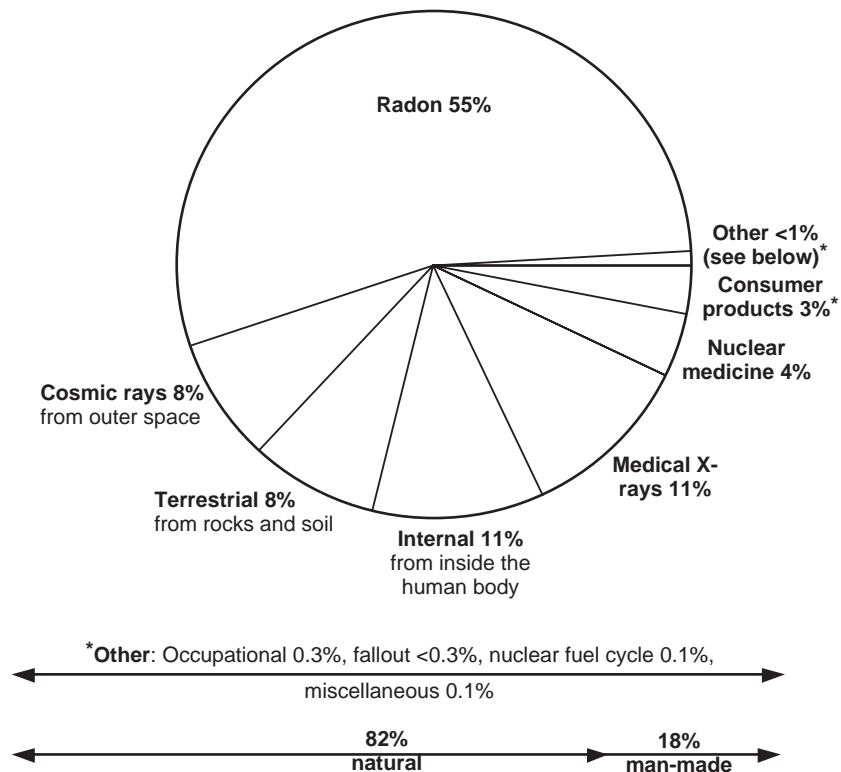


Figure 17.4 Sources of exposure to ionizing radiation to US population. Source: National Council on Radiation Protection and Measurements

²⁵ Materials from the Earth also contain radioisotopes. Coal is one. As it burns, radioactive elements escape into the atmosphere. Residents near a coal-burning power plant have higher exposure to radioactivity than do those living near nuclear-power plants, where emissions are more tightly controlled. Steam from geothermal energy also contains radioactive substances. Phosphate rock, used in fertilizers, contains higher levels of uranium than does surface soil. Groundwater contains higher levels of radioactivity than surface water.

Why radon concerns us²⁶

As a radioisotope decays, it emits *ionizing radiation*²⁷ – an alpha particle, a beta particle, or gamma rays. Any of these can ionize the atoms that they hit by stripping electrons from them. In living tissue, this may damage the genetic material, DNA. The *half-life* of a radioisotope indicates how long it takes for one-half of its atoms to undergo decay. Radon-222 has a half-life of 3.8 days, so the average radon atom breathed into the lungs is breathed out again before it decays. The major problem is not radon-222 itself, but its solid radioactive daughter elements of which *polonium-218* is one; it results from the decay of radon-222 ($^{222}\text{Rn} \rightarrow ^{218}\text{Po} + \text{alpha particle}$). Because polonium-218 and *polonium-214* are solids they can attach to dust particles in the air. Unlike inhaling a gas, if the dust is inhaled, it can deposit onto airway walls and sometimes reside long enough to decay. The solid daughters, polonium-218 and polonium-214 have half-lives of 3 minutes and less than 1 second, respectively. They can decay in the lung emitting alpha particles, which can damage the DNA in dividing lung cells. Cells repair such damage, but not always. When not repaired, cancer can result. Approximately 150 000 lung cancer deaths occur each year in the United States. Radon exposure accounts for an estimated 18 000 of these. *But* it is smokers and people in homes with smokers who bear the brunt of the risk. This is because the radon daughters (^{218}Po and ^{214}Po) attach to tobacco particles, which can be inhaled into the lungs and trapped. See *A citizen's guide to radon*.²⁸

Detecting and reducing radon

In air

- **Testing** A test kit, typically a canister of activated charcoal is left open to the air for 2–7 days, usually in the basement. It is then sealed, and mailed to a laboratory. After analysis, results are sent to the homeowner. If the reading is high, result needs to be confirmed through a longer term test. Some states require radon testing before a home is sold. ■ A number of factors affect radon concentration in indoor air. Levels are lower in summer, when a house is more open, so testing is done in winter to find the highest levels.
- **Reducing radon** Levels can sometimes be much reduced simply by sealing openings in basement floors. Or radon can be diverted through a pipe installed below the basement, which extends up the house walls and vents to the outside with the help of a suction fan. For new homes, the EPA encourages preventive action upfront by installing a diversion system, especially in locales with high potential for radon.

In water

A second source of radon in the home is *well water*, especially water from a deep well. Municipal tap water typically has lower levels even if its source is groundwater. This is true

²⁶ ToxFAQs™ for radon. *ATSDR*, September, 2008, <http://www.atsdr.cdc.gov/tfacts145.html>.

²⁷ ToxFAQs™ for ionizing radiation. *ATSDR*, June, 1999, <http://www.atsdr.cdc.gov/tfacts149.html>.

²⁸ A citizen's guide to radon. *US EPA*, March 26, 2009, <http://www.epa.gov/radon/pubs/citguide.html>.

because radon escapes into the air during processing. Showering and other uses of water in a home allow radon to escape into indoor air. However, only about 1 in 10 000 molecules in water escapes. This amounts to only 1–2% of the total radon in a home's air.²⁹ There is a circumstance in which radon from water can be meaningful: radon can build to high levels in a closed bathroom during showering, but the exposure time is short. Despite the small amount, risk assessment estimates that radon escaping from water may cause 160 lung-cancer deaths a year, about 1% of the lung cancers attributed to radon in air. Also, people who drink water with high radon levels run a slightly greater risk of stomach cancer. An estimated 20 out of 13 000 stomach-cancer deaths in the United States each year may be due to radon in drinking water. ▪ However, the greatest risk by far is from radon seeping from the ground into indoor air. And smokers and their families bear a disproportionate amount of that risk.

Box 17.3

Radon and scientific uncertainty

What could be less controversial than urging people to measure radon levels in their home and to remediate high levels? Scientific groups including a National Academy of Sciences panel agreed that radon causes lung cancer in humans. Moreover, unlike most other carcinogens, for which only animal data is available, we have human information for radon. The association between radon and lung cancer is clear in miners exposed to high radon levels. However, it is difficult to make extrapolations from underground mines to home environments: the association was made by studying miners who worked before the introduction of modern ventilation in mines, most of whom also smoked. The mines also contained radon levels hundreds or thousands of times higher than those in most homes. They were also extremely dusty. Some scientists doubt that lung cancer deaths among such workers can be extrapolated to the conditions of average homes. However, most of these scientists do believe that levels two to four times higher than the EPA's action level of 4 pCi/L can cause cancer. Their caution relates to saying the same about low exposures.

Many studies have examined possible relationships between radon levels in homes and lung cancer incidence. Three studies reported in late 2008 found little evidence of a correlation.³⁰ One conclusion where there *is* widespread agreement is that smokers and those that live with them bear most of the radon risk. Assuming this is true some argue that the EPA should concern itself only with finding homes with much higher radon levels than 4 pCi/l where even non-smokers could be at risk, at least 20 pCi/l of radon. This is an estimated

²⁹ EPA once proposed a maximum contaminant level (MCL) for radon in water of 300 pCi/l. This would have required municipalities having radon levels higher than 300 in their water supplies to reduce them. EPA dropped the proposed MCL, but this represents an interesting case: EPA estimated that an additional 160 lung-cancer deaths per year in the US result from radon that has escaped into air from water. *This risk is greater than that for any other contaminant in the water supply that is regulated by EPA.* Some expressed concern that if we do not regulate radon then industry could claim that, because the pollutants it releases into water present a smaller risk than radon they should not be regulated either. Others countered that society has the right to expect industrial emissions to be more strictly controlled than natural ones.

³⁰ Leary, W. E. Studies raise doubts about need to lower home radon levels. *New York Times*, January 17, 2009, <http://query.nytimes.com/gst/fullpage.html?res=9C00E4DF1038F935A3575AC0A962958260&sec=health&spn=&pagewanted=2>.

50 000 homes in the United States. However, the EPA reminds skeptics that no amount of ionizing radiation is free of risk, and that about 700 deaths a year in the United States are attributed to even the low levels of radon in outside air.³¹ Moreover, some researchers state that “there is no evidence of a threshold below which any exposure would not increase risk.”

Questions 17.1

1. Explain why you are or are not personally concerned about radon.
2. Before buying a home, will you ask that it be tested for radon? Explain.
3. What level would radon have to be in your home before you would voluntarily remediate your home? Explain.
4. (a) If small children lived in the home, would you be comfortable if they regularly played in a basement not tested for radon? (b) If the children only occasionally played there, would that affect your concern?

Indoor air of less-developed countries

The problems

For hundreds of millions of people in less-developed countries as far apart as Bolivia, Kenya, and China, indoor air is a major health risk. The worst offender is smoke. Fuel is often burned inside homes without ventilation especially in cold weather without venting smoke to the outside. Those suffering the greatest exposures to particulates and other combustion pollutants are women as they cook, and their children. Not surprisingly, respiratory diseases are commonplace, often severe. Worldwide, acute respiratory disease causes millions of deaths in children under five each year. ▪ People burn wood, straw, or dried manure, although rural Chinese most often burn coal.³² These fuels are often used for heating too, so adult males are also affected. Chronic bronchitis is common among all adults. In the winter months, when indoor stoves are used for heating as well as cooking, carbon monoxide poisoning is common. ▪ In China where about 800 million people burn coal, problems of contaminants from coal can be serious:³³ some coals burned are as high as

³¹ Recall that for chemicals, an increasing dose has an increasing effect. This holds for radioactivity too. In the mid-1990s investigators reanalyzed lung cancer deaths among uranium miners exposed to radon, pooling data from 11 studies covering 2700 lung cancer deaths among 65 000 miners. They found that as the miners' exposure to radon increased, so did lung cancer. Their results suggested that even average home radon levels pose some risk. The study also found that long-term exposures to low doses of radiation – a condition similar to those found in homes – was more risky than short-term exposure to high doses. The authors understood the difficulty of extrapolating from conditions found in mines to those in homes, but still recommended remediation of homes with radon levels greater than EPA's action level of 4 pCi/l.

³² Hildebrandt, T. and Turner, J. L. Air pollution challenges rural China. *Wilson Center*, April 23, 2003, http://www.wilsoncenter.org/index.cfm?fuseaction=events.event_summary&event_id=28825.

³³ Hricko, A. Environmental problems behind the great wall. *Environmental Health Perspectives*, August 21, 1998, <http://ehp.niehs.nih.gov/docs/1994/102-2/focus.html>.

35 000 ppm arsenic and many are high in fluorine. Thousands have developed severe arsenic poisoning and millions fluorine poisoning. Other coals have toxic levels of elements such as mercury. Lung cancer rates are also very high.

Some solutions

Simple technologies can make a major difference.

- A cooperative project between Beijing's Chinese Academy of Preventive Medicine and the US EPA found that replacing poorly ventilated stoves with well-ventilated ones resulted in less soot and smoke in the air, and a dramatic reduction in lung cancer rates. ■ In Kenya, a project gave women stoves. Although simple in design, they burned more efficiently than traditional stoves, burning 40% less fuel and emitting much less smoke. Thus, respiratory health was improved *and* the women saved hours a day previously spent in collecting biomass fuel. At the same time scarce biomass such as wood was conserved.
- In China's Yunan Province the Nature Conservancy works with the Chinese government and villages to produce biogas (methane) from manure.³⁴ In the mountain village, Haixi, they set up a demonstration project: animal manure and human waste is loaded into a lined pit, and a greenhouse built over it. Heat generated from the digesting manure warms the greenhouse, which grows vegetables for villagers, *and* the fermenting manure emits methane, which is piped into an adjacent schoolhouse. Teachers previously cooked children's lunch over wood fires with not even windows open in this cold climate. Now they use a biogas stove with clean-burning methane. When the waste is no longer fermenting and producing methane, it is used as fertilizer. After this successful demonstration, individual villagers dug their own household fermentation pits, and were given help toward the \$170 cost. Over one year, one cow's manure provides the energy equivalent to 135 gallons (511 l) of gasoline. Some villagers still burn wood. These have been assisted with more energy-efficient stoves, which are vented to the outside. The project is spreading to other villages. With less need for wood, deforestation in the area is reduced as well as indoor air pollution.

SECTION II

Hazardous household products

About 1.5 million Americans visit hospital emergency rooms each year because of poisonings or possible poisonings. About 10% are admitted into the hospital. More than 80% of the cases are among children under 6 years old. These figures do not include the many people who react

³⁴ Gaetz, R. High energy on the edge of the Himalayas. *Nature Conservancy Magazine*, **52**(2), Summer, 2002; or see Smokeless in China. *Earth Report*, <http://www.tve.org/earthreport/archive/doc.cfm?aid=1544>

to hazardous products such as pesticides, solvents, ammonia, or chlorine, but do not report them. In addition to poisonings, some exposures result in injuries to the skin and eyes.

How household products concern us

The words, *toxic*, *corrosive*, *flammable*, and *reactive* were introduced in Chapter 12 to describe characteristics of industrial hazardous waste. Some products used in the home have the same characteristics. A useful web site is Hazardous Substance Information and Education Office, State of Washington.³⁵

Corrosive products

These can directly damage (corrode) skin, eyes, or mouth. Examples are products containing alkali (lye) such as drain openers or oven cleaners. Corrosive products often have the word *poison* on the label and the word, *danger*. Emergency room visits for treatment of skin or eye injuries resulting from improper use of corrosives are common. ■ Diluted with water, a corrosive substance may only be an *irritant*. A much-diluted corrosive may not present a hazard. Although an irritant is less dangerous for most people, it may cause skin redness, itching, or rashes. Cleaners, cosmetics, metals, and polishes are sometimes irritants. ■ An irritant is a greater problem for a person who becomes *sensitized* to it, where repeated use leads to more severe reactions. Since latex gloves have come into common use, many people have become sensitized to latex.

Toxic products

Household products can be toxic. Because all substances are toxic in high doses, treat all products thoughtfully including vitamins, minerals, aspirin, and laxatives. This is especially important if children are in the home. However, only a few household products are legally poisons, and they are clearly labeled. They include oxalic acid, found in a few cleaning products, and methanol, found in windshield washing fluids. Most pesticides³⁶ available to householders are less toxic than those used by professional applicators and are not considered poisons. Nonetheless, home pesticide poisonings occur,³⁷ and children are particularly vulnerable. ■ Toxicity information on the label³⁸ refers to acute toxicity, an adverse health effect occurring soon after exposure. The label does not – often cannot – provide information on chronic toxicity. Significantly, although home-use pesticides may be relatively safe for humans, creatures including some birds, earthworms, or bees can be poisoned.

³⁵ Shoppers' guide: toxic free tips. Hazardous Substance Information and Education Office, State of Washington, no date, <http://www.ecy.wa.gov/toxicfreetips/shoppersguide.html>.

³⁶ An introduction to indoor air quality, pesticides. *US EPA*, November 25, 2008, <http://www.epa.gov/iaq/pesticid.html>.

³⁷ (1) Pesticides: read the label first. *US EPA*, November 7, 2008, <http://www.epa.gov/pesticides/label/>. (2) Pesticide poisoning first aid. *About.com*, 2009, http://firstaid.about.com/od/poisons/qt/07_pesticides.htm.

³⁸ Signal word, toxic fact sheet (answering questions about pesticides). *NPIC*, July, 2008, <http://npic.orst.edu/factsheets/signalwords.pdf>.

Flammable products

A flammable product can catch on fire easily. Household products that contain petroleum distillates are flammable. Examples are oil-based paints, paint thinners, paint strippers, certain furniture and floor polishes, and some rug cleaners. Products that contain organic solvents are often flammable, and many aerosol sprays use flammable hydrocarbons as propellants. A *combustible* substance is similar to a *flammable* one except that it does not as readily catch on fire.

Reactive products

Well-known reactive substances are dynamite, gun powder, and firecrackers. Certain household products are reactive too: dry or liquid bleaches that contain chlorine will, mixed with household ammonia give off highly irritating and toxic fumes. Even some dish-washing detergents contain ammonia and should not be mixed with chlorine-containing products. ■ Chlorine also reacts with acid-containing products such as some toilet and tile cleaners. ■ A general rule is, don't mix any chemical products. Overheated or accidentally punctured aerosol cans may be reactive in a different way, they may explode.

No radioactive products

TV sets emit small amounts of ionizing radiation. Other materials that emit higher than background levels of ionizing radiation are building materials coming from the earth: granite and other rocks, and soil. We do not ordinarily find radioactive substances in the items around us except for tiny amounts in some smoke detectors, exit signs, and Coleman lamp mantles. Our exposure to radioactive substances or ionizing radiation is almost all from natural sources, or from medical procedures (Figure 17.4).

Some products have more than one hazard

A product may have more than one hazard. A prominent example is gasoline. It is flammable and explosive, its fumes are toxic, and it is a skin irritant. Young people who inhale gasoline fumes for a "high" can be poisoned or killed by this practice. Another hazard is accidentally aspirating gasoline into the lungs when (unwisely) sucking it from a motor vehicle's fuel tank. Even small amounts in the lungs can be disabling. These same hazards are present in other products that contain petroleum distillates or organic solvents.

Labeling laws

At the beginning of the twentieth century, perhaps 500 American children a year, mostly under age five reportedly died in accidental home poisonings. Thousands more were burned by the lye (caustic) used to make household soap. This situation changed in 1927 after Congress passed the *Caustic Poison Act* requiring that containers of caustic be labeled. In

1960, the *Hazardous Substances Labeling Act* was passed, a law applying to *all* hazardous products sold to householders. Finally in 1970, the *Poison Prevention Act*, requiring child-proof containers for certain hazardous substances became law. In 2002, although the US population has greatly increased, many fewer children die from poisoning. But we still purchase products containing hazardous ingredients from grocery, hardware, discount, craft and hobby, agricultural product, and drug stores. Information required on product labels follows.

- One or more signal words, *poison*, *danger*, *warning*, or *caution*.
- Principal hazard flammable, harmful or fatal if swallowed, skin and eye irritant, or vapor harmful
- The common or chemical name of the hazardous ingredients.
- The name and address of the product's manufacturer or distributor.
- Statement Keep out of reach of children, or equivalent statement.
- Precautionary measures instructions for safe use of the product.
- First-aid instructions are often on the label, but may be inadequate. Call a poison control center if an accident occurs, 1-800-222-1222.³⁹

Read the label

Look for signal words on a product's label (*poison*, *danger*, *warning*, *caution*). Take special note of the word *poison* or *danger*. *Poison* indicates the greatest level of toxicity whereas *danger* may refer to a corrosive, flammable, reactive, or toxic substance. The US EPA has a *Read the Label First* campaign (Figure 17.5) to promote safe use of pesticides and other products.

- *Caution* indicates a low-hazard product. Detergents commonly have the signal word *caution* on the label, but still lead to home poisoning incidents especially with small children. Fortunately, taste and low toxicity prevents most incidents from being serious. Liquid household cleansers often give off VOCs, enough to lead to adverse reactions if too heavily applied in a closed space.



Figure 17.5

Read Product Labels. Credit: US EPA

³⁹ American Association of Poison Control Centers, March 27, 2009, <http://www.aapcc.org/DNN/>.

- Labels on pesticides are covered by the Federal Insecticide Fungicide and Rodenticide Act, FIFRA, not the Hazardous Substances Labeling Act. For pesticides, *poison* indicates the most toxic product, *warning* refers to medium toxicity, and *caution* to the least.
- *Active ingredients* are those that carry out the function that the product is designed to do. Its *inert* ingredients carry the active ingredient, or make it easy to apply. However, some inert chemicals are hazardous too.
- Sometimes the word *nontoxic* is found on a label, which has no legal meaning. Any substance can be toxic in high enough doses. Nonetheless, a product labeled nontoxic is probably less toxic. Otherwise, a signal word would be on the label.
- A petroleum distillate contains chemicals produced during petroleum cracking. The term *petroleum distillates* is generic as is *organic solvent*. It may refer to acetone, isopropyl alcohol, methylene chloride, or another solvent.

Reducing exposure to hazardous products

Toxics use reduction (TUR)

- TUR is P² that refers to reducing exposure to hazardous substances by eliminating or reducing their use. To protect yourself: read and follow directions on the label. Minimize use of especially hazardous products. If you need to use a hazardous product, then handle it in a way to *minimize exposure*.
 - Use *minimum amount* necessary to do the job.
 - *Always* keep products in original containers, even if only adults are around.
 - Use plentiful ventilation.
 - Do not use aerosol products in closed rooms. That includes latex paint.
 - Use exhaust fan to remove fumes from petroleum-based products (paints, shellacs, etc.).
 - Wait for summer to strip paint from furniture, and do it outside.
 - Get in the habit of using gloves and safety glasses.
 - Don't mix chemical products; in particular, never mix bleach and ammonia.
 - Keep products away from children, including detergents, and vitamin and mineral supplements.

Alternatives

Alternatives are usually available for products with the signal word *danger* or *poison*. For children, buy glue with the word *nontoxic* on the label. For paint, use water-based (latex) rather than oil-based paint when possible. A number of web sites give simple recipes for alternative cleaners and insecticides, etc.⁴⁰ The National Geographic's *Green Guide* has a particularly useful site for do-it-yourself cleaning recipes.⁴¹

⁴⁰ See: ToxicFreeTips for household cleaners. Washington State, 2, <http://www.ecy.wa.gov/toxicfreetips/0804011TFTHouseholdCleaners.pdf>.

⁴¹ McRandle, P. DIY Household Cleaners. *Green Guide*. National Geographic, May 3, 2007, http://www.thegreenguide.com/home-garden/cleaning/diy-cleaners?source=email_gg_20090121&email=gg. The author notes useful items to keep handy and explains how each works. The items are baking soda, borax, distilled white vinegar, hydrogen peroxide, lemon, olive oil, vegetable-based liquid soap, and washing soda. One suggestion: spray hydrogen peroxide and vinegar one after the other (to replace chlorine bleach). Examples of two recipes are: (1) All-Purpose Cleaner: dissolve 1/2 cup borax in a gallon hot water. Mix in pail (or use in spray bottle). After using, wipe clean with rag. (2) For wood floors: Mix 1/4 cup white vinegar in gallon warm water.

Hazards in older homes and buildings

Asbestos⁴²

- The problem Asbestos is a naturally occurring fibrous mineral. Because of its heat resistance, asbestos was widely used to insulate furnaces and furnace pipes. It is still often found in old homes and buildings. Flaking asbestos poses the greatest danger as its particles can become airborne, and may be inhaled. Flaking is much less of a problem for asbestos in floor and ceiling tiles, fireplace gloves, and ironing board covers. *Chrysotile asbestos*, which is considered less dangerous than *amphibole asbestos*, was used in most buildings and homes.
- Lowering the risk Removing asbestos from heating systems is not recommended unless it is deteriorating because the removal process releases asbestos fibers into the air. Rather, ask a professional how best to maintain it in place. Professional advice is also needed to assess whether asbestos is present in old tiles. Leave asbestos-containing tiles in place unless they are deteriorating. Repair or removal of asbestos-containing materials should be done by an EPA-approved professional. Exposure to asbestos, especially at levels found in industrial settings, is associated with asbestosis, lung cancer, and mesothelioma.⁴³ Some risk is associated with ingesting asbestos in drinking water, but the primary risk is inhaling airborne fibers into the lungs, where they may become permanently trapped.

Lead

- The problem Lead paint was once the paint of choice. Lead was added to paints in the United States for many years although in progressively lower amounts until its banning from indoor house paint in 1978. Highest levels are most often found in homes built before 1940. Tiny children may eat flaking lead paint from window sills or woodwork and, of even greater concern they may inhale dust in homes with flaking leaded paint.
- Lessening the risk⁴⁴ Local and state health departments can provide information on identifying lead paint. Using an ordinary vacuum may result in exhausting lead-containing particles back into household air so, unless an especially equipped vacuum cleaner is available, use wet cloths and mops. As with asbestos, if the lead paint is in good condition, leave it undisturbed. Cover it with wall paper or another covering. If painted woodwork is in good condition, wipe it frequently with a wet cloth to lessen the chance of lead dust entering the air. If small children live in the home, consider asking a professional to remove the paint from woodwork or replace the woodwork. Homeowners should not remove leaded paint themselves. Soil around old houses often contains high lead levels, which can be tracked into the home on footwear.

⁴² ToxFAQs™ for asbestos. *ATSDR*, September, 2001, <http://www.rst2.edu/ties/asbestos/university/asbestospdf/lg7.pdf>.

⁴³ The author's brother, a long-time sheet metal worker, developed asbestosis and died of lung cancer in December, 2008.

⁴⁴ Indoor air quality: lead. *US EPA*, November 25, 2008, <http://www.epa.gov/iaq/lead.html>.

Household hazardous waste⁴⁵

- The problem Residues of hazardous products become *household hazardous waste* (HHW).⁴⁶ Waste paint is the most common HHW. Other left-over products in HHW are paint thinners and strippers, pesticides, cleaners and polishes that contain petroleum distillates, and alkaline drain and oven cleaners. Even some discarded cosmetics, such as acetone nail-polish remover contribute small amounts of HHW. Several web sites provide a good description of household hazardous waste, how to handle it and further references.⁴⁷
- Lessening HHW Creation of HHW can be prevented by buying the smallest amount of a product that can do the job desired. This is one time to avoid economy sizes. Once purchased, use it up or give it to someone who will. Some residues can be disposed of, for example if paint is first allowed to dry out (in a place safely away from children), the residue may go in the trash. Sometimes product labels have disposal instructions or a telephone number to call for more information on the product. Although it takes a change in habits, consider making your own products; many of them are simple. See Table 17.2.

Table 17.2 Alternative household products

All-purpose cleaner: 1 gallon hot water, 2/3 cup baking soda, 1/4 cup ammonia, 1/4 cup vinegar (OK to double the ingredients added to the water for a stronger cleaner.)
Window/glass cleaner: 1/4 cup ammonia with 1 quart water (or 1/2 cup vinegar with 1 quart water)
Scouring powder cleaner: use baking soda (For laundry, add 1/2 cup to wash water.)
Furniture polish: mix 1 teaspoon lemon oil and 1 pint mineral oil
Oven cleaner: wash oven with warm water/baking soda mixture. Soften burned-on spills by placing a small pan of ammonia in the oven overnight. Sprinkle salt onto fresh grease spills and then wipe clean
Toilet cleaner: use baking soda, a mild detergent, and a toilet brush
Floor cleaner: 1/2 cup vinegar in a gallon of water
Floor Polish: club soda
Silver cleaner: to small pan of water add 1 teaspoon baking soda, 1 teaspoon salt plus 2" × 2" piece of aluminum foil. Soak silverware overnight.
Rug Cleaner: sprinkle cornstarch on carpets and vacuum
Drain Opener: first spoon baking soda into drain, and then slowly add 1/3 cup white vinegar. Use a plunger to get rid of loosened clog. Prevent clogs by pouring boiling water down drains once a week. Also use drain strainers, and don't pour grease down drains
Moth Balls: put cedar chips or blocks in closets and drawers with clothes. Store clothing clean
Insecticides: mix 2 tablespoons dish-washing liquid with 2 cups water: spray on leaves
Ant poison: clean counter tops with mixture of half vinegar and half water
Fly repellants: use fly swatter or place mint plants on window sills

⁴⁵ (1) Household hazardous waste. *US EPA*, September 30, 2008, <http://www.epa.gov/epawaste/conserve/materials/hhw.htm>. (2) Household hazardous waste. *Land-of-Sky Regional Council's Environmental Planning Division*, 2004, http://www.landofsky.org/planning/p_hhw.html.

⁴⁶ Wastes, ask a question. *US EPA*, January 19, 2009, http://waste.custhelp.com/cgi-bin/waste.cfg/php/enduser/std_alp.php.

⁴⁷ Household hazardous waste. *Ewgateway.org*, August 19, 2008, <http://www.ewgateway.org/progproj/hhw/hhw.htm>.

- HHW Collection Programs In the hands of a householder, HHW is not regulated as hazardous waste, but once it passes into the hands of a collection program, it is strictly regulated. However, community collection programs, although still expensive, are not subject to regulations regarding collection, storage, and transportation of some HHW. However, the waste must be either recycled or properly treated before disposal.

Paint

About half of all HHW is paint. Water-based (latex) paint is less hazardous than oil-based. Alternative “natural” paints containing beeswax, plant waxes, and linseed oil are available, but check the expiration date as some can, literally rot. Buy only the amount needed. If the leftovers are usable, give it away. Encourage your community and state to adopt a paint recycling program or a paint “drop and swap.”

Used Oil and Antifreeze

- Another HHW produced in large volumes is familiar to those who change their own car oil. Used oil is both ignitable and toxic. Never pour used oil on the ground or down a drain, whether it’s a home or storm drain. Check with your city for locations that take used oil. Because millions of do-it-yourselfers make it impractical for the EPA to regulate waste oil, it chose to develop standards for commercial handlers of used oil: if destined for disposal, the oil may fall under hazardous waste regulations. But oil that is to be recycled is treated less strictly.
- Antifreeze too should never be poured on the ground or driveway. Its sweet taste can attract and poison animals and children. Some brands have a bitter-tasting additive to discourage ingestion. Contact the local wastewater treatment plant to inquire if it can handle antifreeze. If it can, then, *little by little* flush the antifreeze down the toilet. Don’t pour antifreeze down the drain if the home has a septic system, as it may kill the system’s microorganisms.

Pesticides⁴⁸

- The problems Most American households use pesticides, commonly lawn and garden pesticides, moth repellents, pet-flea collars, no-pest strips, and disinfectants. Pesticides available to householders are less hazardous than commercial products. However, pesticides may be blown by wind or run off with rainwater into other people’s yards or a local stream or lake. They lead to many bird deaths, and can kill beneficial insects such as honey bees. Pesticides, picked up on footwear and tracked into homes are detected on carpets even in homes not using pesticides. ■ The person most highly exposed to pesticide is usually the one applying it, but others within the home and yard are also exposed.

⁴⁸ (1) What is integrated pest management or IPM? *University of Wisconsin System*, 2005, <http://www.uwex.edu/homeasyst/>. (2) Healthy neighborhoods, going the extra yard (yard environmental health). *Audubon Magazine*, March, 2002, http://audubonmagazine.org/features0203/healthy_habitats.html.

- Pollution prevention Practicing P² can reduce pesticide use within the home: Eliminate the food particles that attract roaches and ants. Use containers with tight-fitting lids to store food. Fill in cracks that allow roaches and other pests to enter the home. A fly swatter can sometimes replace an insecticide. Natural repellents are sometimes useful; boric acid is useful for cockroach and ant control and is less toxic than many pesticides. Some people report that cedar chips in their dog's bed prevent fleas, and that pyrethrum-daisy flowers deter moths. To prevent attracting moths and avoid the use of mothballs, store clothing clean. In a home with carpets or small children, leave shoes at the door to prevent tracking of pesticides into the home. ▀ Outside, allow dandelions, clover, and other "weeds" to inhabit the lawn rather than using herbicides. In the garden, consider companion planting⁴⁹ and crop rotation as means to deter predators. Reduce places with free-standing water that can allow pests to multiply easily.
- Controlling the risk If a pesticide is needed, buy the smallest amount that will do the job. Read and follow label directions. If a spray is used, buy a pump, not aerosol. An aerosol's tiny particles can be inhaled deeply into the lungs. If used within the home, make sure ventilation is good. Check if gloves are needed. Pay attention to how long after spraying that a treated area should be avoided. In particular, consider how to protect children in the area. ▀ Dr. Michael Shelby of the National Institute of Environmental Health Sciences recommends the following for pesticides: "The best advice for anyone, and my advice at home for my wife and children, is (1) don't overuse them; (2) don't expose yourself to them, or if you do, do it at absolute minimal levels; and (3) keep them in a safe place where animals and children cannot get to them."

Questions 17.2

1. As you shower or otherwise use water, what water pollutants may become airborne (a) In a home served by municipal water? (b) In one with well water?
2. What information is of most interest to you personally when you look at a product's label? Why?
3. Are there chemical products you would never have in your home? Explain.
4. Under what circumstances do you (or would you) use pesticides inside and outside your home?
5. Assume you found an *old* house that you wanted to buy.⁵⁰ What environmental hazards would you check the home for: (a) In its interior (including basement and attic)? (b) In the heating system? (c) The plumbing system? (d) Its outbuildings and land?
6. Answer question 5 again, but this time for a home less than 10-years old.
7. (a) Do emissions from new carpets, drapes, or wood paneling concern you enough that you would only install these during the summer? Explain. (b) Would you apply paint or varnish to the inside of your home in the winter? Explain

⁴⁹ Kuepper, G. and Dodson, M. Companion planting: basic concepts and resources. *National Sustainable Agriculture Information Service*, July 2001, <http://attra.ncat.org/attra-pub/complant.html>.

⁵⁰ Hawes, A. A home buyer's guide to environmental hazard. *Consumer Law Page*, 1994–2007, <http://web72345.ntx.net/brochure/home-haz.shtml>.

Delving deeper

Go to the Farm*A*Syst/Home*A*Syst links (<http://www.uwex.edu/homeasyst/>). Choose a topic of interest to you from among the home environmental safety topics given. Follow the links to get enough information to feel comfortable that you know what is necessary or useful to your home. Prepare a brief report. Along with other students who each examine a different topic, make brief oral reports to your class.

Internet resources

- Alliance for healthy housing. 2009. Ventilation and indoor air quality. http://www.afhh.org/dah/dah_ventilation.htm.
- American Association of Poison Control Centers. 2009. <http://www.aapcc.org/DNN/> (March 27, 2009).
- American Lung Association. 1995–2009. Air pollution and your home. http://www.alaw.org/air_Quality/indoor_air_Quality/air_pollution_in_your_home.html.
- American Lung Association. 2008. Diseases A-Z. <http://www.lungusa.org/diseases/>.
- Ewgateway. 2007. Household hazardous waste. <http://www.ewgateway.org/progproj/hhw/hhw.htm> (May 21, 2007).
- Hawes, A. A. home buyer's guide to environmental hazard. *Consumer Law Page*, 1994–2007. <http://www.consumerlawpage.com/brochure/home-haz.shtml>.
- Hildebrandt, T. and Turner, J. L. 2003. Air pollution challenges rural China. *Wilson Center*, http://www.wilsoncenter.org/index.cfm?fuseaction=events.event_summary&event_id=28825 (April 23, 2003).
- McRandle, P. 2007. Do it yourself household cleaners. *Green Guide, National Geographic*, http://www.thegreenguide.com/home-garden/cleaning/diy-cleaners?source=email_gg_20090121&email=gg (May 3, 2007).
- National Safety Council. 2002. Ionizing radiation sources. <http://www.nsc.org/resources/issues/rad/ionize.aspx> (March 25, 2002).
- NPIC. 2008. Signal word, toxic fact sheet (answering questions about pesticides). <http://npic.orst.edu/factsheets/signalwords.pdf> (July, 2008).
- State of Washington. 2009. Shoppers' guide: toxic free tips. <http://www.ecy.wa.gov/toxicfreetips/shoppersguide.html>.
- University of Wisconsin. 2005. What is (home) integrated pest management? <http://www.uwex.edu/homeasyst/>.
- US Consumer Product Safety Commission (CPSC) No date. A guide to indoor air quality (whole booklet here online). <http://www.cpsc.gov/cpscpub/pubs/450.html#Look6>.
- No date. What you should know about combustion appliances and indoor air pollution. <http://www.cpsc.gov/CPSCPUB/PUBS/452.html>.
2008. Carbon monoxide, questions and answers. <http://www.cpsc.gov/CPSCPUB/PUBS/466.html> (September, 2008).

- US EPA 2008. An introduction to indoor air quality: pesticides. <http://www.epa.gov/iaq/pesticid.html> (November 25, 2008).
2008. Household hazardous waste. <http://www.epa.gov/epawaste/conservematerials/hhw.htm> (September 30, 2008).
2008. Indoor air quality: lead. <http://www.epa.gov/iaq/lead.html> (November 25, 2008).
2008. Indoor air quality resources (questions and answers). <http://www.epa.gov/iaq/iaqinfo.html> (November 25, 2008).
2008. Mold resources. <http://www.epa.gov/mold/moldresources.html> (September 18, 2008).
2008. Pesticides: read the label first. <http://www.epa.gov/pesticides/label/> (November 7, 2008).
2008. Remodeling your home? Consider indoor air quality. <http://www.epa.gov/iaq/homes/hip-front.html> (August 26, 2008).
2009. A citizen's guide to radon. <http://www.epa.gov/radon/pubs/citguide.html> (March 26, 2009).
2009. EPA's report on the environment: indoor air. <http://oaspub.epa.gov/hd/home#11> (March 26, 2009).
2009. Indoor air quality. <http://www.epa.gov/iaq/> (January 5, 2009).
2009. Indoor air quality index. <http://www.epa.gov/iaq/atozindex.html> (April 8, 2009).
2009. Wastes: ask a question. http://waste.custhelp.com/cgi-bin/waste.cfg/php/enduser/std_alp.php (January 19, 2009).

“The time has come for humankind not to expect the Earth to produce more, but rather to do more with what the Earth already produces.”

Gunter Pauli, Belgian industrialist

Remember the concept of nature’s services from Chapter 1: conserving nature is absolutely necessary to the sustaining of meaningful life on Earth, its habitats and biodiversity, and its ability to continue to perform the services on which humanity and all life depends. Sustaining nature’s services necessitates producing a minimal amount (“zero”) of damaging wastes and emissions. The Product Life Institute provides a worthwhile introduction to sustainability; see footnote ¹. But how can we speak of zero waste or zero emissions if, as you learned earlier no process is 100% efficient? The answer is that *zero waste* is a philosophy, one that says there is no waste: What we call “waste” or “pollutant” is really a useful resource. However, this philosophy recognizes that waste is now a major problem and, if we aspire to reduce waste 100%, we accomplish more than if our goal was 40% or 80%. Thinking of wastes and pollution in this manner is not contradictory to other concepts covered in this book such as pollution control and pollution prevention because humanity is working at a number of levels, both doing what we must at the present while also working toward the future vision of finding means to a sustainable environment and world.

Dematerialization is emphasized in the first three sections of this chapter, i.e., reducing the quantities of materials we use. Section I asks how well we are doing now in reducing waste and pollution. Section II discusses *industrial ecology*, which has the goal of enmeshing industrial society into the environment. It introduces closed-loop systems and examines the possibility of increasing our efficiency in resource use at least four-fold. Section III examines tools to work toward zero-waste: life cycle assessment (LCA) and design for the environment (DfE) as well as *servicizing* and *product stewardship*. Section IV emphasizes detoxification (*green chemistry*): changing the chemicals we use and how we produce them, to reduce chemical risk to humans and the environment. Section V asks what progress is there toward zero waste – by corporations, cities and countries?

¹ *The Product Life Institute*, 1982–2008, <http://www.product-life.org/en/node>. A sustainable economy and society rests on five pillars: nature conservation; limiting toxicity; maximizing resource productivity; and on social ecology (peace and justice) and cultural ecology (defined at this web site).

SECTION I

Waste and emissions

In the United States, pollution has been reduced – up to a point.

- Air Collectively, US emissions of the six criteria air pollutants² fell more than 50% between 1980 and 2007. This improvement occurred despite a 195% increase in Gross Domestic Product (GDP), 178% increase in vehicle miles traveled, and a population increase of 42%. ■ These are impressive gains. Nonetheless, 159 million Americans live in areas where standards set to protect human health are exceeded for at least one criteria pollutant. Ground-level ozone remains high enough to affect health in many cities. Moreover, greenhouse gas emissions continue to increase in the United States.
- Water is more complicated to assess. The acidity of surface water has decreased in surface water ecosystems sensitive to acid impact. But many waters have too much bioavailable nitrogen; nitrate levels especially have increased in the Mississippi River (Chapter 9). Non-point runoff remains a major problem. Many shallow wells in agricultural areas have detectable pesticides.
- Considering the environment more generally, see Electronic report on the environment. *US EPA*. 2008. <http://www.epa.gov/roe/index.htm>. This site connects you to air, water, land and other environmental trends.

Worldwide, the picture is sobering³ (Table 2.1). Consider Asia where rapid economic growth severely strains the environment.⁴ The Asian Development Bank states that, unless changes are made in economic-development patterns to address pollution and natural-resource degradation Asian cities will increasingly become unlivable, and available resources further degraded.^{5,6} Equally serious problems exist in many places in addition to Asia. ■ Meanwhile, the complexity of environmental problems increases and problems will worsen without decisive action. Major action is needed to greatly increase citizens' environmental awareness and the will of governments, businesses and organizations to act.

² (1) Earthday 2008 fact sheet. *The National Center for Public Policy Research*, 2008, <http://www.nationalcenter.org/EarthDay08Progress.html>. (2) Air trends, basic information. *US EPA*, November 21, 2008, <http://www.epa.gov/airtrends/sixpoll.html>. (The criteria air pollutants are carbon monoxide, lead, sulfur dioxide, nitrogen oxides, ground-level ozone, and particulate matter.)

³ Vitousek, P. M., Mooney, H. A., Lubchenco, J. and Melillo, J. M. Human Domination of Earth's Ecosystems. *Science*, 277, July 25, 1997, 494–499.

⁴ The Long-Term Strategic Framework of the Asian Development Bank (2008–2020). *Asian Development Bank*, December, 2007, 8–9, <http://www.adb.org/Documents/Policies/LTSF-W-Paper/LTSF-W-paper.pdf>.

⁵ The Asian Development Bank stated (2002) that “environmental degradation – air pollution, biodiversity loss, land degradation, exhaustion of aquifers, water pollution and exposure to hazardous waste – is now ‘pervasive, accelerating and unabated.’” Its five-fold policy to turn this around is: reduce poverty, take the environment into account in bank operations and when addressing economic growth, promote regional and global cooperation, work with partners to reverse environmental degradation.

⁶ Starting in 2008, a severe economic downturn may indeed be altering economic development worldwide, but such a precipitous drop in economic activity is definitely not a path we would deliberately choose to take.

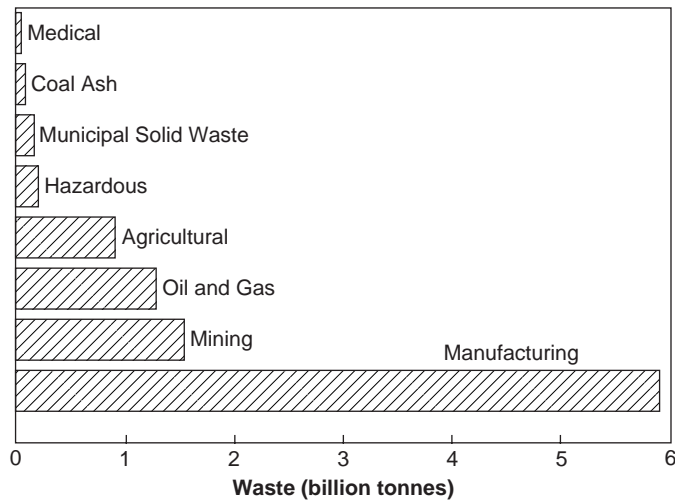


Figure 18.1 Amounts of waste generated by various sectors (billions of tonnes). Source: US Congress, Office of Technology Assessment

Resources necessary to solve environmental problems are sorely lacking, especially in poor countries. Nonetheless, as seen in this chapter, progress, although not in the spotlight, is being made. We may not reach the elusive zero waste, but with a mindset of zero, surprising reductions can be achieved even in resource-poor societies.

How much waste?

The United States generates about 12 billion tons (10.9 billion tonnes) of waste per year. See Figure 18.1 for the types of wastes such as mining operations, oil and gas recovery and agriculture. By weight, most is manufacturing waste produced to make a multitude of products from chemicals to computers, bread to cigarettes, automobiles to clothing, and much more. It may be too obvious to state that if we are generating so much waste, it is because we are using the Earth's resources. How can we cut resource use – *dematerialize* our societies?

SECTION II

Industrial ecology⁷

Industrial ecology (IE) was introduced in Chapter 2. The goal of IE is ambitious: enmesh our industrial society seamlessly into the environment – a framework in which industrial society

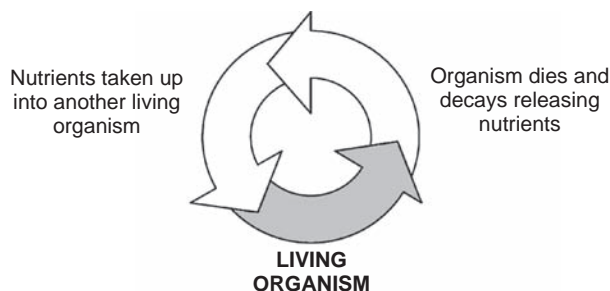
⁷ What is eco-efficiency? *Industry Canada*, November 24, 2008, http://www.ic.gc.ca/eic/site/ee-ee.nsf/eng/h_ef00010.html.

and ecosystems function together holistically, a framework for sustainability.⁸ Instead of isolation from the living world industrial society would work in concert with other life.

Closed-loop systems

One author stated “the ultimate goal of industrial ecology is bringing the industrial system as close as possible to being a closed-loop system, with near complete recycling of all materials.” A major characteristic of biological systems is that they work within closed loops. This principle is also expressed as cradle to cradle⁹: there is no end of life for a product. See Figure 18.2. The wastes excreted by living creatures are degraded into what serves as nutrients for living organisms. Likewise, when living creatures die, they biodegrade into nutrients. So, for IE to succeed, we must find ways to mimic nature,¹⁰ transform

NATURAL SYSTEM: CIRCULAR FLOWS OF MATERIAL AND ENERGY



TRADITIONAL INDUSTRIAL SYSTEM: LINEAR FLOWS



Figure 18.2

Flows of materials and energy, natural and industrial¹¹

⁸ In 1987, *sustainable development* was defined as meeting the needs of today without compromising the ability of future generations to meet their needs (report of UN-sponsored World Commission on Environment and Development). What sustainable development means in daily practice is the subject of discussion and controversy: to what extent can we impact our environment without harming its ability to provide natural services such as water and air purification, pollination, fertile soil, decay of organic materials in the environment, and many others? Other frameworks exist for looking at a sustainable world. An approach called *sustainability science* emphasizes the great importance of economic and social sustainability as part of a sustainable environment.

⁹ About cradle to cradle design. MBDC, March 28, 2009, <http://www.mbdc.com/index.htm>.

¹⁰ Ask nature. *The Biomimicry Institute*, 2009, <http://www.biomimicryinstitute.org/>. The mission of the Institute is to nurture and grow a global community of people who are learning from, emulating, and conserving life's genius to create a healthier, more sustainable planet.

¹¹ A plant or a photosynthetic microbe directly captures the sun's energy whereas an animal obtains the sun's energy indirectly by eating plants or other animals. Human industrial systems depend on the sun too – oil, coal, and gas arose from living plants. Solar panels use the sun directly. Wind turbines are powered indirectly by the sun, etc.

Box 18.1

Space ecology

Manned space flights store their wastes and bring them back to Earth. This would be impractical for long-term missions. In 1978, NASA began studying a self-sustained system for living in space, an *Advanced Life Support System*.¹² Long-term flights would need systems to produce food, purify water, regenerate oxygen, and prevent air pollutants and wastes from building up – they need closed-loop systems. Green plants would be grown as food. Plants would also absorb the carbon dioxide that humans respire, while emitting the oxygen that humans need. Plant transpiration would provide pure water. Plant and human wastes would be resources. “All systems would have to operate under the restrictions of minimizing volume, mass, energy, and labor.” A computer would integrate this complex system, which would need intensive testing on Earth. Knowledge gained in developing this system would also have applications on an Earth that contains more human beings, more wastes, and fewer virgin resources. • Both Biosphere 2 and the NASA program teach us more about how natural systems work. They help clarify how we may adapt ourselves to nature rather than continuing in a naïve expectation that nature can boundlessly adapt to humans.

society’s activities into closed loops. This future world would create useable by-products – nutrients – not wastes. You have already seen the example of Kalundborg Figure 2.2) with its extensive use of industrial symbiosis. Kalundborg has reached the IE goal, but is pointing the way. In closed-loop systems, by-products continuously recycle within closed loops. Biodegradable materials could be discarded in amounts and under circumstances where we know they will degrade without harming the environment. There have been attempts to set up closed-loop systems experimentally. See Box 18.1 and remember Biosphere 2 (Box 1.1).

Recycling is not enough

Recycling only *slows* the linear – as opposed to closed loop – flow of materials. Industrial symbiosis (Chapter 2) is a great improvement, but needs to be applied widely and to all types of industrial systems. As architect William McDonough stated, “We should recycle, but it is not the first thing we should do, it is the last. Redesign first, then reduce, and finally recycle, if there is no other alternative.”

Is it possible to use resources ten times more efficiently?

To achieve closed loop systems we must use resources with much greater efficiency: we must use less material and less energy. • Some believe that to maintain today’s living standards we need a *factor ten*¹³ improvement in efficiency, i.e., produce the same amount of goods and services with 90% fewer resources. Others go further and think *factor twenty*. • Why would we need such dramatic increases in efficiency? One major reason is that our already large human population continues to grow. At the same time, billions of the world’s people live in poverty,

¹² Braukus, M. and Matthews-Schmidt, L. Team begins test of *Advanced Life Support System*. *NASA*, January 31, 2009, http://findarticles.com/p/articles/mi_pasa/is_ai_3053565124.

¹³ The Product Life Institute, 1982–2008, <http://www.product-life.org/en/about>.

many in absolute poverty not knowing where their next meal is coming from: they need more food and material goods, thus we need to increase economic activity to satisfy basic needs. But if society increases economic activity using “business as usual” there will not be enough resources. Nor, most likely, will the environment continue to efficiently provide natural services. Because factor ten seems a daunting goal *factor four* is seen as a more reachable challenge.

Designing to use less material

Computers became remarkably more useful when size was reduced. Even if, 50 years ago it had been possible to use a computer as a word processor, that computer would have filled a room. Remarkable advances in technology made possible the micro computers of today, which use conspicuously less material. Changing computer technology was not motivated by the environment, but it shows us what can be accomplished. Today, we need to deliberately use DfE to find ways to use fewer material resources and less energy and water to make products. The emerging field of nanotechnology has a vision of making machines the size of molecules. But nanotechnology aside, there are already tools we can use to lessen material and energy use.¹⁴ Is the computer a special case or could factor of four, or more be applied to many more products? There are products, which cannot fulfill their purpose if built with much less material. What if, instead of discarding such products, we reuse them or their parts in a continuous loop? In the process, we *dematerialize*, i.e., use fewer materials. ■ Think about a sofa. We could and should find ways to lessen the amount of energy and water needed to make the sofa. But assuming we want a full-sized sofa, what do we do? We must design durability into the sofa. Keep the sofa indefinitely, re-upholstering as necessary. All its components, upholstery, foam, wood and metal would be reusable and recyclable. Design it for disassembly so that when parts need replacing or the sofa is finally “discarded,” its parts are not. The sofa would “live” indefinitely. The social question remains: how do we change ourselves to desire durable products? For any product, design it so that minimal waste and pollution are produced during all steps of its life cycle including disassembly and reuse.

SECTION III

Tools for dematerialization, moving toward a zero-waste society

Pollution prevention (P^2)¹⁵ reduces waste and pollution, while conserving energy, water and materials. But P^2 seldom eliminates all waste. Before using P^2 or design for the environment

¹⁴ Although computers and other electronics are very small compared to their antecedents, many people in industrialized societies use many more electronics, and discard them frequently as they are replaced with newer products with ever-increasing efficiency and attractive features. To deal with this, the EU and Japan are requiring manufacturers to be responsible for their electronic products throughout their entire lives. This stimulates DfE. However, it does not address the perceived need of our industrial society to grow forever.

¹⁵ Pollution prevention. *US EPA*, January 14, 2009, <http://www.epa.gov/p2/>. This site has a number of useful links to other sites relevant to P^2 .

Table 18.1 Environmental impacts that may be evaluated during an LCA

The impacts noted below are illustrative, not complete

Type of impact ¹	Example of pollutant, which can cause the effect
Global warming	Greenhouse gas such as carbon dioxide
Acidification	Acid substance such as sulfuric acid
Eutrophication	Nutrient such as nitrate
Photochemical smog	Hydrocarbons
Terrestrial toxicity ²	Pesticide
Human health	Chemical such as arsenic
Other types of effect	Explanation
Resource depletion	Quantity of resource used compared to how much remains
Land use	Quantity of waste disposed into a landfill
Damage to biodiversity, etc.	

¹ Consideration is also given to whether the impact is local, regional, or global (See Table 2.2).² Toxicity to plants, animals of all types, and microbes.

(DfE) effectively, we need to know as much about the product as it now exists as possible. For that, a major tool is life-cycle assessment (LCA).¹⁶

Life-cycle assessment

LCA allows us to study the flows of materials, energy and water throughout the life of a product (or a process such as fossil fuel combustion) as it now exists. It examines the environmental impacts at each point in its life, see Table 18.1 Once flows and impacts are understood, then both P² and DfE can more effectively come into play. LCA can be useful for examining a piece of paper, plastic bag, car, or a food item such as an apple. ▪ Look at the four life cycle stages (Figure 18.3). 1. The impacts of acquiring the raw materials for the product. 2. The impacts of manufacturing it. 3. The impacts of using (reusing) and maintaining it. 4. The impacts of recycling or otherwise managing the product at the end of its useful life. For *each* of the four stages we analyze:

- Inputs (left of diagram) for raw material acquisition: How much material, energy and water are used?
- Outputs (right): What – for each of these inputs – are the outputs in terms of pollutants, wastes and by-products?

LCA can be very complex¹⁷

Most products contain more than one component – each step of the LCA must be done on each component. Often LCA is an ambitious, time consuming, and expensive undertaking.

¹⁶ Life cycle assessment. *US EPA*, October 17 2008, <http://www.epa.gov/nrmrl/lcaccess/>. This site will link you to sites such as LCA 101.

¹⁷ Life Cycle Inventory. *Environment Canada*, February 2, 2001, <http://www.mindfully.org/Plastic/Life-Cycle.htm>.

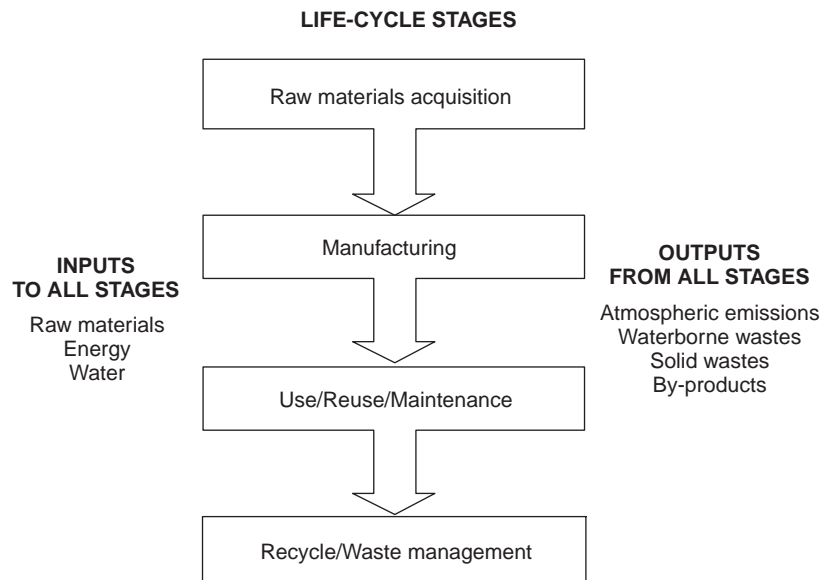


Figure 18.3

Information needed for a life-cycle assessment. Credit: US EPA

Think of one fairly simple product, a disposable diaper: it contains a plastic covering, a super-absorbent polymer, and paper. ▪ Moreover, as you think about the environmental impacts of a product, remember that good information is not always available. ▪ Still, many years have gone into developing LCA. More years will go into making it more reliable, simplifying it, and providing realistic results.

LCA one product at a time

▪ Industry increasingly uses LCA to examine the environmental impacts of its products, often with the goal of reducing those impacts. Volvo performed an LCA on its vehicles and used the results to design environmentally better vehicles. ▪ Sometimes LCA can be simplified by studying only one aspect of a product as when Proctor&Gamble analyzed energy consumption over the life cycle of its laundry detergents. It found the most energy-intensive step was heating washing machine water. It then designed detergents that work well in cold water or when less water is used. ▪ Generally, LCA provides invaluable information: the more designers know about a product's environmental impacts at each stage of its life cycle, the better a DfE can be.

LCA to compare products

LCA can be used to compare two or more products that serve the same function. Which is environmentally preferable, has the smaller environmental impact? Which is better – a disposable polystyrene cup or a paper cup? A cloth diaper or a disposable diaper? A truck using diesel fuel or one using propane gas fuel? (Box 18.2). Product comparisons are useful,

Box 18.2

Questions on environmentally preferable products

- Are disposable paper cups better than plastic cups? An LCA indicated that a plastic disposable cup is probably no worse than the paper one. Both are disposables so perhaps a different – better? – question is which is environmentally preferable, a disposable cup or a reusable one? Is the reusable cup obviously preferable? The LCA concluded that a glass cup must be used hundreds of times to be preferable to a disposable cup. This is because making a glass cup generates more pollution than making a disposable one, takes more resources and energy in its making and transportation to market. Moreover, each time a reusable cup is washed, more energy and water are used, and polluted wastewater produced. Furthermore, a prosperous householder usually has many glass cups. If the householder owned only a few cups, and each was reused a great many times and washed only when the dishwasher was full, etc., glass cups could be preferable. The real problem appears to be that prosperous households have many glass cups *and* many disposable ones too.
- Are cloth diapers preferable to disposable diapers? The issues are similar to those for throw-away versus reusable cups. Cloth Each time cloth diapers are laundered, water is used, energy is needed to heat the water, contaminated wastewater is generated, and, unless diapers are dried on a clothesline, energy is used to dry them. If a diaper service is used, transportation to and from the laundry adds to energy used and pollution produced. Disposable diapers create more waste than do cloth diapers. This waste is difficult to recycle although a few cities do so. If disposable diapers are burned in a waste-to-energy incinerator, some energy is recovered, but some pollution produced. A strong negative is that the plastic does not biodegrade. Buried in a landfill it takes many years to break down; when it finally does break down, it is into ever smaller particles – the plastic components are still there.

Comparison

It is difficult to compare even simple products. And it is a much more ambitious undertaking still to compare complicated products with many components and materials.

but always have uncertainties One product may use recycled materials, but otherwise generate more pollution during manufacture or use. One product needs less energy to manufacture but requires more hazardous chemicals. Another may be manufactured with little pollution, but presents major problems at the end of its useful life. You could make a long list of difficult-to-compare factors. Nonetheless, used conscientiously, LCA is useful for comparisons. The US EPA used it to help develop guidelines for *environmentally preferable products* (Box 11.1).

Design for the environment¹⁸

After delving into a product's environmental impacts the next question is: what impacts can we reduce or entirely design out of this product? Earlier, we saw illustrations of DfE, e.g.,

¹⁸ (1) Design for the environment, basic information. *US EPA*, November 13, 2008, <http://www.epa.gov/dfe/pubs/about/index.htm>. (2) DfE publications. January 5, 2009, <http://www.epa.gov/dfe/pubs/index.htm>.

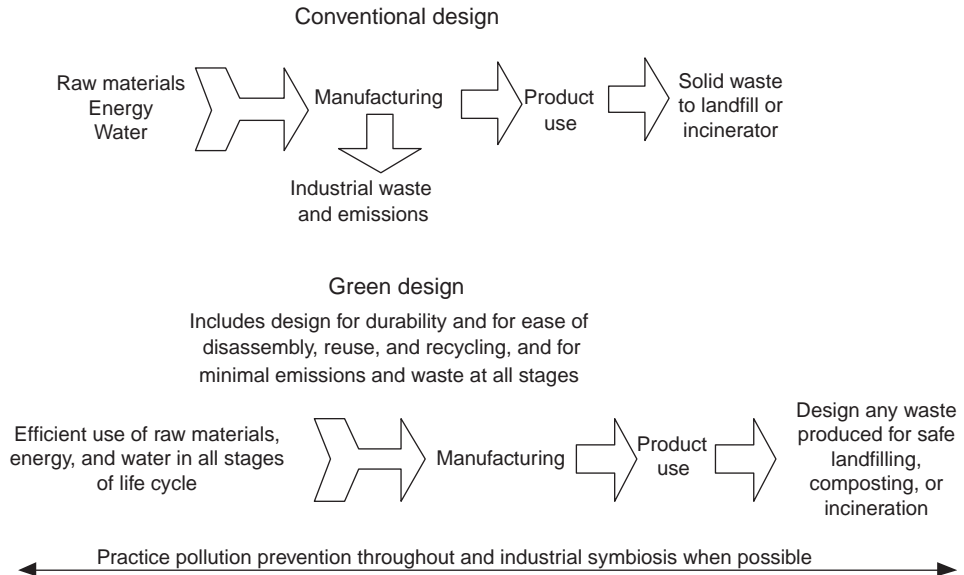


Figure 18.4

Conventional and green product design

removing cadmium from disposable batteries or hazardous metals from packaging and newspapers. ▪ The Xerox Corporation uses a comprehensive DfE approach. Xerox has been renting and taking back its copying machines from users since the 1960s. This was significant, especially as compared to other companies of the period, but DfE was not integral. In 1990, Xerox started using DfE from the moment a new product idea is conceived. Criteria were added with the intent of producing a longer-lived durable product, one easier to disassemble to recover components for recycling or to remanufacture into new copiers. Also *remanufacturing convertibility* is built into product design, i.e., design product components in a way that allows them to have more than one use, as when a photocopier part finds a second life in an electronic printer. ▪ Designers strive for a product that – considered over its entire life cycle – uses the least material, energy, water, and hazardous chemicals. And increasingly, designers look at disassembly of their product for reuse or remanufacturing, and recycling. A major aspect of DfE is designing for durability¹⁹ (Figure 18.4).

Questions 18.1

1. Why is product durability such an important factor in increasing the efficiency of resource use?
2. The example of a “live forever” sofa was given in Section II. Become more specific on how the sofa can be designed, used, and reused. Include the social components – getting ourselves to desire such a sofa, thinking about servicing the sofa, the types of jobs generated, etc.

¹⁹ Lovins, L. H. Chapter 3: Innovations for a sustainable economy. In *State of the World 2008*. New York: World Watch Norton, 2008, 32–44, http://www.worldwatch.org/files/pdf/SOW08_chapter_3.pdf.

3. Choose a simple product. Using a diagram as you proceed, design the product to have a minimal environmental impact. Be prepared to discuss and justify your approach before fellow students.
4. Renting rather than selling products impacts how Xerox manages its products. Why is its approach likely to be more environmentally benign than if it sold its products?
5. Develop an example of *servicizing* (not one given in this text), either real or one you think could work. Explain how it works and how it would save resources (energy, materials, water).
6. Do servicing and EPR have the same purpose? Do a comparison.

Product stewardship²⁰

Product stewardship means a producer takes responsibility for a product throughout its entire life cycle. Stewardship can be freely chosen by a forward-looking company. Or, as in the EU and Japan *take-back* laws (or *extended producer responsibility*, EPR) impose stewardship. EPR provides a major incentive for manufacturers to redesign their products.²¹ This is because it is expensive to handle a take-back product as waste. It can be profitable or much less expensive to take back a product that retains value – as when Xerox takes back its copiers. ■ Producers begin to ask: is the product durable enough to retain value after the consumer gives it up? Can this car, this computer, or other product be disassembled efficiently? Can its component parts be recycled or remanufactured? Are component parts non-toxic, and so easily dealt with at end of life?

European and Japanese take-back laws

In Chapter 11 you saw that for fairly simple products such as packaging EU producers began to use less packaging when required to take back packaging.

- Japanese and EU manufacturers also take back electronics products – not just computers and TVs, but any product containing electronics including refrigerators, stereo equipment, even some toys. When a program begins, unless manufacturers are well forewarned, take back is difficult because products already sold or on the market were not designed for disassembly, reuse, remanufacturing, or recycling. In fact, there may be aspects of the product that the producer is unaware of such as purity of potentially recyclable materials, possible unknown hazardous constituents, or even the product's material composition.
- Take-back laws for motor vehicles require EU manufacturers to reuse or recycle at least 80% of the vehicle by weight; this increases to 85% by 2015.

²⁰ Product stewardship. *US EPA*, September 25, 2008, <http://www.epa.gov/epaoswer/non-hw/reduce/epr/>.

²¹ Thorpe, B. How producer responsibility for product take back can promote eco-design. *Clean Production Action*, 2008, www.amrc.guelph.org/proceedings/fall2008/Bev%20Thorpe.ppt.

European and Japanese electronics and automobile take-back laws have already stimulated DfE even in the United States where Ford designed a car to meet requirements of Europe's program. Take back in the United States, when present at all is voluntary, but some proactive US companies are working on pilot programs, e.g., IBM has an electronics recycling effort.

Product stewardship: barriers and drivers

- Barriers Producers often resist product stewardship. EPR means producers must develop detailed knowledge of their products and of their products' life cycles, which can be costly and time consuming. Some virgin industries have been receiving government subsidies, which they resist giving up. Remaking a take-back product to the same specifications as the virgin-material product may be difficult or more costly.
- Drivers Purchasers who buy large volumes of products – federal, state, and local agencies, universities/colleges and other institutions – can *drive* product stewardship if they choose products designated environmentally preferable (Chapter 11). This provides an incentive for producers to make environmentally preferable products.

Servicizing²²

Transforming a product into a service is *servicizing*. The consumer pays for the function of a product, its *service*, not a physical product. How does this promote dematerialization?

- Recall that Xerox Corporation has leased products for many years, thus stimulating itself to design products that retain usefulness when reclaimed. Xerox has a *Xero-Waste* Initiative, and in 1998 had an 88% recycling rate worldwide. ■ Interface Corp. leases some of its carpets to business: it lays down the carpet as tiles. In heavily-used places, tiles wear out fairly quickly. A representative comes, removes and replaces only those tiles, not the whole carpet.
- *Servicizing stimulates producers to make durable products* because durability is related to profitability. It's an advantage to Interface Corp. that its products be durable. Also, such a business has an incentive to do more with less – less material, less energy, and less water. Servicizing stimulates LCA too because to redesign products producers need to know as much about their life cycles as possible. As one author noted, “information is the lubricant of the transition to a service economy.” Servicizing is a deliberately chosen form of EPR.

Servicizing chemicals^{23,24}

As with other products, the value of chemicals lies in the functions they perform such as cleaning, coating, or lubricating.

²² Nassos, G. Servicizing: a business model for a sustainable environment. *Sustainable Enterprise*, May 12, 2008, <http://www.sustainability.com/blog/2008/05/servicizing-a-b.html>.

²³ Reiskin, E. D., Whie, A. L., Kauffman Johnson, J. and Votta, T. J. Servicizing the chemical supply chain, *Journal of Industrial Ecology*, 3, 2000, 18–31.

²⁴ Stoughton, M. Servicizing: the quiet transition to extended product responsibility. *The Tellus Institute*, 2000, <http://www.epa.gov/nrmrl/std/mtb/pdf/stoughton.pdf>.

- If you sell paint by the gallon, you want to sell as many gallons as possible. But what if a car manufacturer hires you to paint its cars? What the manufacturer wants is not quantity of paint, but a quality paint job. This frees the paint seller to ask, how can I increase the efficiency of paint application and use as few gallons as possible? In one case, a Raytheon facility analyzed its operations and found ways to increase its paint application efficiency and, at the same time reduce paint waste by 71%.
- Navistar produces truck engines. Another company, Castrol Chemical sells coolants, cleaners, and additives to Navistar. Since 1987 the two companies working together reduced coolant use 50% and coolant waste 90%.
- Motorola has begun to have outside managers handle their chemical use with an emphasis on efficiency of chemical use, i.e., using the least amount of chemicals while also using the least hazardous chemicals that will do the job and handling them with maximum safety.

Value of these tools

Regulations are useful for mandating limits on pollutant emissions during production, reuse, recycling and disposal. However, take back and servicing go further. They lead to greater efficiency in the use of materials and energy. When producers retain custody, they have an incentive to look at their products in a totally new way, from “cradle to cradle.”

SECTION IV

Detoxification

When thinking of chemicals, society must consider that many are hazardous or have properties that accentuate toxicity such as persistence or being bioaccumulative (PBT chemicals, Chapters 14 and 15). *Detoxification* involves reducing the use of toxic substances.

Green chemistry: designing chemicals for the environment^{25,26,27}

Green chemistry is DfE applied to chemicals: it “aims to design hazards out of chemical products and processes.” It is sometimes defined as “doing chemistry the way nature does

²⁵ Wiion, S. L. Green chemistry is practical, profitable. *Chemical & Engineering News*, **75**(31), August 4, 1997, 35–43.

²⁶ Hjerresen, D. L. Green chemistry: progress and challenges worldwide. *Environmental Science & Technology*, **35**(5), March 1, 2001, 114A–119A.

²⁷ Green engineering, *US EPA*, September 13, 2007, <http://www.epa.gov/oppt/greenengineering/>. This website includes excerpts from the textbook, *Green Engineering: Environmentally Conscious Design of Chemical Processes*. It also has the complete Green Engineering Educator’s modules in PowerPoint format. Other topics, such as available software tools and additional resources, are also highlighted.



Figure 18.5

The US EPA's design for the environment logo

chemistry.”²⁸ The US EPA has a DfE program that emphasizes chemicals²⁹ (Figure 18.5).³⁰ Green chemistry has one or more of the following goals.

- Change the product: find or design a safer one that performs the same function as the more hazardous substance.
- Change the process: make a chemical using a more environmentally benign process. A process is the series of steps or operations used in manufacturing a substance or product. ■ Careful changes in a process can also result in dematerialization, i.e., more efficient operations that produce less waste.
- Other possible changes include those resulting in less hazardous waste, reduced energy use, or improved competitiveness of chemical manufacturers.

Japan, Italy, the United Kingdom, China, Australia, and the United States are among the countries pursuing both research and applications of green chemistry, working toward alternative chemicals and alternative ways to synthesize them. To promote innovative green chemical technologies, the US EPA makes yearly awards for outstanding achievements, the Presidential Green Chemistry Challenge Awards for projects developed by industry or by the academic world.³¹ The US state of California has started an active green chemistry program.³²

Change the chemical product

The global market for the polymer, *polyacrylate* is about 2 billion pounds(0.9 billion kg) a year. Polyacrylates are used in industry, agriculture, and consumer products. Polyacrylate is the super-absorbent component of disposable diapers. Polyacrylates are inexpensive and

²⁸ Partnerships for safer chemistry. *US EPA*, January 12, 2009, <http://www.epa.gov/dfe/>.

²⁹ (1) DfE screens for safer chemical ingredients. *US EPA*, February 19 2009, <http://www.epa.gov/dfe/pubs/projects/gfcp/index.htm>. (2) Design for the environment, basic information. *US EPA*, November 13, 2008, <http://www.epa.gov/dfe/pubs/about/index.htm>.

³⁰ What does the DfE label on a product mean? *US EPA*, November 13, 2008, <http://www.epa.gov/dfe/pubs/projects/formulat/label.htm>.

³¹ Green chemistry award winners. *US EPA*, August 26, 2008, <http://www.epa.gov/gcc/pubs/pgcc/past.html>.

³² California officials launch green initiative; the plan would help gauge the safety of chemical products. *ASH Institute*, December 22, 2008, http://www.enn.com/top_stories/article/38911.

easy to manufacture. Unfortunately, they “last virtually forever.” ▪ Some years ago, chemists at Donlar and Bayer Corporations noticed that a natural biopolymer, *polyaspartic acid* is chemically similar to polyacrylate. Shellfish produce polyaspartic acid to mold their calcium carbonate shells. It is biodegradable, and moreover, can be synthesized from a non-hazardous chemical, aspartic acid (an amino acid). Markets are potentially huge, but polyaspartic acid is still more expensive than polyacrylate. However, polyaspartic acid has found other uses in agriculture and in water treatment. ▪ Producers continue to seek safer pesticides. One 2008 Green Chemistry award went to Dow for developing the pesticide, Spinetoram, which has low toxicity to non-target species and is effective at 10–34 times lower levels than traditional insecticides, is less persistent, and has low toxicity to non-target species. Spinetoram is now in commercial use.³³ ▪

Change the process used to produce or use the chemical

- US households spend about \$1.5 billion a year on termite control. This typically involves surrounding their homes with a chemical barrier. The SENTRICON system works differently. Monitoring stations containing wood are set up around the home. When, during periodic inspection, termites are detected, bait containing *hexaflumuron* is loaded into the stations. This chemical prevents termites from making chitin, an essential part of their exoskeleton – they cannot molt and they die. Hexaflumuron is not used until termite activity is detected, and then only inside the stations. It is in commercial use, although some question its effectiveness. However, in 2008, China selected it as an alternative to traditional hazardous termite killers.³⁴
- The risks of even an extremely hazardous chemical can be reduced: manufacture it only at the rate it is used so it doesn't accumulate. The very useful, but extremely hazardous chemical, chlorine dioxide provides an example. Processes were developed to make it on site only as needed. And remember (Chapter 1) the extremely hazardous chemical, methyl isocyanate (MIC) used to produce insecticides. It is a chemical that was involved in killing thousands in Bhopal, India. MIC is still used, but can now be made from much less hazardous chemicals. Moreover, once produced it is immediately consumed in a closed-loop process, so that – unlike the situation at Bhopal – large volumes do not accumulate.
- Looking into the future, miniature chemical plants are envisioned as a means to reduce risk. Designers anticipate making chemicals at the sites they are needed using tiny microchip-based chemical reactors – there would be no need for shipping or storing hazardous chemicals. Reactors could be installed wherever needed. If an accident or worker exposure did occur, it would be very small.

Reduce the waste associated with making chemicals

Synthesizing complex chemicals such as some pharmaceuticals can involve multiple step processes. Each step generates some, sometimes much, waste. Thus, “The greenest course of

³³ Designing greener chemicals, Dow Agrosiences, Spinetoram. *US EPA*, August 26, 2008, <http://www.epa.gov/greenchemistry/pubs/pgcc/winners/dgca08.html>.

³⁴ China selects the SENTRICON system as environmentally responsible termite control alternative. *Dow*, July 25, 2008, <http://www.dow.com/greaterchina/en/news/20080807a.htm>.

action is to minimize the number of reactions.” ▪ Zoloft is a well-known prescription drug. To synthesize sertraline, Zoloft’s active ingredient, previously took three steps. A new procedure uses only one step. And, whereas it previously took 60 000 gallons (227 000 liters) of solvent per ton to synthesize sertraline, it now takes 6000. The new process eliminated 485 tons (440 tonnes) of waste titanium dioxide-methylamine hydrochloride salt, 165 tons (150 tonnes) of 35% hydrochloric acid, and 110 tons (100 tonnes) of 50% sodium hydroxide.

Major changes in how chemicals are made

Using green chemistry signals a major change in perspective of how chemicals are made. However, changes are made only on one or at most a few chemicals at a time. Now, green chemists want to “introduce radical new technologies that will transform the nature of chemical use and manufacture.” A futuristic approach to do this was mentioned above, developing miniature chemical plants. Other approaches are to use natural systems, *living organisms or the enzymes that they produce*. Some chemical syntheses are already done using organisms or enzymes, but these are limited whereas chemists envision synthesizing many different chemicals and materials in these manners and to do so using *waste biomass*.

Using natural systems – microorganisms

You have seen how useful microorganisms can be in degrading the organic materials in wastewater, in landfills, and some hazardous wastes (Chapters 10, 11 and 12). However, the talents of microbes can also be used to make specific chemicals. Microbial *fermentation* is already used to make some pharmaceuticals and a few other chemicals. Fermentations with which you are probably familiar include those for making alcohol and vinegar. Compare manufacturing chemicals from petroleum as compared to microbial fermentations (Table 18.2). ▪ **Petroleum** Producing chemicals from petroleum typically requires high temperature and pressure, and also often requires hazardous metal catalysts and hazardous chemicals; hazardous waste is often produced. ▪ **Microorganisms** Microbial fermentations work at low temperature, sometimes room temperature and low pressure. The catalysts used by microbes are enzymes; the enzymes are, of course, synthesized by the microbes themselves. Microbes do not need (cannot usually tolerate) hazardous metals or hazardous chemicals, and microbial waste is biodegradable.

A major obstacle to using microbes to make chemicals is that microbes ordinarily make the chemicals they need for themselves, not what humans desire. Sometimes, incidentally as when a mold synthesizes certain antibiotics, they make enough to satisfy the humans that culture it. However, in other cases we can manipulate microbes using special growing conditions or feedstocks to induce them to make larger amounts of chemicals we desire. ▪ A way we can program microbes to synthesize specific chemicals is *bioengineering* (genetic modification). As noted in Chapter 16, this technique introduces new genes into a microbe so that it synthesizes the desired chemical. Example Billions of pounds of *adipic acid* are

Table 18.2 Chemicals made from petroleum or made by living organisms: how they differ

Chemicals made using	Temperature	Pressure	Catalysts	Type of chemicals made	Waste produced	Closed cycle
Petroleum	Often high	Sometimes high	Hazardous metals often used	Some are not biodegradable; many are toxic	Some is not biodegradable	Not usually
Living organisms or enzymes from them	Ambient temperature	Ambient pressure	Enzymes Metals used are nutrients	Biodegradable, usually non-toxic, but some toxins are made.	Biodegradable	Yes

produced each year as a feedstock to make nylon and other valuable chemicals. Historically, the chemicals, benzene and toluene have been used to make adipic acid. But benzene and toluene are from petroleum, can be risky to use, can contribute to air pollution, and produce hazardous waste. Recently, researchers genetically modified *Escherichia coli* bacteria to induce them to synthesize adipic acid when given the sugar, glucose. The glucose given to the bacteria now comes from cornstarch, but research is ongoing to obtain glucose from agricultural wastes such as corn stalks. In the future, the *E. coli* process may be a valuable means of producing adipic acid and other useful chemicals.

Using natural systems – enzymes

Microorganisms are living organisms. Enzymes are protein catalysts found within all living organisms that catalyze reactions necessary to the lives of those organisms. Thousands of different enzymes exist. Each catalyzes one or a limited number of reactions. So instead of using the whole microorganism, we can extract and purify individual enzymes from microorganisms, plants, or animals. ▪ The isolated enzyme catalyzes a specific reaction (or few reactions) to produce the specific chemicals dictated by that enzyme. This is unlike microbial fermentations where the desired chemical is but one among many chemicals made. Again, because enzymes are selective, there are fewer unwanted by-products. ▪ Other positive attributes are that like living organisms, enzymes cannot tolerate toxic chemicals, hazardous metal catalysts, or high temperature (Table 18.2). Some require a metal to do their work, but the metals are nutrients such as iron. ▪ Certain enzymes make polymers, which may be of special economic importance, polymers that are biodegradable. ▪ There is much hope that enzymes will begin to replace petroleum in the synthesis of many chemicals including some polymers.

Using agricultural and other biological by-products

As noted above, living microbes can make the valuable chemical, adipic acid from glucose. It would be extremely useful if the glucose to be used by the microbes came from waste

organic material (biomass), not from starch. There are many organic wastes: agricultural wastes (corn stalks, rice straw, etc.) as well as waste paper, cheese whey, and industrial sludge from biological processes.³⁵ One company, BioEnergy International has built a pilot-scale plant to produce ethanol and eventually specialty chemicals from organic wastes such as wood and agricultural residues.³⁶ ■ Another attractive feature of waste materials is their “negative cost.” Instead of needing to pay to dispose of waste, it may be possible to obtain the waste for the cost of transport.

Using biochemicals and biopolymers does not eliminate all problems

Both microbial fermentations and enzymes produce waste, often *much* waste such as great masses of microbes (as happens in wastewater treatment plants). As bio-wastes, these can be composted or used as fertilizer. However, whenever large quantities of wastes are produced, transporting and otherwise dealing with them can be difficult. ■ An important reason biomass is considered an attractive source of chemicals and polymers is because it is renewable. This concept is appealing. Corn is promoted as a source of ethanol to add to gasoline (as an oxygenated chemical to promote cleaner burning or just as a fuel). Corn is also used as a source of glucose used to make biodegradable biopolymers. But the net environmental effect may not be positive: much energy is needed to grow corn, so are large amounts of fertilizer and pesticides, which run off into water along with eroded soil. Indeed, there are great concerns that when growing high-volume crops, of which corn is a major example, soil is being mined rather than farmed sustainably. ■ Other questions: should land be used for growing food not for growing biomass to make chemicals? Should it be left as much-needed wildlife habitat? ■ Dow Chemical and Cargill Inc. have built a facility that uses corn as a source of glucose to make the biodegradable polymer, *polylactide*. The biodegradable polylactide can be used in clothing, carpet, diapers, packaging and other products. In the future, producers hope to use agricultural waste from crops such as wheat, rice and other crops as a glucose source. This is a more difficult proposition than using corn. Using waste may make the process more attractive environmentally. However, impacts on soil from which the waste has been removed are not yet clear.

³⁵ There is even hope that manure and sewage sludge could become chemical feedstock. Manure is already used to generate methane (used as a fuel). A prison in Washington State (a US state) generates its own electricity using methane as a fuel. The methane is produced by allowing anaerobic microbes to ferment manure in a closed digester. The manure comes from farm animals maintained on site. ■ Some dairies in Oregon State (USA) also produce methane from dairy manure. ■ And some households in very-poor countries generate enough methane from fermenting manure (produced by their cows) to use as fuel in their homes. But the use of manure or sewage envisioned in this chapter is to use these materials as feedstocks useful in the synthesis of a variety of chemicals.

³⁶ Pennsylvania announces major corn-ethanol plant, cellulosic-ethanol pilot plant. *Green Car Congress*, 17 August 2006, http://www.greencarcongress.com/2006/08/pennsylvania_an.html.

Recycling carpet “forever”

Nylon is a plastic and very difficult to recycle. So when the DuPont Corporation developed an almost closed-loop recycling for nylon carpet, it marked a special success.³⁷ The United States alone uses about 1.4 billion pounds (0.6 billion kg) of new nylon carpet each year. Discarded carpets go to landfills where they don’t biodegrade, enduring indefinitely. Unlike plastic containers such as soda or milk bottles, nylon is not a *thermoplastic*, i.e., it cannot be melted down and then remolded. ▪ To recycle nylon, it must first be depolymerized, broken down into the subunit chemicals from which it was made, processes that do produce some waste. Then the subunits must be purified to meet the same standards as chemicals made from virgin resources. Only then can carpet of quality equivalent to virgin ones be made. ▪ Glues, backing, and other matter associated with old carpets are wastes to be dealt with too. And collecting carpets isn’t easy. Some recyclers obtain used carpets directly from local commercial establishments that rip them out. Dupont and other companies have begun asking municipalities to do curbside carpet collections. They recycle 55 million pounds (25 million kg) of carpet each year. This may seem like a great deal except that the United States alone landfills more than a billion pounds of nylon carpet each year, plus large quantities of other carpets. ▪ Dupont and Evergreen recycle nylon carpets only, but there are many types of carpets, wool and cotton plus other synthetic carpets. An association of European carpet makers collects all kinds of carpets for recycling. In the past these were sorted by hand, but now there is an automated sorting system.

SECTION V

Progress toward zero waste³⁸

Hans van Ginkel, Vice-Secretary General of the UN and Rector of the United Nations University states that “The ultimate goal of Zero Emissions is to create a new type of society that seeks to achieve a social and industrial transformation whereby humankind mimics the sustainable cycles found in the world of nature.”³⁹ Another quote, one from the Grassroots Recycling Network is “Zero waste maximizes recycling, minimizes waste, reduces consumption and ensures that products are made to be reused, repaired or recycled back into nature or the marketplace.”⁴⁰ See Figure 18.6.

³⁷ (1) Tullo, A. H. DuPont, Evergreen to recycle carpet forever. *Chemical & Engineering News*, **78**(4), January 24, 2000, 23–24, http://gertrude-old.case.edu/276/materials/C&ENews/CENNylonfiberrecycle_files/7804bus2.htm
(2) Life cycle studies, nylon. *World Watch Magazine*, November/December, **21**(6), 2008, inside cover, <http://www.worldwatch.org/node/5906>. Also see Block, B. 70 years of “miracle fiber.” *WorldWatch*, October 3, 2008. <http://www.worldwatch.org/node/5899>.

³⁸ Case studies on the way to zero-waste worldwide, <http://www.grn.org/zerowaste/kit/briefing/case1.pdf>.

³⁹ The idea of zero emissions. *United Nations University*, 2002, <http://www.unu.edu/zeff/about.html>.

⁴⁰ Working toward a world without waste. *Zero Waste International Alliance*, <http://www.zwia.org/index.html>.

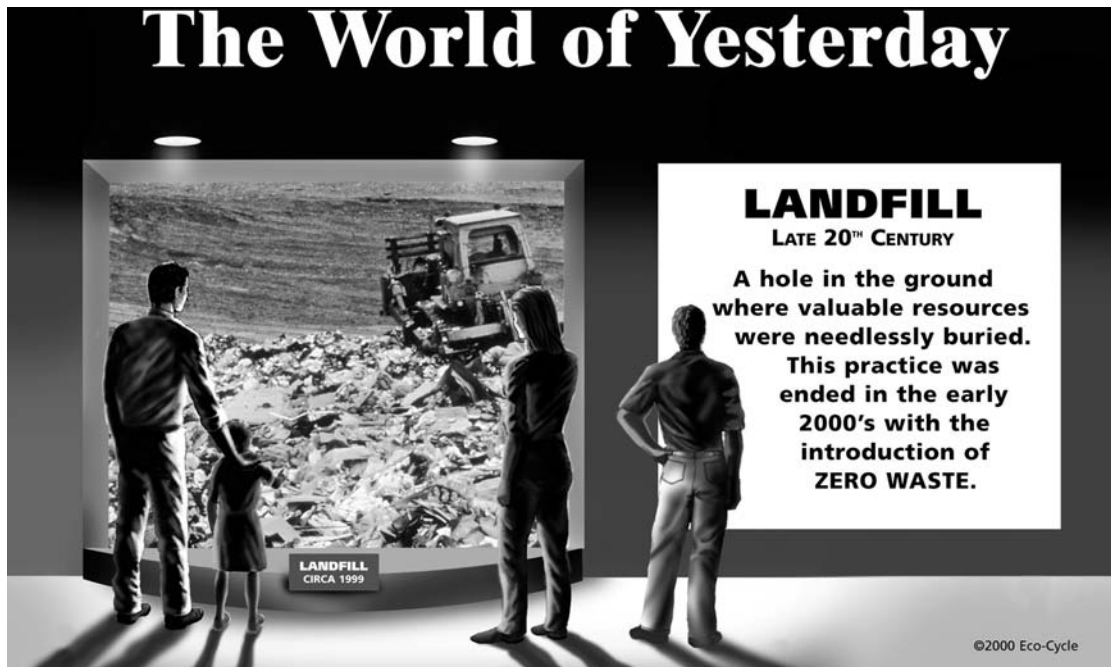


Figure 18.6

Thinking of a landfill in the past tense. Credit: Eco-cycle

Delving deeper: product durability

1. To think about durability, consider a building.^{41,42} A new building can be “green,” state-of-the-art using 40% recycled materials, and be highly energy efficient. Nonetheless if it is built to replace an old building, demolished to make space for it, the new building will take 65 years to recover the energy lost in demolishing and replacing the old one. Demolishing the old building creates huge amounts of waste and pollution and takes energy; subsequently constructing the new building consumes energy and natural resources too. With such information in mind, architect Philip Bess said: “Durability is the most sustainable thing an architect can do.” This situation also implies that retrofitting is worth the cost and effort. ▪ However, people resist durable buildings because they cost more, and many don’t value the long-term benefits or old buildings. For buildings, as for so many other products, the higher initial cost of durably made products represents a barrier to making them.

⁴¹ (1) Sustainability Case Studies (applied to renovation of historic buildings). 2009, <http://www.preservationnation.org/issues/sustainability/sustainability-preservation.html>. (2) Sustainable stewardship, historic preservation’s essential role in fighting climate change. March 27, 2008. www.preservationnation.org/.../Sustainable-StewardshipBerkeley-CA.pdf.

⁴² Leadership in Energy and Environmental Design. *US Green Building Council*, 2008, <http://www.usgbc.org/LEED/>.

2. Choose a product of interest to you, one that you think *should* be durable. Decide how long a time period would represent durability for your product. Then plan whatever combination of actions would be necessary to maintain your product for that period of time, whether it be recycling, disassembling to recover reusable components, remanufacturing, or? Realistically, how long is “forever”? For example, what losses would occur when your product was subjected to an action such as recycling? Under what circumstances could such losses be close to zero or very low? Note social barriers to making the product durable. Summarize your conclusions.

Corporations committing to zero waste and sustainability⁴³

Some corporate facilities have greatly reduced their solid waste generation.⁴⁴ See the Subaru example in Box 18.4. Xerox’s xero-waste program has been noted too. Other examples are Epson, an Oregon computer-printer maker that recycles 90% of its materials and incinerates the rest for energy. Other companies include Pillsbury (Minnesota), which diverts 96% of its waste and is working toward 100%.

- Fetzer Vineyards in California cut its garbage generation 93% and is aiming for zero. It did so by composting large quantities of grape seeds and corks, committing to buying recycled products, and using recyclable packaging for all its products. Fetzer is also using lighter glass bottles.⁴⁵ It also developed enough solar capacity to power its buildings and fill and cap 1.2 million bottles of wine each year. Fetzer also converted its vineyards to organic agriculture, which eliminated pesticide emissions.
- *Being sustainable means more than zero-waste.* A company must also rethink all stages of the life cycle for each of its products. Interface, Inc. is a carpet company, vigorously pursuing the goal of sustainability. To Interface this means “to take nothing from the Earth that is not renewable and do no harm to the biosphere.” One of Interface’s programs, Evergreen Lease was noted above.⁴⁶ ■ Other companies are also striving to varying extents to pursue principles of sustainable development.

⁴³ Dow Jones Sustainability Indexes. 2008, http://www.sustainability-index.com/07_html/sustainability/corpsustainability.html.

⁴⁴ Orzech, D. At clean plants, it’s waste not. *WIRED*, August 10, 2005, <http://www.wired.com/science/planetearth/news/2005/08/68448>.

⁴⁵ Fetzer vineyards convert to lighter glass bottles. *GreenBiz*, October 19, 2008, <http://www.greenbiz.com/news/2008/10/19/fetzer-vineyards-converts-lightweight-glass-bottles>.

⁴⁶ *Interface, Inc.* 2008, <http://www.interfaceglobal.com/Company/Mission-Vision.aspx>. “We believe that there’s a cure for resource waste that is profitable, creative and practical. We must create a company that addresses the needs of society and the environment by developing a system of industrial production that decreases our costs and dramatically reduces the burdens placed upon living systems. This also makes precious resources available for the billions of people who need more. What we call the next industrial revolution is a momentous shift in how we see the world, how we operate within it, what systems will prevail and which will not . . . Our vision is to lead the way to the next industrial revolution by becoming the first sustainable corporation, and eventually a restorative enterprise.”

Box 18.3

A government intervention to promote reuse of PVC

Dealing with the plastic, polyvinyl chloride (PVC) at the end of its useful life is a problem.⁴⁷ If landfilled, it does not degrade. If incinerated, hydrochloric acid and other pollutants are produced. In Japan a PVC recycling system was set up. Construction waste is carefully collected and sorted. PVC waste is recycled into new PVC pipes and window frames. Recycled PVC costs more than virgin PVC. To overcome this cost difference, the Japanese government subsidizes PVC recycling, obtaining the funding to do so by imposing a tax on construction sites. The result is a market price for recycled PVC window frames similar to virgin PVC. To further boost sales, the government encourages the construction industry to choose recycled window frames. This action has led to a transition from using virgin PVC to recycled PVC.

Box 18.4

Environmentally benign manufacturing (EBM)⁴⁸

EBM addresses the question of “how to achieve economic growth while protecting the environment.” A panel examining EBM asked the question, “Is ‘*environmentally benign manufacturing*’ an oxymoron?” The EBM panel (sponsored by the US National Science Foundation and the US Department of Energy in the late 1990s) examined manufacturing sectors making plastics, electronics, automobiles, and metal products in the United States, EU, and Japan. EBM, sometimes called smart or lean production focuses on technologies that can ameliorate manufacturing’s environmental impact. (Also see green engineering.⁴⁹) The panel, chaired by Dr. Timothy Gutowski of the Massachusetts Institute of Technology visited EU, United States, and Japanese sites producing metal products, polymers, automobiles, and electronics. Their report discussed environmental problems of each sector starting with raw materials extraction to manufacturing, product use and recycling. It identified technologies that would be needed if EBM were to become a reality. EBM also leads to advantages such as efficient production, flexibility from regulatory agencies, and a more positive corporate image.

Progressive companies see striving for absolutely minimal waste as the thing to do. The EBM panel found one Toyota assembly plant in Japan producing only 40 lb (18 kg) of landfill waste per vehicle produced. Today (2009) a zero-waste philosophy has spread beyond Japan. A Subaru factory in Indiana diverts 99.8% of its waste from the landfill, doing so by separating, reusing, or recycling various materials. Importantly it strives to use fewer resources to begin

⁴⁷ Environmental issues of PVC. *Commission of the European Communities*, July 26, 2000, http://www.pvcinformation.org/assets/pdf/EU_PVC_wasteReport.pdf.

⁴⁸ Gutowski, T., Murphy, C., Allen, D. *et al.* Environmentally benign manufacturing: observations from Japan, Europe and the US. *Journal of Cleaner Production*, 13, 2005, 1–17, [http://web.mit.edu/ebm/www/Publications/EBM in Japan, Europe and US.pdf](http://web.mit.edu/ebm/www/Publications/EBM%20in%20Japan,%20Europe%20and%20US.pdf).

⁴⁹ (1) What is green engineering? *US EPA*, September 13, 2007, http://www.epa.gov/oppt/greenengineering/pubs/whats_ge.html (This site has an excellent figure, “Proliferation of environmental laws and regulations.”) (2) Anastas, P. T. and Zimmerman, J. B. Design through the 12 principles of green engineering. *Environmental Science & Technology*, 37(5), March 1, 2003, 94A-191A. (3) Green engineering for a sustainable environment. *US EPA*, September 13, 2007, <http://www.epa.gov/oppt/greenengineering/>.

leaving less waste.⁵⁰ Illustrations: the Subaru factory stamps out its car roofs and bodies from a sheet of metal of a size calculated with such precision that very little metal remains behind to be recycled. When defects occur in plastic bumpers, these are ground into pellets used to make new bumpers. Personnel found that some protective shrink wraps used for shipping could be eliminated. Styrofoam inserts that protect engine parts during shipping are reused until they no longer can be and, thereafter, the styrofoam is recycled. Many other often small changes have been made to reduce waste. Indeed, factory personnel find themselves thinking about and discussing other means to reduce waste; they have had a change in mindset.

The EBM panel compared Japan, Europe, and the United States in terms of how geographic constraints, cultures, and governments affected EBM strategies. Japan has a strong culture of avoiding waste and saving resources; it practices *kaizen*, continuous improvement which has as one tenet – muda – reducing waste. The EU, like Japan also pays close attention to how it uses increasingly scarce green space, and there is a strong relationship between industry and government. In the EU, issues such as recycling are ingrained in its citizens, and take-back product stewardship has become important. • An encouraging finding was that manufacturers, especially international firms showed “a clear trend towards ‘internalization’ of environmental concerns”⁵¹ Moreover, the companies that successfully pursued EBM were also able to integrate “technology, economic motivation, regulatory actions and business practices.” The EBM panel came away convinced that many companies really do understand that their long-term success is based on a sustainable business policy and environmental sustainability.

Cities and countries committing to zero waste⁵²

Cities

- Canberra, Australia (population 340 000) has adopted zero waste as a goal. To demonstrate its commitment, Canberra is working to eliminate its landfills and replace them with Resource Recovery Estates, each with a processing plant to separate and reprocess useful materials. Some products are recycled; other companies on the site use “wastes” as resources to make other products (See Figure 2.2).⁵³
- Seattle, Washington (population 600 000) had been discouraged because, despite persistent effort, its recycling rate remained under 40%. In 1998, Seattle decided to change its philosophy and go zero waste,⁵⁴ “managing resources instead of waste, conserving natural resources through waste prevention and recycling, turning ‘trash’ into jobs and

⁵⁰ Woodyard, C. It’s waste not, want not at super green Subaru plant. *USA TODAY*, February 19, 2008, http://www.usatoday.com/money/industries/environment/2008-02-18-green-factories_N.htm.

⁵¹ World Business Council for Sustainable Development, 1997–2009, <http://www.wbcsd.org/templates/TemplateWBCSD5/layout.asp?MenuID=1>

⁵² (1) Local governments for sustainability. *ICLEI*, 1995–2008, <http://www.iclei.org/index.php?id=643>. (2) Around the world, http://www.grn.org/zerowaste/zw_world.html.

⁵³ Canberra Australia zero-waste initiative. *Canberra*, 2005, http://www.green-alliance.org.uk/uploadedFiles/Our_Work/Canberra.pdf.

⁵⁴ Zero-waste goal in city’s solid waste plan. *Zero Waste*, http://www.grn.org/zerowaste/articles/seattle_1998.html.

products, promoting durable products and materials, and discouraging products that can only become trash after use.”

- Several other US cities have created resource recovery parks wherein a city creates a central location for recycling, composting, and reuse facilities. New manufacturing and retailing facilities co-locate to use incoming materials. ▪ Many communities compost leaves and yard waste, but still leave much compostable materials in their municipal solid waste (MSW) stream. About 15% of US MSW is food. Perhaps twice that much is un-recyclable paper such as contaminated fast food wrappers. Such organic material can be composted. ▪ There are many other ways to reduce MSW; see Section II of Chapter 11.

Countries embracing or actively moving toward zero waste

- New Zealand⁵⁵ is committed to zero waste. Its government issued a challenge to its citizens in 1999: move from waste management to waste elimination by 2020. Its vision applies three core principles: 1. End cheap waste disposal, which it believes has helped create a “hugely inefficient industrial system that externalizes costs to the environment and future generations.” 2. Design waste out of the system by incorporating waste-reduction technologies at all points along the supply chain, DfE. Anyone designing a product will first think about the need for it, and then ensure that no waste is created in its production, use, and final return to the human economy or nature. 3. “Engage . . . every person at a national and community level in our quest for Zero Waste. . . . unleash the creativity and energy of communities, businesses and institutions in its pursuit.”
- Japan is making great strides in reducing waste and energy use. In Box 18.4, note Japan’s strong work with EBM. And, recall that Japan is, along with the EU at the forefront of take-back programs. ▪ More generally, Japan is committed to “the 3Rs – reuse, recycle, and reduce.” With little space for land fills (Figure 11.10) Japan incinerates 80% of its waste. One city, Yokohama⁵⁶, gives residents a 27-page booklet with detailed instructions on how to sort 518 items of garbage into 10 categories. This exacting effort is seen as no more expensive than incineration. Japan also does “urban mining,” extracting precious metals from waste electronics and other metal-containing products.⁵⁷ But recall (Chapter 12) that great quantities of waste electronics are dumped in less-developed countries for “recycling.” Japan works to prevent such illegal trade. Moreover, it assists less-developed countries to develop the capacity to properly treat waste electronics and other recyclables. It also requires the recycling of all cell phones. ▪ Energy: a New York Times article noted that “Japan’s single-minded dedication to reducing energy use is a commitment that dates back to the oil shocks of the 1970s that shook this resource-poor

⁵⁵ Zero waste. *New Zealand Trust*, 2008, <http://www.yha.co.nz/Sustainability/WhatWeDo/ZeroWaste/>. See also Target zero, Canada, <http://www.grm.org/zerowaste/articles/tzc.html>.

⁵⁶ Onishi, N. How do Japanese dump trash? Let us count the myriad ways. *New York Times*, May 12, 2005, <http://www.nytimes.com/2005/05/12/international/asia/12garbage.html>

⁵⁷ Newcomb, A. Japan as ground zero for no-waste lifestyle. *Christian Science Monitor*, December 16, 2008, <http://www.csmonitor.com/2008/1216/p01s04-woap.html>. A Dow Eco-System Recycling Co. official stated that a ton (0.9 tonnes) of earth may yield 5 g of gold when mined, while causing significant environmental damage. However, a ton of cell phones contains 1.1 pounds (400 g) gold as well as 0.9 pounds (500 g) silver and 0.1 ounce (4 g) palladium.

nation.”⁵⁸ Japan is “by many measures the world’s most energy-frugal developed nation.” In 2005, Japan consumed half as much energy per dollar’s worth of economic activity as the EU or the United States, and one-eighth as much as China and India. Even when energy was cheap it continued to invest in energy research and development. Lower energy use means, of course lower carbon dioxide emissions and lower emissions of other significant air pollutants (Chapter 5). ■ However, Japan does not have a sustainable environment. The fact that this nation, which is making a major effort, still has far to go indicates how greatly other nations need to be following Japan’s path

Delving deeper

1. Go to the web and further investigate Kalundborg, how the industrial symbiosis system got started, why it is useful to them, what is working well, what problems have arisen, and what else needs to be done. Prepare an oral or written report. Also address why the United States finds setting up such systems to be more difficult than do European countries.
2. Durability is a key need for the products that we produce, but how do we let go of the “need,” the desire for something new, with new being perceived as better? Develop your own ideas individually while several others do the same. Then, discuss the issue as a group. Come up with a report that next year’s class can use as a *starting* point for their own deliberations.
3. Reduced consumption could damage the economy. How could this be mitigated or even avoided? Start with examining material from the International Society for Ecological Economics: <http://www.ecoeco.org/>. Write a report or make a presentation.
4. An individual commitment to zero waste: to further develop your environmental consciousness and what meaningful actions you could take, carry out the following exercise: choose an internet site (one given here⁵⁹ or one of special interest to you). Spend time pondering the information provided. Then – as if you really intended to follow your own plan – design a project to reduce waste and pollution, one that you could start by yourself, with friends or your community. What will you accomplish and how will you accomplish it?

The Environmental Performance Index⁶⁰

Early in this chapter you noted the reductions in air and water emissions made in the United States. More generally, how well are humans caring for their environments? There is a lack

⁵⁸ Fackler, M. Japan sees a chance to promote its energy-frugal ways. *New York Times*, July 4, 2008, <http://www.nytimes.com/2008/07/04/world/asia/04japan.html>.

⁵⁹ Possible internet sites include the following. (1) Wastes, what you can do (in your home, community, office and at the store). *US EPA*, October 8, 2008, <http://www.epa.gov/epawaste/wycd/index.htm>. (2) Fisk, U. A consumption manifesto: the top ten principles of good consumption. *WorldWatch*, <http://www.worldwatch.org/node/1470>. (3) The Consumer’s Handbook for Reducing Solid Waste. *US EPA*, September 12, 2008, <http://www.epa.gov/epawaste/wycd/catbook/index.htm>. (4) In the quest for sustainable stuff, <http://susdev.agecon.vt.edu/worksheets/Green%20Technologies%20Worksheets.pdf>.

⁶⁰ (1) Environmental Performance Index. *Yale and Columbia Universities*, 2008, <http://epi.yale.edu/Home>. (2) Guterl, F. and Sheridan, B. Green Countries, a global report card on nations doing the most, and least, to clean up the environment. *NEWSWEEK*, July 7–14, 2008, <http://www.newsweek.com/id/143678/output/print>. (3) Also

of good data to answer this question, and some nations do not speak truthfully about their environment. So it's often difficult to precisely rate the performance of various governments, let alone to discuss sustainability and zero waste/zero emissions. ▪ Despite these constraints, Yale and Columbia University researchers using the best information they could find, analyzed and ranked the world's countries using an *Environmental Performance Index* (EPI). The highest score is 100.

▪ Not surprisingly, Japan has a high EPI. So do many EU countries, especially Germany and France. Among factors contributing to Germany's rating is good regulation of pesticides, of water use and quality, good management of natural resources, good recycling, and investment in alternative energy. The United States does not rank as highly among nations in its income class (including the EU and Japan) primarily due to high greenhouse gas emissions, much of which result from coal burning. Other rich countries that didn't do well on the EPI were Belgium and, surprisingly the Netherlands.

The EPI study had some revealing results. ▪ Recall from earlier chapters the description of China's pollution and environmental degradation. China claims that it cannot afford superior environmental performance. However, China's EPI ranking was the lowest among the 15 nations in its income group even behind Vietnam. ▪ It is true that poor countries generally have poor ratings. Take India where hundreds of millions of people lack proper sanitation, clean drinking water, or reliable energy, and where often severe air pollution affects both human health and the environment. ▪ However, *good governance*, even in poor countries can enhance environmental performance. In sub-Saharan Africa many countries have poor EPI scores. But one sub-Saharan country, Tanzania, ranks ahead of even the wealthy United Arab Emirates. It also ranks highest among those nations (the poorest 10% of nations) in its income group. One reason for this is that Tanzania has a stable government, one which works to care for its environment.

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This chapter assumes that the student has had little or no chemistry. First, recognize that chemicals are not something “out there.” The whole Earth is composed of chemicals. So is your body. You breathe in chemicals with each breath, you eat chemicals – all food is composed of chemicals – and you excrete chemicals. So chemicals are not just synthetic chemicals, i.e., not just chemical pollutants. Rather, everything you touch, taste, or smell is chemical in nature.

After introducing necessary concepts, the chapter selects several pollution issues from earlier chapters in this text and explains them from a simple chemical perspective. Section I introduces the atom and its subatomic particles, as well as isotopes; and then goes on to chemical bonds and valence. Section II overviews organic and inorganic chemicals, and then moves on to free radicals and their capability to sometimes help solve pollution problems but, in other cases worsening them. Section III looks at oxidation reactions from the perspective of burning fossil fuels. Avogadro’s constant and the mole are also introduced. Finally, Section IV uses simple chemistry to overview two major acid pollution problems: acid deposition and ocean acidification.

SECTION I

Atoms^{1,2}

An element is the fundamental form of matter. Each element is composed of atoms, which cannot be further subdivided. There are 92 natural elements. Among them are familiar names such as iron, gold, sodium, calcium, and carbon. ▪ The atom of every element contains a nucleus and a shell of electrons. Within the nucleus are found protons and neutrons. ▪ A proton³ is a subatomic particle found in the nucleus of the atom; it has an electric charge of +1 and an atomic mass (weight) of 1. The number of protons in the nucleus is specific to a particular element and the number of electrons is equal to the number of protons. Because the number of protons and electrons is equal, the atom has no net charge.

¹ M. J. Farabee *Atoms and molecules*. 2007, <http://www.emc.maricopa.edu/faculty/farabee/BIOBK/BioBookCHEM1.html>.

² Barbalace, R. B. Anatomy of the atom, *Environmentalchemistry.com*, 1995–2009, http://environmentalchemistry.com/yogi/periodic/atom_anatomy.html#AtomicMass.

³ Proton. *Wikipedia*, February 22, 2009, <http://en.wikipedia.org/wiki/Proton>.

Box 19.1

Hints of a greater complexity

Many simplifications are necessarily used in this chapter. ▪ One is the formula given for a molecule. It is written as if the atoms and molecules are linear structures, e.g., H-O-H or CH₄. In actuality, most molecules are three-dimensional as indicated for water and methane in Figure 19.1. However, these representations are also inadequate. But a few molecules really *are* linear; carbon dioxide, CO₂ or O::C::O is one. Knowing orientations is helpful in understanding what happens in chemical reactions. ▪ Or, in Figures 19.3 through 19.6 the electrons around an atom are shown as solid dots. Although electrons are believed to be “point particles,” they are believed to exist as electron clouds surrounding the nucleus in specific orbitals. Exactly where one is located at any time is not known.

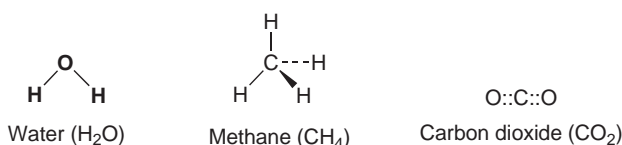


Figure 19.1

The configuration of H₂O, CH₄, and CO₂

▪ Another particle is also within the nucleus, the neutron.⁴ The neutron has no charge, but has the same mass as a proton. ▪ The electron⁵ has an electric charge of -1 . In comparison to the proton and neutron, an electron is tiny, weighing 1836 times less than the proton. Nevertheless, electrons add greatly to the *size* of the atom because they are spread out in “electron clouds” at varying distances from the compact nucleus.

The periodic table⁶

Follow the periodic table of the elements (Figure 19.2) as you read the next few paragraphs. The first element in the periodic table (upper left) is hydrogen (H).

- The 1 above the H is its *atomic number*, which equals the number of protons in an element. With only one proton, H has an atomic number of one. ▪ The number of electrons equals the number of protons meaning the H atom has one electron.
- The *atomic mass* (atomic weight) of the element equals the number of protons plus the number of neutrons in an atom of the element. The atomic mass is the number shown below each element. For H, the atomic mass is 1.008. (The reason its value is slightly more than 1 will be given below.)

⁴ Neutron. *Wikipedia*, February 23, 2009, <http://en.wikipedia.org/wiki/Neutron>.

⁵ Electron. *Wikipedia*, February 28, 2009, <http://en.wikipedia.org/wiki/Electron>.

⁶ The periodic table. *Wikipedia*, February 23, 2009, http://en.wikipedia.org/wiki/Periodic_table.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.007 94	2 He 4.002 602	3 Li 6.941	4 Be 9.012 182	5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.998 4032	10 Ne 20.1797	11 Na 22.989 770	12 Mg 24.305	13 Al 26.981 538	14 Si 28.0855	15 P 30.973 761	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955 910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938 049	26 Fe 55.845	27 Co 58.933 200	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.64	33 As 74.921	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.4678	38 Sr 87.62	39 Y 88.905 85	40 Zr 91.224	41 Nb 92.906 38	42 Mo 95.94	43 Tc 97.9072	44 Ru 101.07	45 Rh 102.905 50	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.904 47	54 Xe 131.293
55 Cs 132.905 45	56 Ba 137.327	57–71 lanthanoids	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.966 55	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.980 38	84 Po [209.9871]	85 At [209.9871]	86 Rn [222.0176]
87 Fr (223.0197)	88 Ra (226.0254)	89–103 actinoids	104 Rf (261.1088)	105 Db (262.1141)	106 Sg (266.1219)	107 Bh (264.12)	108 Hs (277)	109 Mt (268.1388)	110 Ds (271)	111 Rg (272)							
57 La 138.9055	58 Ce 140.116	59 Pr 140.907 65	60 Nd 144.24	61 Pm (144.9127)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.925 34	66 Dy 162.500	67 Ho 164.930 32	68 Er 167.259	69 Tm 168.934 21	70 Yb 173.04	71 Lu 174.967			
89 Ac (227.0277)	90 Th 232.0381	91 Pa 231.035 88	92 U 238.028 91	93 Np (237.0482)	94 Pu (244.0642)	95 Am (243.0614)	96 Cm (247.0704)	97 Bk (247.0703)	98 Cf (251.0796)	99 Es (252.0830)	100 Fm (257.0951)	101 Md (258.1097)	102 No (259.1010)	103 Lr (262.1097)			

Figure 19.2 The periodic table⁵⁰ of the elements. Credit: International Union of Pure and Applied Chemistry, November 1, 2004

Notice that H, atomic mass of 1.008, is the lightest of any element in the periodic table. For any given row, the atomic mass of elements increases as you move from column 1 to column 18 of the table. Likewise, within any given column the atomic mass increases as you move down the column. As an illustration, find the row beginning with Cs (cesium), atomic mass 133. Move along this row until you reach Hg (mercury) with its atomic mass of 200 and then Pb (lead) with a mass of 207. An atom of mercury weighs nearly 200 times more than hydrogen, and lead nearly 207 times more. And notice the atomic numbers for mercury and lead. Mercury has 80 electrons and lead has 82. Within each column of the table, the elements have characteristics that they share in common. For example, the elements in column 1 (except for hydrogen) are the alkali metal elements, those in column 17 are the halogens and those in column 18 the inert (or noble) gases.

Neutrons

Look at Li (lithium) the element below H in the periodic table. Its atomic number is 3 meaning it has three protons, so its unit weight is 3. However, its atomic mass is 6.941. The reason is that each nucleus contains *neutrons* as well as protons⁷, with each neutron weighing as much as a proton. So, the atomic mass equals the number of protons plus the number of neutrons. At this point, you might guess that, with a mass of 6.94, there are four neutrons in Li. But if this is the case, why isn't the atomic mass an even 7?

Isotopes

▪ The reason that the atomic masses shown below each element are not even numbers is because the number of neutrons can vary within any given element – an element has *isotopes*. An isotope has the same atomic number but a different mass. ▪ Go back to H with its atomic mass of 1.079. From this uneven number you may guess that even this smallest of elements has isotopes. Hydrogen-1 (^1H) – atomic mass 1 – is, by far the most abundant isotope and has no neutron. ▪ But there is also a hydrogen-2 (^2H) called deuterium; much less abundant than ^1H it *does* have a neutron (so one neutron plus one proton yields an atomic mass of two. Hydrogen-3 (^3H) called tritium is the third isotope of H; with two neutrons its atomic mass is three. Tritium is very rare in nature. The atomic mass of hydrogen is 1.079 because it averages the mass of all three isotopes including the relative abundance of each. ▪ Going back to Li: its atomic mass, 6.941 averages the mass of five isotopes, and the relative abundance of each. Except for properties related to mass, the properties of isotopes are the same.

The existence of isotopes is often very useful to environmental chemists. ▪ One of a number of instances is in the analysis of ice-core bubbles. Remember (Chapter 7) the ability to calculate the temperature of years long past by examining the relative abundance of oxygen-16 to that of the isotope, oxygen-18 in air bubbles trapped in ice cores. Oxygen-18 is

⁷ ^1H is an exception among the elements in that it has no neutrons. However ^2H has one neutron and ^3H has two.

not just rare compared to oxygen-16 (the predominant oxygen isotope) but, because it is heavier than oxygen-16, less of it evaporates into the air during cooler weather. Using this fact as a starting point, and the relative proportion of oxygen-18 to oxygen-16 in ice core bubbles, it became possible to calculate the temperature corresponding to each point in the ice core going back hundreds of thousands of years.⁸

Radioactivity Some isotopes are stable, i.e., the number of neutrons in the nucleus of a given isotope always remains the same. However, some isotopes have one difference in addition to a different mass. To explain, let's examine H again: deuterium with its one neutron is a stable isotope, but tritium with its two neutrons is not. It undergoes radioactive decay, it is a radioisotope. ■ You saw above that Li has five isotopes; two of these are radioactive. ■ The radioactive isotopes of various elements are also very useful to earth and environmental scientists.

Electron configurations and valence⁹

In Figures 19.3–19.6, the electrons around the elements are represented as solid dots in the circles around the nucleus. Also, for each element in these figures, note that there is an innermost shell with two electrons, which is all that particular shell needs to be full. It is the electrons in the outer shell, the valence electrons that we pay attention to. As you examine Figure 19.3, think of the number eight. To be stable (*not* reactive) an element needs eight electrons in its outer shell, the stable octet.

- Look at *neon* (Ne), a noble element with its full outer shell of eight electrons. As is the case with the other elements in column 18 of the periodic table, Ne is stable and does not participate in chemical reactions. **Keep in mind:** when other elements react with one another, they do so in a way that will result in a stable octet.
- Now examine *fluorine* (F) in this figure. F is an atom that is very reactive. Count the number of electrons in its outer shell – there are seven. F needs one more electron for a full valence shell. F is *electronegative*, needing to take an electron from another atom or molecule to become stable.
- Finally, look at *lithium* (Li). It has only one electron in its outer shell. It is also very reactive but, in this case, it is reactive because it needs to give up that one electron. Lithium is *electropositive*, readily giving up an electron to another element or molecule.



Figure 19.3

Representations of the atoms neon, fluorine, and lithium

⁸ Thomas, E. The behavior of isotopes of hydrogen and oxygen: heavy and light rain. *Wesleyan University*, <http://ethomas.web.wesleyan.edu/ees123/isotope.htm>.

⁹ Electron Dot Structure: Shell Diagrams For The First 20 Elements. *Green-Planet-Solar-Energy.com*, February 27, 2009, http://environmentalchemistry.com/yogi/periodic/atom_anatomy.html#AtomicMass. Also see: The electron dot diagram, the basics of bonding. *Green-Planet-Solar-Energy.com*, February 27, 2009, <http://www.green-planet-solar-energy.com/electron-dot-diagram.html>.



Figure 19.4

Representations of the atoms oxygen, nitrogen, and carbon

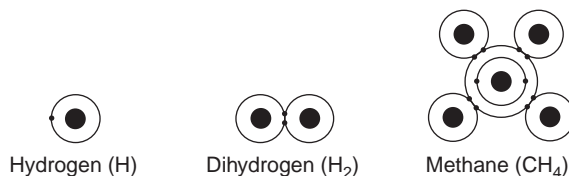


Figure 19.5

Representation of the hydrogen atom plus two simple compounds of hydrogen

Valence¹⁰

The word *valence* means the number of electrons that an atom must gain or lose to achieve the stable octet. Another way to consider valence is as the “combining capacity” of an atom as “determined by the number of electrons that it will lose, add, or share when it reacts with other atoms.”

- Look again at Figure 19.3.
 - Fluorine has seven electrons in its valence shell, needing only one more to form the stable octet. It has a valence of one. The highly reactive F atom readily bonds with many elements, including itself. If it bonds with another F atom, the product is F₂. In F₂, the two F atoms share electrons, so both have a stable octet.
- Go to Figure 19.4.
 - Oxygen (O), the first element illustrated has an outer shell with six electrons. It needs two more to form the stable octet. Its valence is two. As shown, e.g., in the water molecule, H₂O (or H-O-H) oxygen is bonded to two hydrogen atoms. (You may correctly surmise from this that the valence of H is one.)
 - Note that nitrogen (N) has five electrons. It needs three more, so its valence is three. A common compound that N forms is ammonia with three hydrogens, NH₃.
 - And carbon (C) – so all important to life – has only four electrons. It needs four more.¹¹ Its valence is four. The simplest example of an organic C compound is methane, CH₄ (Figure 19.5).

¹⁰ Reusch, W. Virtual text of organic chemistry: structure and bonding. 1999, <http://www.cem.msu.edu/~reusch/VirtualText/intro2.htm>.

¹¹ Metal atoms such as copper and iron often have more than one valence.

Hydrogen and lithium

Several very light elements are *exceptions* to the stable octet as they have too few electrons. For these elements, think about the innermost shell, which needs only two electrons to be full. Examine Figure 19.5.

- Hydrogen (^1H) has only one electron. It needs one more to be stable. So H has a valence of one. If another H atom is available, the two will react to form H_2 gas (Figure 19.5): they share the pair of electrons. Other examples given in the paragraph above also indicate the valence of one for hydrogen: H_2O , NH_3 , and CH_4 . ■ Hydrogen very often reacts with carbon to form organic compounds (described later in this chapter). A major group of compounds formed by the reaction of H with C is the hydrocarbons such as those in petroleum or coal. The simplest hydrocarbon is methane. A carbon atom with its valence of four reacts with four hydrogens to form methane, CH_4 (Figure 19.5).
- The very reactive lithium (Figure 19.3) is another light element. Li has two electrons in its inner shell, but only one in its outer shell. To be stable, it must lose that outer electron. So Li, like H, has a valence of one.

Chemical bonds

A molecule is a chemical that contains two or more atoms held together by chemical bonds. The atoms in a molecule can be from the same element¹² or different elements (as with carbon and hydrogen in hydrocarbons, or hydrogen and oxygen in water). Most molecules contain at least two elements. ■ As indicated above, the one group of atoms that doesn't bond with other elements is the inert (noble) gases (column 18 of the periodic table, which begins with helium (He) at the top and ending with radon (Rn) at the bottom. It is difficult to get these six elements to react and form chemical compounds as each already has its eight electrons.

Covalent bonds¹³

In a covalent bond the atoms *share* electrons – as shown for H_2 in Figure 19.5. Also see the diagram for methane, CH_4 . Notice that each of the four hydrogens in CH_4 is sharing a pair of electrons with carbon. Each H now has a stable configuration, and carbon has formed the stable octet. ■ Covalent bonds are found in countless chemicals. You may remember from earlier chapters the names of chemicals such as carbon monoxide (CO), methane (CH_4), ammonia (NH_3), oxygen (O_2), nitrogen (N_2), formaldehyde (HCHO), benzene

¹² About 99% of the Earth's atmosphere is composed of *diatomic* molecules, molecules containing two atoms of the same element. Nitrogen (N_2) accounts for 78% of the atmosphere. Oxygen (O_2) accounts for 21%. Other diatomic molecules include hydrogen (H_2), fluorine (F_2), and chlorine (Cl_2).

¹³ Clark, J. Covalent bonds—single bonds. 2000, <http://www.chemguide.co.uk/atoms/bonding/covalent.html#top>.

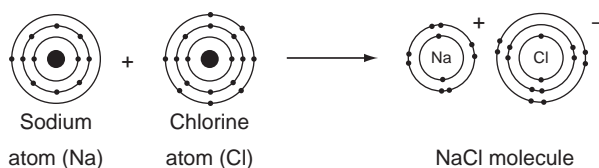


Figure 19.6

Sodium and chlorine react to give sodium chloride

(C_6H_6 ¹⁴), etc. All these have covalent bonds. ▪ The atoms and chemicals shown in this chapter are deliberately chosen to be simple. However, many chemicals with covalent bonds are complex, some extremely complex such as proteins and nucleic acids synthesized by living creatures.

Ionic bonds

Even in a covalent bond, sharing a pair of electrons does not mean that they are shared equally. For instance, the very electronegative fluorine takes more than its share of the electric charge. Such a bond is called polar covalent. ▪ Knowing that an unequal sharing can occur, an *ionic bond* may not surprise you. In an ionic bond, the elements involved do not share electrons. Rather, one element takes one or more electrons away from the other, gaining a negative electric charge in the process leaving the other element with a positive charge. ▪ Common table salt, sodium chloride, NaCl, has an ionic bond, which results from a reaction between sodium (Na) and chlorine (Cl).¹⁵ See Figure 19.6.

- As noted above, fluorine (in the halogen family, column 17) is very electronegative, i.e., strongly attracted to electrons. So is its relative, chlorine (although Cl is less intensely electronegative).
- Also noted above, lithium (in the alkali metal family, column 1) is electropositive with a strong tendency to donate an electron. So is its relative, sodium (although Na is less electropositive than Li.)
- So when Na and Cl meet, they readily react to yield NaCl: sodium gives up its one electron to become a positive ion, a *cation*. Chlorine takes that electron to become a negative ion, an *anion*.

¹⁴ Benzene is different than the other chemicals in this list of compounds. It is a cyclic molecule with three *double* bonds. It is the simplest of the so-called aromatic compounds. A double bond means that the elements involved in the bond share *two* pairs of electrons. Quite often you see aromatic compounds represented with inner circles rather than the line representation for double bonds. Sharing the electrons in the way that benzene and other aromatic compounds do makes them stable. Conversely, non-cyclic molecules, which contain double (or triple) bonds are very reactive. An example of a simple linear molecule is *pentane* which will be seen when discussing gasoline combustion. The structure of an aromatic chemical more complex than benzene is seen in Figure 19.7.

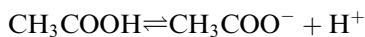
¹⁵ See column 1 of the periodic table: sodium is in the same family of elements as lithium. A family, in this case the alkali metal family, shares similar chemical properties. Sodium is a heavier element than lithium and has 11 protons and 11 electrons. Now see column 17. Chlorine is in the same chemical family as fluorine. Chlorine is a heavier element than lithium with 17 protons and 17 electrons.

- The fact that one element takes and another gives up electrons doesn't mean that ionic species are not bonded. There are strong electrostatic forces. ▪ Note something else about ionic bonds: Na^+ is smaller than Na, the parent atom because it has given up an electron. The chlorine atom is about the same size as it has only added one more electron to its outer shell.

Ionic compounds share several characteristics. ▪ An ionic compound is formed by a reaction between a metal and a nonmetal; here the reaction was between an alkali metal Na or Li and a halogen, Cl or F. ▪ Ionic compounds are solids. ▪ However, like NaCl, ionic compounds generally dissolve freely in water. ▪ Once dissolved ionic compounds easily conduct an electric current. With that information, you may guess that certain ionic compounds are useful in making batteries. Although they were not identified as ionic, ionic compounds have been mentioned earlier, e.g., the metal salts that predominate in incinerator ash (Chapter 11). An important point to remember about ionic compounds is that they are not molecules in the same sense that covalently bonded compounds are.

Molecules with both covalent and ionic bonds

From the above discussion of covalent and ionic bonds, you may conclude that the atoms in a molecule can form only covalent bonds or only ionic bonds. However, many chemicals have both covalent and ionic bonds. As just one of a great many examples, look at Figure 14.2, which shows the structure of sodium perfluorooctanate. Note that sodium's bond to oxygen is ionic with sodium having a positive charge and oxygen a negative. However, also note that all the other bonds in the molecule are covalent. It is worthwhile to note that carbon forms only covalent bonds. However, when carbon is bonded to, for example, oxygen as in Figure 14.2, the oxygen can participate in an ionic bond. ▪ Common molecules with which you are familiar that have both covalent and ionic bonds are detergents. A detergent has a water-loving (ionic) bond at one end whereas the body of the molecule is hydrophobic and has only covalent bonds. The ionic interaction of Na^+ and -O^- keeps the detergent soluble in water whereas the hydrophobic body of the molecule is attracted to organic molecules. Thus the hydrophobic portion of the molecule interacts with organic materials such as the grease in dirty clothes. When the clothes are subsequently rinsed the grease rinses out with the detergent. ▪ Another molecule with which you are familiar is acetic acid, CH_3COOH , in vinegar. CH_3COOH itself has only covalent bonds. However, in water it is a weak acid with a small portion of the acetic acid dissociating to give the acetate ion CH_3COO^- and a proton, H^+ .



Molecular mass (molecular weight)¹⁶

How heavy is a molecule? You learned above that the atomic mass of an element equals the number of protons plus the number of neutrons in its nucleus. The atomic mass of each

¹⁶ Molecular mass (molecular weight) *AUS-e-TUTE*, <http://www.asetute.com.au/mmcalcul.html>.

element is below its symbol in the periodic table. Li is 6.94, Ca is 40.07, etc. Let's look at several examples of calculating molecular weight (MW). (To simplify calculations, round off the mass of each element to the nearest whole number.)

Look at the two molecules in Figure 19.5, H_2 and CH_4 .

- Each H atom has an atomic mass of one so the MW is $1 + 1 = 2$.
- Methane has four hydrogens (4) plus the mass of one carbon (12) as seen in column 12 of the periodic table. The MW of a methane molecule is $4 + 12 = 16$.

See the NaCl molecule in Figure 19.6

- Add the mass of the Na atom (23) as seen in column 1 to that of chlorine (35) as seen in column 17. The MW is $23 + 35 = 58$.

Other molecules mentioned here include CO, NH_3 , and HCHO.

- CO: add the atomic mass of oxygen (16) as seen in column 16 to the atomic mass of carbon (12). The MW is $16 + 12 = 28$.
- NH_3 : add the mass of three hydrogens (3) to that of nitrogen (14) seen in column 15. The MW is $3 + 14 = 17$.
- HCHO: add the mass of two hydrogens (2) to that of carbon (12) and that of O (16). The MW is $2 + 12 + 16 = 30$.

Basically, as you can see, to get the MW of a molecule: take the atomic mass of each element and multiply it by the number of atoms of that element in the molecule. Do that for each element in the molecule. Finally, add together the masses.

SECTION II

Two categories of chemicals: organic and inorganic

Many people think of the word, organic in the context of organic farming, farming that does not use synthetic pesticides or fertilizers. That use of the word, organic is historic as it was once believed that only living organisms could synthesize organic compounds: a "life force" was needed. Then in 1828, Friedrich Wohler synthesized the organic chemical, urea $\text{H}_2\text{N}-\text{CO}-\text{NH}_2$.

Organic chemicals

- Organic chemicals contain the element *carbon* and there are millions of carbon compounds. Except for very simple compounds such as methane (CH_4), organic chemicals contain more than one carbon atom, tens, sometimes hundreds or more, linked in carbon-carbon bonds. ▪ Those that contain only carbon and hydrogen are called

hydrocarbons; a simple example is $\text{H}_3\text{C}-(\text{CH}_2)_3-\text{CH}_3$ (pentane). Organic chemicals commonly contain other elements too, such as oxygen, nitrogen, or sulfur. An *organo-metallic* chemical has a carbon atom bonded to a metal as in tetraethyl lead. Some organometallic chemicals are found naturally, e.g., hemoglobin (iron) and vitamin B_{12} (cobalt), and many other proteins and enzymes,

- Many organic chemicals are *synthetic*, i.e. produced not by living creatures, but manufactured by human beings. However, the feedstocks from which the chemicals are made come from nature. Commonly synthetic organic chemicals are made from petroleum or natural gas feedstock; these are often called *petrochemicals*. ▪ Coal or wood also sometimes serve as feedstocks for organic chemicals. Some organic chemicals are produced too by cultures of molds or bacteria. Plastics are synthetic organic chemicals. Even so-called bioplastics, produced from plant materials, involve some synthetic chemistry. Some commercial organic chemicals are produced too by cultures of molds or bacteria; such chemicals must then be purified from these cultures by human actions.
- Most chemicals found in petroleum are hydrocarbons. Methane (CH_4) found in natural gas is the simplest hydrocarbon. Often, to make the desired chemicals other elements such as oxygen or chlorine must be added to hydrocarbons. Synthetic chemicals may be simple as is formaldehyde (HCHO), used for purposes ranging from making plastics to embalming corpses. Other synthetic chemicals such as some pharmaceuticals, certain vitamins, or peptides can be much more complicated.
- A *biochemical* is an organic chemical synthesized by a living creature. Proteins, fats, and carbohydrates are biochemicals. Sucrose (table sugar) and the sour acetic acid (in vinegar) are examples of simple biochemicals. Many more complicated chemicals are synthesized by living organisms too: these include proteins such as enzymes, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). ▪ Many biochemicals can also be made synthetically, not only simple chemicals such as vinegar or the sugars, sucrose and xylose, but also complex ones. If the structure of a chemical made by synthetic means is exactly the same as that found in nature, it is indeed the same chemical – the body treats both in exactly the same way so there is no biological difference between them either. Chemicals synthesized by living creatures can also be extensively manipulated during extraction and purification and still legally be called natural. The word “natural” is often misused or used without explanation.

Inorganic chemicals

- An inorganic chemical is one *not* containing carbon although there are a few exceptions, i.e., chemicals that contain carbon and yet are considered inorganic. These include sodium bicarbonate (baking soda) and sodium carbonate (washing soda).
- Inorganic chemicals may contain almost any element in the periodic table – nitrogen, sulfur, lead, arsenic, etc.
- Many inorganic chemicals are found naturally – salts in the ocean, minerals in the soil, the silicate skeleton made by a diatom, or the calcium carbonate skeleton made by a coral.

- Inorganic chemicals are also often manufactured by humans. Ammonia used as a nitrogen fertilizer is a major example. Simple inorganic chemicals can be manipulated to make more complicated ones. However, the total number of inorganic chemicals is much smaller than the number of organic chemicals.

Free radicals

Let's start looking at some of the chemistry associated with pollution issues, starting with free radicals.

Electrons normally come in pairs. You have seen that the inner shell of atoms have two electrons (one pair). The outer shell contains up to eight electrons (four pairs). A free radical is an atom (or a fragment of a molecule) that has *at least one unpaired electron*. That electron is very reactive. Some elements are free radicals. Consider the lithium atom: with only one electron in its outer shell, it is extremely reactive. Exposed to air or water lithium reacts violently. To a lesser extent sodium (Na) and potassium (K) – in the same family as lithium and also with only one electron in the outer shell – are also very reactive. Free radicals are extremely important in a number of circumstances including pollution events. Some will be noted below.

The hydroxyl radical as a solution

▪ The environmental fate of a number of pollutants is noted in this text. In soil and water, microorganisms can break down many organic pollutants and materials into carbon dioxide and water. A major means of degrading pollutants in the atmosphere is via the *hydroxyl radical*, $\bullet\text{OH}$. Although present in the atmosphere in only tiny concentrations, $\bullet\text{OH}$ destroys many pollutants.¹⁷ In fact, it is sometimes called “the detergent of the troposphere.” Its importance was noted in Chapter 5 (Air pollution) because it participates in the destruction of many VOC pollutants and a number of inorganic pollutants as well including sulfur dioxide and ozone.¹⁸

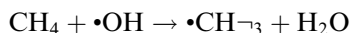
▪ The hydroxyl radical, composed of one oxygen and one hydrogen, is represented as $\bullet\text{OH}$ where the dot represents the unpaired electron. Between them the oxygen and the hydrogen have only seven electrons. So $\bullet\text{OH}$ is highly reactive, needing an eighth electron in order to regain stability. ▪ How is destruction initiated by $\bullet\text{OH}$ carried out? Consider below what happens to methane, the simplest hydrocarbon when it is attacked by $\bullet\text{OH}$. Follow the movement of the radical \bullet . The names of the chemical entities are not important to remember – the important thing is to note that the chemical entity to which the radical is attached changes at every step of the reaction. That happens because, when $\bullet\text{OH}$ attacks an atom, that atom gives up an electron and now it holds the unpaired electron. In its turn the

¹⁷ Hydroxyl radical. *Wikipedia*, January 13, 2009, http://en.wikipedia.org/wiki/Hydroxyl_radical.

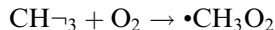
¹⁸ Borrell, P. *Tropospheric Chemistry, an essay in the Encyclopedia of Ecology and Environmental Management*. Peter Calow (ed.). Oxford: Blackwell Science, 1998, <http://www.luna.co.uk/~pborrell/p&pmb/tropchem.htm>.

new radical attacks another atom, which in turn becomes a free radical, etc. This is often referred to as a chain reaction. The reaction will continue until interrupted in some way.

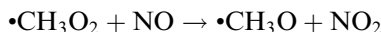
- (1) The $\bullet\text{OH}$ comes in contact with a CH_4 and removes a H from it. The H becomes part of a stable water molecule. The electron is now associated with a methyl fragment $\bullet\text{CH}_3$.



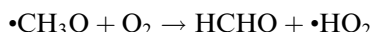
- (2) The $\bullet\text{CH}_3$ radical reacts with atmospheric O_2 to form the methylperoxy radical $\bullet\text{CH}_3\text{O}_2$.



- (3) If the reaction is happening in a locale where nitric oxide, NO is in the atmosphere, the methylperoxy radical converts the NO to NO_2 , and in the process becomes a methoxy radical, $\bullet\text{CH}_3\text{O}$.



- (4) The methoxy radical reacts with O_2 and forms formaldehyde, HCHO.



At this point, notice that there is no trace of the original CH_4 . It has been converted to formaldehyde, HCHO and yet another radical. Formaldehyde is also a pollutant, but can, in its turn, be destroyed. Eventually, the products are CO_2 and H_2O . More complicated hydrocarbon pollutants go through a longer series of reactions. Not all organic molecules degraded by a free radical are converted to CO_2 and H_2O , but are often broken down to chemicals that can deposit onto the Earth, or into chemicals such as acids which are soluble in water and can be rained out.

Inorganic molecules are also attacked by the $\bullet\text{OH}$.

The hydroxyl radical as a problem

The above example showed a free radical destroying pollutants in the atmosphere. In Chapter 8 we saw free radicals in a different light. CFCs swept into the stratosphere are destroyed by the sun's ultraviolet radiation. In the process, CFCs release chlorine as the chlorine free radical $\text{Cl}\bullet$. (A bromine radical, $\text{Br}\bullet$ is released from halons.) It is these free radicals that destroy the stratospheric ozone that serves the protective function of absorbing high energy radiation from the sun that could otherwise reach and damage life on Earth. A major substitute for CFCs are the HCFCs (hydrochlorofluorocarbons). Because HCFCs contain some hydrogen-carbon bonds, they are often destroyed in the lower atmosphere by $\bullet\text{OH}$ before they can reach the stratosphere. Thus, HCFCs are fortunately less persistent in the environment and less likely to reach the stratosphere. Another CFCs replacement, HFCs (hydrofluorocarbons) contain no chlorine and are even more subject to destruction by free radical reactions in the lower atmosphere.

Box 19.2

Avogadro's constant and the mole

Avogadro's constant equals 6.022×10^{23} . It is a fundamental constant in chemistry.

Look at the periodic table. Notice carbon, the first element in column 14. Its atomic mass is 12. *Now note:* in 12 g of carbon there are 6.022×10^{23} atoms. Also, 12 g of carbon equals a *mole*.

So a mole of carbon, indeed a mole of *any* element contains exactly the same number of atoms, 6.022×10^{23} . A mole of ^1H (1.008 g) contains 6.022×10^{23} atoms. So does a mole of aluminum, ^{13}Al (26.98 g) or a mole of silver, ^{47}Ag (107.87 g) or a mole of any other element.

One can also speak of a mole of *molecules* (such as a mole of H_2 or a mole of H_2SO_4). A mole of any one of these contains 6.022×10^{23} molecules. The term can also be used for *ions*. A mole of Na^+ ions has 6.022×10^{23} ions. The mole along with Avogadro's constant gives a sense of great order to the discipline of chemistry.

Stoichiometry

Before examining the oxidation reactions that follow, it is important to introduce the concept of stoichiometry. The two sides of a chemical reaction must always be balanced.

- First consider any molecule, let's say water. On the basis of what you already know about valence you can say that the molecule H_2O always has two atoms of hydrogen and one atom of oxygen; *the molar proportion* of hydrogen to oxygen is two to one. You can also say *the stoichiometry* of hydrogen and oxygen in H_2O is 2:1.
- All chemical reactions take place in definite ratios. For instance: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$
- This simple equation tells you the quantities of reactants (left side) must balance with the quantities of products (right side) in a chemical reaction. Seeing this equation you can say that two moles of H_2 plus one mole of O_2 yields two moles of water. There are four hydrogens and two oxygens on both sides of the equation. The water example is a simple one, but the stoichiometry holds for any chemical equation: one must balance out the quantities of reactants and products.

SECTION III

Oxidation reactions¹⁹

Many chemical reactions noted in this text involve adding oxygen to hydrocarbons. The best-known examples are of oxygen atoms added to hydrocarbons during the combustion of fossil fuel (Box 1.2 and Table 13.1). In such oxidation reaction, the proportion of oxygen in the molecule is increased. Because adding oxygen to an element or molecule generally means that it is losing electrons the word *oxidation* has a much broader meaning: it is a

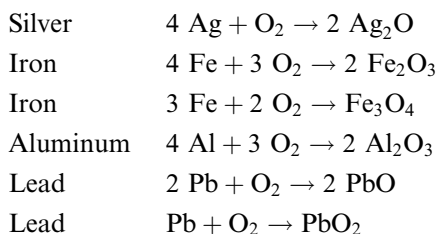
¹⁹ Oxidation and reduction. *Columbia Encyclopedia*, 2003, <http://www.answers.com/topic/redox>.

reaction in which an element or molecule loses electrons. The converse of oxidation is *reduction*: adding electrons to an element or molecule. Consider the reaction of lithium with chlorine: $\text{Li} + \text{Cl} \rightarrow \text{LiCl}$. In this reaction lithium loses an electron, it was oxidized. Conversely chlorine gains an electron, it was reduced. Overall, it is called a *redox* reaction.

Below, see illustrations of adding oxygen to elements or molecules in gasoline during combustion. In developed countries, significant amounts of these pollutants are removed by catalytic converters and other changes in the operation of the vehicle,²⁰ but significant quantities are still emitted.

Oxidation reactions of metals

Many metals are present in trace amounts in gasoline.²¹ Metal oxidation will be examined first. Metals, when combusted, react with atmospheric O_2 to yield metal oxides, tiny particulate pollutants released in car exhaust. Many particulates are captured by modern vehicle emissions controls. Four metals have been chosen to illustrate metal oxidation. Assume that the valence of oxygen is two in each of the following cases, then determine for yourself the valence of each metal. Many elements (for reasons not covered here) can have more than one valence state. Notice that each equation is – must be – balanced, i.e., the number of atoms of each element on the left side of the equation must equal those on the right.

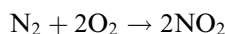
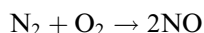


Oxidation reactions of nitrogen and sulfur when burning gasoline

The sulfur and nitrogen compounds in gasoline are also oxidized when it is burned (Box 1.2). At the high temperature of gasoline combustion, atmospheric O_2 also reacts with atmospheric nitrogen (N_2) resulting in nitrogen oxides (NO_x), released in the exhaust.

²⁰ (1) Catalytic converter. *Wikipedia*, March 3, 2009, http://en.wikipedia.org/wiki/Catalytic_converter. (2) Automobile emissions control. *Wikipedia*, March 5, 2009, http://en.wikipedia.org/wiki/Automobile_emissions_control.

²¹ Metals found in gasoline in trace amounts include cadmium (Cd), arsenic (As), vanadium (V), manganese (Mn), nickel (Ni), antimony (Sb), chromium (Cr), zinc (Zn), copper (Cu), boron (B), calcium (Ca), magnesium (Mg), silver (Ag), aluminum (Al), iron (Fe), and lead (Pb) – all released as metal oxides in car exhaust. Fortunately, in most countries Pb is no longer added to gasoline, so this once large contaminant is now present in very small amounts. Nonetheless, remember that metals cannot degrade; they can build up in soils along roads. Also recall that these metals are found in trace amounts in coal too; with more than a billion tons of coal burned each year in the United States, even trace amounts can slowly but surely add up as these pollutants first released into the air deposit onto soil.

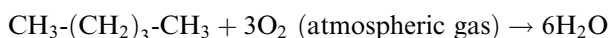


Again notice that the two sides of the equation are balanced. Because NO, NO₂, and N₂O are major pollutants (referred to as NO_x), we are fortunate that more than 85% of the N₂ is not oxidized, but is released unchanged in the car's exhaust. However, enough is released to lead to significant environmental problems; see NO_x pollutants in Chapter 5, 6, 9, and 13. The NO_x contribute greatly to ozone formation. One NO_x gases, N₂O is a powerful greenhouse gas. NO_x also contributes to acid deposition. ▪ Similar reactions oxidize the sulfur compounds in the gasoline to sulfur oxides.

Oxidation of hydrocarbons in gasoline²²

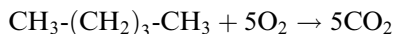
There are hundreds of different hydrocarbon compounds in gasoline.²³ Hydrocarbons with one to four carbons are not found in gasoline because they are gases. So, for purposes of illustration, the smallest liquid hydrocarbon, pentane (with five carbons) is used here to examine the oxidation of a hydrocarbon. The formula for pentane is CH₃-CH₂-CH₂-CH₂-CH₃, abbreviated as CH₃-(CH₂)₃-CH₃. ▪ Remember that the valence of hydrogen is one and that of carbon is four, so hydrogen is bonded to only one other atom, but carbon is bonded to four. At both ends of the hydrocarbon molecule carbon is bonded to only one other carbon and to three hydrogens whereas in the molecule's center carbon is bonded to two other carbons and two hydrogens. Assume that the gasoline is burning at 495° F (232°C) and that the pentane is being oxidized to CO₂ and H₂O.

- First consider the reaction of hydrogen with atmospheric O₂. There are 12 hydrogens in the pentane molecule and two hydrogens in each H₂O, so ...



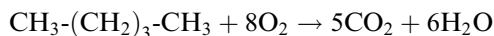
Note that the two sides of the equation are balanced for oxygen and hydrogen: 12 hydrogen atoms require 6 O atoms (left side of equation) to produce the 6 water molecules.

- Then consider the reaction of carbon and oxygen.



Here the two sides of the equation must balance: five carbon atoms require 10 oxygen molecules to yield five molecules of CO₂.

- The overall reaction is the sum of those first two equations.



²² Hydrocarbon chemistry. *Encyclopedia of Earth*, February 4, 2007, http://www.eoearth.org/article/Hydrocarbon_chemistry.

²³ Hamilton, B. FAQ: Automotive gasoline. January 8, 1995, <http://www.turborick.com/gsxr1127/gasoline.html>.

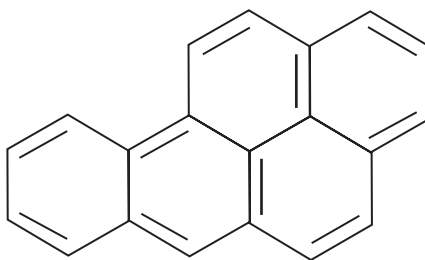


Figure 19.7

Structure of benzo[*a*]pyrene (a polycyclic aromatic hydrocarbon, PAH)

At the end of Box 1.2, you were asked the following question: assume that a gallon (3.8 liters) of gasoline weighs ~6 pounds²⁴ (2.7 kg). How then can nearly 20 pounds (9.1 kg) of carbon dioxide be emitted per gallon of gasoline (in the car's exhaust)?²⁵ Probably, the answer to that question is now obvious. ▪ Notice how much oxygen it takes to oxidize a hydrocarbon, and thus how much carbon dioxide – the major greenhouse gas – that a motor vehicle is churning out.

Incomplete oxidation of hydrocarbons

Another important point is that the internal combustion engine burns gasoline with as little as 20% efficiency,²⁶ so large quantities of *incomplete* products of combustion are being formed.²⁷ Although significant quantities of these are captured in the modern environmental controls now in cars, the pollution still represents major problems (Chapter 5). Worse, in less-developed countries, the emissions are often truly obnoxious. Below are a number of incomplete products of combustion.

- **CO** (carbon monoxide) is a major product of incomplete combustion. In urban areas up to 90% of CO emissions are from vehicle emissions (Table 13.1).
- Another important set of incomplete product of combustion are the **VOCs** (volatile organic chemicals). Most VOCs emitted from motor vehicles are hydrocarbons. These pose a major problem in urban environments.
- **Soot** is fine black carbon particles released by very poorly tuned vehicles, and by two-stroke engines used in a number of applications, not just motor vehicles.
- **PAHs** (polycyclic aromatic hydrocarbons) are formed in small amounts, but a number are very toxic. Observe in Figure 19.7 the structure of benzo[*a*]pyrene (BaP), a carcinogenic and mutagenic PAH.²⁸ Also see Box 19.3.

²⁴ A gallon of gasoline (3.8 liters) weighs between 5.8 and 6.5 pounds (2.6–3 kg). The average formula of gasoline is two atoms of hydrogen for each atom of carbon (CH₂). So, by weight gasoline is ~86% carbon. The density of gasoline is ~6.1 lb/gal (0.71–0.77 g/cm³). Because gasoline is lighter than water, which has a density of one, it floats on water.

²⁵ See: (1) Emission facts: average carbon dioxide emissions resulting from gasoline and diesel fuel. *US EPA*, February 13, 2009, <http://www.epa.gov/oms/climate/420f05001.htm>. (2) Frequently asked global change questions. *Carbon Dioxide Information Analysis Center*, <http://cdiac.ornl.gov/pns/faq.html>.

²⁶ Internal combustion engine. *New World Encyclopedia*, July 17, 2008, http://www.newworldencyclopedia.org/entry/Internal_combustion_engine#Gasoline_ignition_Process.

²⁷ Although it doesn't happen under real world conditions, combustion can be forced to completion in a laboratory setting by using pure oxygen, producing almost entirely CO₂ and H₂O.

²⁸ Sander, L. C. and Wise, S. A. Polycyclic aromatic hydrocarbon structure index. http://ois.nist.gov/pah/sp922_Detail.cfm?ID=189.

Box 19.3

More on BaP

The double lines shown in the BaP structure (Figure 19.7) represent double bonds, i.e. the atoms involved share two pairs of electrons. However, saying that two carbon atoms share two pairs of electrons in such rings is a simplification; rather the electrons are “spread” among the carbons. The atoms that make up BaP are not shown because it is assumed that the carbons and the hydrogens are present; each apex represents a carbon atom. Benzene, the simplest aromatic ring compound has a formula of C_6H_6 . Examine the BaP molecule and determine why each ring is able to have less than six carbons.

SECTION IV

Acid pollution²⁹

▪ First, consider *water*³⁰ (H_2O or $H-O-H$). The oxygen atom in the H_2O molecule strongly attracts the two hydrogen atoms to which it is bonded. However, the O also attracts the H atoms in other water molecules, resulting in a phenomenon called *hydrogen bonding*. Hydrogen bonding leads to water molecules clustering closer together than would otherwise happen. ▪ Pure water is mostly composed of intact $H-O-H$ molecules, but it does slightly dissociate into H^+ ions (cations) and OH^- ions (anions). The H^+ is characteristic of an acid and OH^- is characteristic of a base (also called alkali). ▪ *Acids* are compounds of hydrogen. Remember that the hydrogen atom has one proton and one electron. When acting as an acid, H loses its electron, leaving only the proton, H^+ . But the proton is not bare. In water, H^+ is associated with a H_2O molecule, and is represented as H_3O^+ ; it is a hydrated H^+ .³¹ However, the proton is typically represented as H^+ , not H_3O^+ .

Acids

- pH ^{32,33} is a measure of how acid or alkaline a water solution is. It has a scale of 0 to 14. The pH of pure water is 7, which is neutral. If an acid such as hydrochloric acid (HCl) is added, it dissociates into Cl^- anions and H^+ cations. Because of H^+ , the water becomes acidic. As more H^+ is added, the solution becomes progressively more acidic, and its pH becomes progressively lower.³⁴ Examine Box 6.3 for examples of the acidity of common substances.

²⁹ Acid. *Wikipedia*, February 18, 2009, <http://en.wikipedia.org/wiki/Acid>.

³⁰ Water (molecule). *Wikipedia*, February 24, 2009, [http://en.wikipedia.org/wiki/Water_\(molecule\)](http://en.wikipedia.org/wiki/Water_(molecule)).

³¹ H_3O^+ is a cation called *hydronium*. See Hydronium. *Wikipedia*, February 19, 2009, <http://en.wikipedia.org/wiki/Hydronium>.

³² What is pH? *US EPA*, June 8, 2007, <http://www.epa.gov/acidrain/measure/ph.html>

³³ pH. *Wikipedia*, February 24, 2009, <http://en.wikipedia.org/wiki/pH>.

³⁴ Conversely, if a base such as sodium hydroxide (NaOH) is added, the solution becomes alkaline, and the pH becomes progressively higher as more base is added.

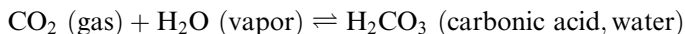
- An *acid*³⁵ is a chemical compound that, when dissolved in water, releases H^+ and gives rise to a solution with a pH below 7. A pH of 7 means the solution is neutral. Some acids (hydrochloric acid and nitric acid, HNO_3) are strong, meaning all their hydrogens are released as H^+ ions, they ionize completely.³⁶ However, a weak acid such as acetic acid (CH_3COOH) found in vinegar only partially ionizes into CH_3COO^- and H^+ .
- The converse of an acid is a *base*. A base releases OH^- when dissolved in water. When the base, sodium hydroxide ($NaOH$) is added to water, it dissociates into Na^+ cations and OH^- anions and the pH rises. The solution becomes progressively more alkaline as more OH^- is added. (Note: *don't confuse* the OH^- ion with the $\bullet OH$ radical. The OH^- ion has an octet of electrons whereas the $\bullet OH$ radical is so unstable because it has only seven electrons.)
- When OH^- ions, are added to H^+ ions, the solution begins to move toward 7. If just enough OH^- ions are added to reach a pH of 7, the solution is *neutralized*. One mole of OH^- ions added to one mole of H^+ ions means the solution is no longer acidic or basic; it is neutral.

Acid deposition²⁷

In Chapter 6 you saw the problems of water and soil acidification resulting from acid deposition. Pollutants emitted to the atmosphere were transformed into acids, then deposited onto earth and water.

Carbonic acid

Even without acids generated by human actions, rain has a slightly acid pH. That is because carbon dioxide (CO_2) is always present in the atmosphere. So, to varying extents is water vapor. Thus the following reaction occurs.



The reversible arrows indicate that the reaction between CO_2 and H_2O to form H_2CO_3 doesn't go to completion. Carbonic acid also dissociates back into CO_2 and H_2O . Carbonic acid is a weak and natural acid. It does affect the pH of rain, but the problematic acids in acid deposition are sulfuric acid (H_2SO_4) and nitric acid (HNO_3). The atmospheric transformations of SO_2 and NO_x to these acids are complex, and simplified versions are presented here.

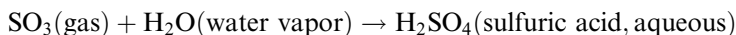
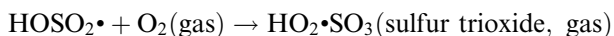
Sulfuric acid

Coal-burning power plants and other sources release SO_2 . There are three means to convert SO_2 to H_2SO_4 . One involves the hydroxyl radical ($\bullet OH$).³⁷

³⁵ Acid. *Wikipedia*, February 18, 2009, <http://en.wikipedia.org/wiki/Acid>.

³⁶ Sulfuric acid (H_2SO_4), which is heavily involved in acid deposition is also a strong acid. However, only the first H^+ is completely released.

³⁷ Atmospheric reactions of sulfur and nitrogen. *Northern Arizona University*, April 14, 2008, http://jan.ucc.nau.edu/~doetqp-p/courses/env440/env440_2/lectures/lec37/lec37.htm.



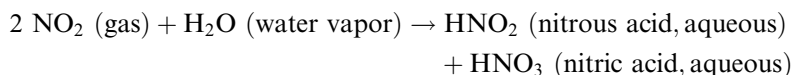
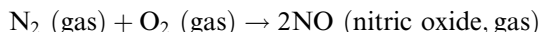
The sulfuric acid is washed out of the atmosphere by rain into the soils and waters below. Or, in dry conditions, the sulphate (SO_4^{2-}) is formed and settles from the atmosphere. There are also bases in the atmosphere of which the volatile ammonia (NH_3) is the most common. It can react with H_2SO_4 .



Ammonium bisulfate is a salt. It is strongly attracted to water, in which it dissolves. It is washed out with rain or other precipitation, or if it remains dry, can settle out as particles.

Nitric acid

Most nitrogen oxides (NO_x) results from the high-temperature reaction of atmospheric nitrogen with atmospheric oxygen during fossil-fuel combustion. Consider how this oxidation happens in the atmosphere.



Ocean acidification^{38,39,40,41}

▪ In the past 200 years, the oceans have absorbed about 550 billion tons (499 billion tonnes) of CO_2 from the atmosphere, about a third of the CO_2 emissions for which humans have been responsible.⁴² That oceanic absorption of CO_2 still continues.⁴³

³⁸ The acid ocean: the other problem with CO_2 emission. *Real Climate*, July 2, 2009, <http://www.realclimate.org/index.php?p=169>.

³⁹ Petkewich, R. Off-balance ocean: acidification from absorbing atmospheric CO_2 is changing the ocean's chemistry. *Chemical & Engineering News*, **87**(8), February 23, 2009, <http://pubs.acs.org/cen/science/87/8708sci2.html>.

⁴⁰ Ocean acidification. *Wikipedia*, February 22, 2009, http://en.wikipedia.org/wiki/Ocean_acidification.

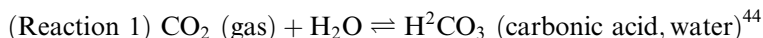
⁴¹ Young, R. O. What is causing ocean acidification? *Articles of Health*, November 27, 2008, <http://articlesofhealth.blogspot.com/2008/11/what-is-causing-ocean-acidification.html>.

⁴² Carbon dioxide. *Wikipedia*, February 27, 2009, http://en.wikipedia.org/wiki/Carbon_dioxide.

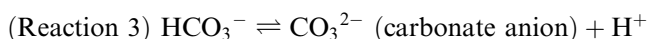
⁴³ That so much CO_2 has been absorbed into the oceans from the air has had a major positive aspect: there is less CO_2 in the atmosphere to absorb the infrared radiation coming from the Earth. This mitigates the warming compared to what could otherwise occur. Unfortunately, that CO_2 is affecting the pH of the oceans, as discussed here.

Carbonic acid and the fall in ocean pH

The following three reactions have always occurred in the oceans, making use of some of the CO₂ absorbed into the ocean's waters.

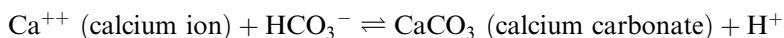


The problem with the increased and increasing CO₂ concentration is that more and more is being converted into carbonic acid.⁴⁵ ■ Carbonic acid, a weak acid, as Reaction 2 shows, partially dissociates into the acidic H⁺ cation and the bicarbonate anion (HCO₃⁻). And as seen in Reaction 3, the HCO₃⁻ partially dissociates into the second H⁺ and carbonate (CO₃²⁻).



The consequence of increased hydrogen ions in the ocean

Although carbonic acid is weak and, in turn, only a small proportion of the protons are dissociated from the HCO₃⁻, such great quantities of carbonic acid have formed over the years that the pH of the oceans' surface waters has decreased about 0.1 pH unit (from about pH 8.2 to pH 8.1). This does not sound like much, but because pH is a logarithmic function, this small drop represents about a 30% rise in acidity.⁴⁷ With increasing concentrations of H⁺ in the water, CO₃²⁻ reacts with H⁺ more often to form bicarbonate (HCO₃⁻) than was the case before the ocean began acidifying.⁴⁸ ■ What does this matter? Geologists tell us that the pH of the oceans has been stable for many millions of years. A great many tiny creatures at the base of the ocean food chain depend on calcium carbonate to build their shells (coral, and the many plankton, protozoa and algae that form calcium carbonate shells).



For millions of years, calcium carbonate shells have been stable because there has always been more than enough carbonate to maintain them: the waters have been "shell friendly." However, with more CO₃²⁻ moving back toward HCO₃⁻ (Reaction 3), there is less calcium

⁴⁴ Carbon dioxide. *Wikipedia*, February 27, 2009, http://en.wikipedia.org/wiki/Carbon_dioxide.

⁴⁵ As noted above, the reversible arrows indicate that the reaction goes in both directions, and H₂CO₃ can dissociate to release CO₂. If you drink carbonated beverages, you have seen what happens to the carbonic acid added to these beverages. When you remove the cap, the release in pressure allows the CO₂ to begin gassing out, thus pulling the reaction to the left.

⁴⁶ Bicarbonate is used as an antacid NaHCO₃ (bicarbonate of soda), as baking soda, and for cleaning purposes. Na₂CO₃ may be familiar to you as washing soda; it is also used, with sand to make glass.

⁴⁷ The pH of the ocean is actually slightly alkaline, about pH 8.2. What is happening is that the ocean is becoming less alkaline. It is easier to refer to this as ocean acidification as the pH is indeed moving ever lower.

⁴⁸ Most of the inorganic carbon in the ocean, about 88%, is bicarbonate. The concentrations of carbonate ion and CO₂ are about 11% and 1%, respectively. NASA educational workshop, the basics of ocean chemistry. *NASA SeaWiFS Project*, <http://oceancolor.gsfc.nasa.gov/SeaWiFS/TEACHERS/CHEMISTRY/>.

carbonate with which to form shells. To date, the change has not been great enough to cause obvious harm. However, in controlled studies, it is clearly seen that as H^+ continues to increase shell formation is harmed. ■ Moreover, not only creatures that form their shells from calcium carbonate are in danger. A change in ocean pH can affect other fundamental biological and geochemical processes in the oceans.⁴⁹

You now see that every pollution issue in this text could be examined from the perspective of the chemistry involved. For those interested in going further, consider:

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- An on-line environmental chemistry course from Northern Arizona University is found at http://jan.ucc.nau.edu/~doetqp-p/courses/env440/env440_2/index.htm.

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⁴⁹ (1) Zeebel, R. E., Zachos, J. C., Caldeira, K. and Tyrrell, T. Carbon emissions and acidification. *Science*, **321**(5885), July 4, 2008, 5152. (2) Kerr, R. A. The many dangers of greenhouse acid. *Science*, **323**(5913), January 23, 2009, 459.

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Index

accidents and major exposures

- arsenic, “largest mass poisoning”, 451
- Bhopal explosion, 18
- Chernobyl explosion, 393
- Danube cyanide spill, 14
- Exxon Valdez oil spill, 246
- Minamata, mercury poisoning, 444
- Rhine chemical spill, 14
- TVA ash pond, failure, 430

acetic acid, 557

acetone, 504

acetylcholine, 466

acid deposition

- acid-forming pollutants, 155
- aerosols, 155
- buffers, 157
- carbonic acid, 156
- dry and wet, 156
- formed of, 155
- high stack emissions, 156
- history, 156
- ill effects, 159–162
 - aluminum, 431
 - erosion, haze, 162
 - forests, 160
 - mercury, 431
 - metals, 431
 - water and aquatic life, 159
- international
 - Asia, 167
 - China, 167–168
 - Europe, 166
- NAPAP, 158, 159, 160, 164
- pH, 158
- recovery from, 164
- reducing
 - nitrogen oxides, 163
 - sulfur dioxide, 162
- soil
 - base cations, 157
 - ill effects, 431
- sources, 162
- transboundary, 165

acid from mining, 428

adipic acid, 526

Afghanistan, 343

Africa, 28, 74, 83, 88, 143, 144, 147, 181, 302, 343, 414, 475, 477, 478, 479

agencies

- US Centers for Disease Control, 25, 70, 85, 91, 289, 290, 422
- US Consumer Product Safety Commission (CPSC), 487
- US Department of Agriculture, 472
- US Department of Energy, 47, 331, 352, 359, 361, 384, 532
- US DOE, *see* US Department of Energy
- US EPA, 12, 24, 39, 42, 47, 71, 98, 102, 104, 110, 111, 112, 113, 118, 121, 125, 126, 131, 134, 135, 138, 144, 198, 199, 232, 248, 249, 251, 253, 254, 255, 256, 261, 263, 266, 271, 272, 276, 277, 282, 287, 288, 289, 290, 291, 292, 296, 297, 299, 300, 308, 318, 319, 324, 333, 339, 352, 353, 356, 359, 360, 366, 368, 379, 389, 391, 410, 414, 417, 418, 422, 425, 430, 433, 434, 436, 437, 444, 445, 447, 450, 451, 460, 464, 465, 469, 470, 471, 472, 483, 489, 492, 494, 497, 498, 500, 503, 505, 507, 519, 524
- US EPA's Science Advisory Panel, 165
- US Fish & Wildlife Service, 471
- US Food and Drug Administration, 84, 102, 299, 418, 444, 447, 465
- US Geological Survey, 320
- US National Academy of Sciences, 498
- US National Aeronautics and Space Administration, 8, 219
 - closed-loop system, 515
- US National Oceanic and Atmospheric Administration, 178, 213, 221, 255
- US National Research Council, 102, 114, 269, 279, 289, 443, 447

Agenda 21, 21, 305, 334

AIDS, 27, 28, 72, 298, 302

air pollutants

HAPs

- examples, 139
- summary
 - Table 5.1, 119
 - Table 5.3
 - sulfur and nitrogen oxides, 129

air pollutants, criteria

- ambient air standards, 118
- as principal air pollutants, 118
- carbon monoxide, 119–121
 - Box 5.1, 120
 - fate, 120
 - ill effects, 120
 - produced of, 119
 - reducing, 120
 - sources, 120

lead, 135

- sources, 135

nitrogen oxides, 128–130

- aerosols, 128
- fate, 128
- ill effects, 128
- produced of, 129
- reducing, 130, 279, 386
 - low-NOx burners, 391
- sources, 128

ozone, 190–191

- fate, 124
- ill effects, 122–123
- ill effects, continuum, 124
- intractable, 125
- motor vehicles, 124
- peroxyacyl nitrate, 122
- photochemical smog, 122
- produced of, 123
- reducing levels, 379
- sources, 123
- tropospheric, 122
- particulates, 130–134
 - description, 130
 - epidemiology, 132
 - fate, 134
 - ill effects, 132
 - PAHs, 133
 - exposure, 133
 - ill effects, 133
 - reducing, 133
 - sources, 133
 - PM10 PM2.5, 131, 132
 - reducing, 134
 - reduced levels, 512
 - sources, 132
- sulfur dioxide, 125–127
 - aerosols, 125
 - China haze, 127
 - fate, 127
 - ill effects, 126
 - reducing, 127
 - fluidized bed, 391
 - scrubbers, 391
 - sources, 126

air pollutants, HAPs

- ill effects, 138

- maximum available technology (MACT), 140
- reducing, 140

air pollutants, hazardous air pollutants (HAPs), 138–140**air pollutants, principal, see air pollutants, criteria****air pollutants, summary**

- Table 5.1, 129

air pollutants, toxics, see air pollutants, HAPs**air pollutants, VOCs, 136–137**

- fate, 137
- ill effects, 136
- reducing, 137
- sources, 136
- VOCs and ozone, 136

air pollution

- brown Asian haze (ABC), 149
- Calcutta, 149
- Eastern Europe
 - reducing, 151
- from desertification, 148
- from space, 142–144
 - carbon monoxide, 142
 - dust storms, 144
 - NASA, 142
 - smoke, 143
- less-developed countries, 148
 - children, 148
 - reducing, 150
- seen from space, 142–144
- Shenzhen
 - cause, 150

air pollution and desertification

- reducing, 148

air toxics, see air pollutants, HAPs**Alaska, 232, 402****Algeria, 397****allergies, 72, 73, 77, 126, 139, 447, 486, 490, 492, 493, 494****alveoli, 74****ambient air pollutants, see air pollutants, criteria****ammonia, 558****Anopheles mosquito, 471****Antarctic, 144, 174, 175, 177, 181, 211, 219, 221, 222, 224, 226, 233, 234, 257, 348, 420, 422, see also stratospheric ozone****antibiotic drugs**

- resistance
 - development of, 471

antifreeze, 102**Apollo Project**

- “energy, jobs”, 406

Aral Sea, 147**Arctic, 257, 420, 435, 449**

- PCB levels, 15
- POP accumulation, 15

Argentina, 302, 469**Aroclor**

- see PCBs, 1939.1

- Arrhenius, Svante**, 170
- arsenic**, 12, 288, 293, 294, 295, 308, 309, 451, 452, 453, *see also* **water contaminants**
 as syphilis treatment, 432
 inorganic compounds, 452
 uses, 452
- asbestos**, 64, 94, 139, 370, 484, 505
 exposure, 12
- Asia**, 21, 109, 143, 144, 146, 147, 148, 149, 150, 153, 167, 169, 189, 190, 269, 302, 343, 426, 435, 440, 451, 453, 477, 480, 512
 arsenic exposure, 432
- aspirin**, 59, 61, 69, 501
- Atlantic Ocean**, 21, 143, 144, 152, 178, 207, 272, 278, 370
- atmospheric deposition**, *see also* **acidic deposition** (“acid rain”)
 atrazine, 464
 atropine, 59
- Australia**, 265, 450, 475, 533
- Bacillus thuringiensis (Bt)**, 461
- baculoviruses**, 461
- Bangkok**, 150
- Bangladesh**, 12, 302, 344, 371, 453
 arsenic, 293
 steel recycling, 370
- banks**
 Asia Development Bank, 21, 512
 Inter-American Development Bank, 480
 World Bank, 23, 148, 280, 302, 405, 444
- base deposition**
 produced of, 157
- batteries**
 energy to manufacture, 341
 EU regulations, 342
 lead acid, 336
 metal reclamation, 342
 Ni-cad, 342
 rechargeable, 342
 reclaiming metals from, 342
 waste management hierarchy, 341
- Beijing**, 81, 145, 146, 151, 345, 387, 500
- Belgium**, 536
- benzene**, 78, 94, 527
 exposure, 140
 ill effects, 139
 VOCs, 136
- benzopyrene**, 76
 as PBT, 415
- benzopyrene**, 76
- Bhopal**, 1, 18, 19, 32, 39, 42, 444, 525
- bioaccumulation**, 411
 land based, 16
- biodiesel**, 383
- biofuels**
 LCA, 55
- biomass fuels**
 algae, 383
- biomonitoring**, *see* **chemicals in the body**
- biosolids**, *see* **wastewater treatment**
- Biosphere 2**, 7, 515
- bio-treatment**, *see* **solid waste, municipal: composting**
- bisphenol A (BPA)**, 83–85
- Black Sea**, 278, 279
- black-lung disease**, 386
- “blue baby” syndrome**, 293
- Bolivia**, 499
- Bombay**, 27
- botulinum toxin**, 59, 60
- Brazil**, 21, 109, 149, 209, 302, 311, 337, 345, 346, 383, 448, 536
 Curitiba, 25
- brownfield**, *see* **hazardous waste sites**
- Bt**, 473
- Buenos Aires**, 302
- cadmium**, 70, 139, *see also* **metals**
- CAFOs**, *see* **confined animal feeding operation**
- calcium carbonate shells**, 559
- Calcutta**, 149, 150
- California**, 12, 148, 256, 264, 319, 366, 369, 399, 401, 404, 468, 475, 531
 motor vehicles, 380
- Cambodia**, 364, 478
- Cameroon**, 144, 205
- Canada**, 15, 76, 257, 299, 300, 441, 464, 494
 Arctic animals, 416
- Canberra**, 533
- cancer**
 causes, 80, 83, 94
 infection, 80
 pollutants, 80
 development, 79–80
 dose-response, 79
 initiation and promotion, 79
 organ affected
 bladder, 98, 294
 liver, 74, 94, 294
 lung, 12, 78, 94, 294, 450, 498
 scrotum, 94
 skin, 225, 293
 vagina, 83
- carbofuran**, 469
- carbon monoxide**, 60, 119, 120, 135, 142, 143, 376, 379, 392, 487, 509, *see also* **air pollutants, criteria**
- carbon tetrachloride**, 220
- carbonic acid**, 557
- Caribbean**, 144, 147, 432
- cars**, *see* **motor vehicles**
- cataracts**, 225
- caustic**, 502

- CCA alternatives**, 452
- CFL light bulbs**, 387
- chemical**
 - bioavailability, 66
 - persistence, 35
 - PCBs, dioxins, 65
 - reference, 44
- chemical effects**
 - body organs, 71–74
 - irritant, 63
 - local, 73
 - multiple chemicals, 62
 - additive, 19, 63
 - antagonists, antidotes, 19, 63
 - synergism, 19, 63, 74
 - synergism, 74
 - target organs, 65
- chemical exposure**, 89
 - children, 76
 - multiple chemicals, 62
 - one chemical, 63
- chemical risk**
 - impoverished countries, 109
 - occupational, 109
- chemical risk assessment**, 34–35, 98–108
 - animal tests, 105
 - cancer, 104–108
 - dose-response, 105
 - excess tumors, 105
 - exposure assessment, 105
 - hazard identification, 104
 - no safe dose, 105
 - potency factor, 106
 - risk
 - assumptions, 107
 - risk characterization, 106
 - upper-bound risk, 108
 - cancer dose-response assessment, maximum tolerated dose, 105
 - definition, 34
 - dose response
 - reference dose, 101
 - safety factor, 101
 - dose-response
 - NOAEL, 101
 - dose-response assessment, 100, 101, 105
 - ecosystem assessment, 108
 - exposure assessment, 100
 - most highly exposed, 103
 - route of, 103
 - source, 103
 - worse-case, 103
 - future of, 113
 - hazard, 98
 - hazard assessment, 100
 - hazard identification, 100
 - hazardous waste sites
 - indicator chemicals, 99
 - human subjects, 102
 - non-cancer, 100–104
 - pesticides
 - cumulative risk, 104
 - risk characterization, 100
 - hazard quotient, 104
 - safety factor
 - children, 465
 - factors of 10, 102–103
 - what it compensates for, 99
 - what it is not, 99
 - when warranted, 99
 - why do, 99
- chemical risk management**, 110–113
 - factors considered, 110
 - laws and regulations, 110
 - legislative tools, 110
 - negligible risk, 110
 - take-back laws, 111
- chemical toxicity**, 62
 - aflatoxins, action level, 74
 - ammonia, 218
 - arsenic**, 64, 453
 - drinking water, 293
 - epidemiologic studies, 295
 - exposure
 - chronic, 293
 - drinking water, 451
 - sources of, 453
 - exposure levels, 295
 - gangrene, 294
 - in utero, 295
 - key environmental health problem, 451
 - local and systemic effects, 73
 - mass poisoning, 293
 - murders, 452
 - reducing risk, 294–295
 - asbestos, 12, 73
 - atrazine, 114
 - benzene, 65
 - cadmium, 70
 - caffeine, 62
 - carbofuran, 469
 - carbon monoxide, 72, 388
 - carbon tetrachloride, 62
 - DDT, 413, 415
 - DES, 83
 - dibromochloropropane, 76
 - diethylene glycol, 102
 - dioxins, 413
 - endosulfan, 469
 - ethyl alcohol, 62, 72
 - formaldehyde, 63, 64, 73

chemical toxicity, (cont.)

- insecticides, 466–468
 - carbamates, 467
 - DDT, 466
 - organochlorines, 466
 - organophosphates, 466
- iron, 427
- lead
 - IQ and memory, 435
- mercury
 - inhalation, 66
- metals, 72, 427, 432
- methylmercury**, 66, 447
 - wildlife, 444
- neomycin, 73
- nitrite
 - methemoglobin, 293
- nutrition and toxicity, 432
- oxalic acid, 62
- parathion, 65
- particles, 73
- PCBs, 413, 417
 - fetal brain, 417
- pesticides, 73, 466–469
- pesticides and children, 77
- radon, 12
- reactive gases, 73
- solanine, 62
- teratogens, 75
- thalidomide, 76
- tin, organo-, 433
- tobacco products, 76
- toxic element, 427
- trichloroethylene, 107
- vitamin A, 76

chemicals in the body

- absorption, 64–65
 - ingestion, 64
 - portal blood, 64
 - inhalation, 64
 - lung alveoli, 64
 - skin, 65
- ADME, 64–68
- bioaccumulation, 35, 67
- biomagnification, 67
 - methylmercury, 67
- biomonitoring, 91
- body burden, 91–93
 - chemicals found, 91
- CDC studies, 91
 - usefulness, 93
- distribution and target organs, 65
- excretion
 - how occurs, 67
- metabolism, 65
 - biotransformation, 65
- storage, 66

chemistry

- acids, 556
- analytical, 19
 - vanishing zero, 42
- atomic mass, 540
- atomic nucleus
 - neutrons, 539
 - protons, 539
- atomic number, 540
- atoms, 539
- Avogadro's constant, 552
- balancing reactions, 552, 554
- chemical bonds, 547
 - covalent, 545
 - ionic, 546
- electron, 540
 - configuration, 543
- electrostatic forces, 547
- elements, 539
 - electronegative, 543, 546
 - electropositive, 543
 - hydrogen, 540, 545
 - deuterium, 542
 - tritium, 542
 - lithium, 545
 - noble, 543
- free radicals, 550
- hydroxyl radical
 - atmospheric roles, 550
- incomplete products of combustion, 555
- isotopes
 - environmental chemistry, 542
 - lithium, 542
 - mercury, 441
 - oxygen, 175
 - radioisotopes, 175, 393, 543
 - stable, 543
 - what they are, 542
- metal primer, 426
- molecular mass
 - calculating, 547
- neutralization, 557
- oxidation
 - hydrocarbons, 554
- oxidation reactions, 552–555
- periodic table, 540
- pH, 556
- reduction reactions, 553
- stable octet, 544
- stoichiometry, 552
- subatomic particles, 539
- valence, 544

chemistry, chemicals

- acids, 556–558
 - ocean, 556–558
- acids, strong, 557
- acids, weak, 557

- bases, 557
- benzo(a)pyrene, 556
- biochemicals, 549
- corrosive examples, 349
- flammable examples, 349
- formula, 540
- inorganic, 17, 549
- organic, 548–549
 - definition, 548
- polyhalogenated examples, 411
- reactive examples, 349
- water
 - hydrogen bonding, 556
- Chernobyl**, 393
- Chesapeake Bay**, 243, 258
- Chicago**, 270, 299
- children**
 - drinking water pollution, 302
 - hazardous products, 501, 503
 - indoor air pollution, 77, 499
 - less-developed countries
 - air pollution, 148
 - nontoxic products, 504
 - pesticide exposure, 77
 - tolerances, 465
 - pesticides
 - wood preservative exposure, 451
 - smoke
 - exposure
 - children, 499
- children and in utero**, 75–78, 469
- Chile**, 225
- China**, 22–24, 40–41, 81, 127, 144, 145, 147, 149, 150, 151, 167, 168, 229, 280, 281, 282, 304, 344, 347, 366, 369, 387, 396, 403, 478, 499, 500, 525
 - acid deposition, 168
 - air pollution, 145–146
 - banning plastic bags, 345
 - cancer villages, 23, 81, 87
 - carbon dioxide emissions, 202
 - coal burning, 81, 167, 194, 202, 375, 387, 499
 - coal reserves, 386
 - consumption, 28
 - desertification, 145
 - dust and sand storms, 146
 - dust storms, 145
 - economic growth, 24, 41, 387
 - energy use
 - coal, 387
 - economic activity, 535
 - inefficiency, 387
 - renewables, 387
 - energy use per capita, 375
 - environmental health, 81
 - environmental laws, 40
 - environmental organizations, 40
 - Environmental Performance Index, 536
 - exported products, 28
 - export-related pollution, 150
 - food production, 127
 - green chemistry, 524
 - green technology, 319
 - human dominance culture, 22
 - laws, 40–41
 - lead in children's blood, 436
 - mercury
 - workplace exposure, 445
 - multinational operations, 41
 - name and shame, 41
 - pesticide use, 478
 - pollution
 - air, 23
 - coastal, 281
 - drinking water, 23, 281, 282, 302
 - energy use, 387
 - indoor air, 499
 - metals, 430
 - reducing pollution, 281, 500
 - rivers, 280
 - waste, 312
 - waste electronics, 367
 - waste, silicon tetrachloride, 398
 - water, 81
 - unregulated emissions, 281
 - pollution and population, 281
 - polysilicon production, 396
 - power plants
 - emission controls, 392
 - reducing pollution, 40–41
 - greenhouse emissions, 209
 - right-to-know, 44
 - sand and dust storms, 145–146
 - solid waste, 312
 - solid waste issues, 344, 345
 - State Environmental Protection Administration, 23, 145, 280
- chloracne**, 68, 417
- chlordane**, 416
- chlorine**, 502
- chloroform**
 - exposure, 140
 - ill effects, 139
- cholera**, 308
- chromated copper arsenate (CCA)**, 451–452
- Clean Air Act**, *see laws*
- Clean Water Act**, *see laws*
- climate change**
 - IPCC, 172
- closed-loop systems**, 514–515
 - Biosphere, not successful, 515
 - closed-loop recycling, 515
 - cradle to cradle, 356, 514, *See dematerialization*

closed-loop systems, (cont.)

- LCA
 - cars, 331
- DfE, 516
- factor 4, factor 10, 515
- how nature does it, 514
- industrial ecology, 513–516
- Kalundborg
 - first model, 515
- NASA
 - Advanced Life Support System, 515
- need to dematerialize, 513
- recycling
 - not enough, 515
 - wastes and emissions
 - as resources, 511
 - zero waste, zero emissions, 511

closed-loop systems, dematerialization

- computer design, 516
- designing for, 516
- durability, 520, 530
- environmentally benign manufacturing, 532
- environmentally preferable products, 519
- extended producer responsibility
 - (EPR), 521
- product stewardship, 521–523
 - barriers, 522
 - drivers, 522
- servicizing
 - chemicals, 522
 - definition, 522
 - durability, 522
 - EPR, 522
- take-back laws, 521
- tools
 - design for the environment (DfE), 519
 - LCA, 517
 - comparing products, 518
 - complexity, 517
 - P², 516
 - zero waste
 - progress toward, 529

closed-loop systems, detoxification, 523–526

- green chemistry, 365, 523
 - biodegradable, 525
 - carpets, 529
 - change chemical used, 524
 - change production process, 525
 - goals, 524–526
 - major future changes, 526–528
 - reduce chemical waste, 525
 - using enzymes, 527
 - using microbes, 526
 - using wastes, 527

coal

- amounts burned, 430
- ash from burning, 386

- externalities, 385
- increase in usage, 385
- life cycle assessment, 386
- reserves of, 386
- sulfur
 - reducing, 386

coal burning

- ash ponds, 430
- metal emissions, 453
- pollution from
 - reducing, 391
- power plants, 429
 - ash amounts, 430
- power plants, retrofitting, 392
- radioactive metal emissions, 453

Coeur d'Alene

- Superfund mining site, 351

coliform, fecal, 289**colony collapse disorder, 468****Colorado, 71, 83, 144, 200, 276, 399****combustion, 12, 76, 335, 429, 483, 546, 555**

- gasoline, 11
- incomplete products of, 11

command-and-control, 39

- limitations, 41

comparative risk assessment, 35–38**copper**

- mining, ancient practices, 431

coral reefs, 6, 188, 208**corporations**

- 3M, 46, 421
- AMOCO, 42
- Androscooggin Energy, 390
- Bayer, 525
- BMW, 331
- BP-Amoco, 390
- Bruce Mansfield, 392
- Castrol Chemical, 523
- Caterpillar, 320
- Chevron, 388
- Chisso, 444
- Donlar, 525
- Dow, 525
- Dow Chemical, 19, 415
- Duke Energy, 388
- DuPont, 415, 529
- Epson, 531
- Fetzer Vineyards, 531
- Fiat, 331
- General Electric, 418
- Hewlett-Packard, 369
- Honda, 380
- Hooker Chemical, 350
- Interface, 522, 531
- International Paper, 390, 531
- LL Bean, 333
- Maine Oxy, 402

- Motorola, 523
- Navistar, 523
- Nokia, 320
- Occidental Chemical, 350
- Panasonic, 369
- Pillsbury, 531
- Proctor & Gamble, 415
- Proctor & Gamble, 518
- Raytheon, 523
- Renault, 331
- Rohm and Hass, 391
- Sony, 369
- Sunoco, 380
- Toyota, 380, 532
- Unilever, 50
- Union Carbide, 18, 42
- Volvo, 331, 518
- Wal-Mart, 325
- Xerox, 520, 522, 531
- cotinine**, 91
- crabs**, 242, 274, 277
- cradle to cradle**, 356
- criteria air pollutants**, *see* **air pollutants**,
 criteria
- Cryptosporidium parvum**, 289, 300
- curare**, 59
- Curitiba**, 25, 311, 337, 345, 346, 536
- Czech Republic**, 151
 - right-to-know, 44
- Davis**, 475
- DDT**, 15, 17, 35, 66, 67, 75, 77, 82, 83, 86, 92, 106, 107, 108, 156, 248, 258, 410, 412, 415, 416, 420, 421, 423, 457, 458, 459, 466, 467, 471, 478, 481 *see also* **persistent organic pollutants (POPs)**; *see also* **pesticidal chemicals**
 - biomagnification, 466
 - malaria, 415
 - metabolite, 92
 - one of “dirty dozen”, 415
- dead zones**
 - Black Sea, 278
 - recovery, 278
 - description, 277
 - Gulf of Mexico, 276–278
 - nitrate fertilizer, 277
 - reducing
 - CAFOs, 279
 - fertilizer, 279
 - water pollution, nitrogen glut, 273
- dematerialization**, 516
- Denmark**, 51, 107, 399, 447
 - industrial symbiosis, 51
- DES**, 83, 84, 93, 94
- desert**
 - Gobi, 144, 146
 - Sahara and Sahel, 144
- desertification**, 6, 145, 146, 147, 148, 153, 202
 - and pollution, 145
- design for disassembly (DfD)**, 320
- design for the environment**, *see also* **DfE**, **closed loop systems**
 - design for disassembly, 320, 369
 - cars, 331
 - remanufacturing examples, 320
- design for the environment (DfE)**
- Detroit**, 361
- DfE**, 48, 316, 365, 370, 516, 517 *see also* **green chemistry**
 - and design for disassembly, 320, 331
 - design changes, 324
 - design for durability, 520
 - design for waste minimization, 334, 369, 534
 - electronic equipment, 324
 - examples of, 519
 - green chemistry, 523
 - redesigning electronics, 369
 - reducing excess material, 333
 - reducing hazardous waste, 365
 - take-back programs, 333
- Dhaka**, 344
- dibromochloropropane**, 76
- dichlorodiphenyltrichloroethane**, *see* **DDT**
- diethylene glycol**, 102
- diethylstilbestrol**, *see* **DES**
- dimethyl sulfoxide (DMSO)**, 65
- dioxins**, 14, 17, 35, 37, 44, 65, 67, 68, 90, 92, 93, 114, 134, 338, 350, 351, 363, 412, 415, 416, 417, 418, 420, 444, 448, 488
 - air emissions, 14
 - as PBTs, 414
 - bioaccumulation, 67
 - bioavailability, 66
 - biomagnification, 90
 - cannot totally ban, 416
 - chloracne, 417
 - chlorine-using processes, 90
 - combustion, 90
 - processes that produce, 416
- dissolved oxygen**, 241, 242, 259, 276, 279
- Dobson units**
 - see* stratospheric ozone depletion, 221
- Dominican Republic**, 146
- drinking water**
 - background, 286
 - bottled
 - compared to tap, 299
 - environmental impact, 299
 - standards, 299
 - contaminated, 300
 - human waste, 300–303
 - ill effects, 300
 - issues
 - most sensitive groups, 298
 - population, 298

drinking water (cont.)

- less-developed countries, 300–302
 - cholera, 308
 - point-of-use treatment, 305–306
 - reducing pathogens, 305
- safe
 - greatest medical milestone, 300
- safety
 - aging systems, 297
 - small systems, 297
 - water-borne illness, 290
 - why treat, 289

drinking water contaminants

- arsenic, 293
 - Asia, 432
 - mass poisoning, 293
 - removing, 295
 - source, 293
 - well water, 293
- chloroform and trihalomethanes, 291
- DBPs, removing, 291
- DBPs, risk, 291
- disinfection byproducts, 290
- fluoride
 - controversy, 288
- lead, 437
- microbes, 289
 - fecal coliform, 289
- nitrate
 - ill effects, 292
 - immediate threat, 292
 - sources, 292
- pathogens
 - disinfection, 290–292
 - ill effects, 289
 - immediate threat, 289
 - reducing, 290
 - sources, 290

drinking water contaminants, emerging

- antibiotics, 296
- hormones, 296
- treatments for, 297

drinking water disinfectants

- chlorine, 290–291
- non-chemical methods, 292
- non-chlorine chemicals, 291
- reducing, 292

drinking water standards

- maximum contaminant level, 287
- primary, 287–288
 - examples, 288
- secondary, 296
 - public welfare, 296
 - taste, color, odor, 296

drinking water, less-developed countries

- boiling water, 302
- children, impact on, 302

- diarrhea, 302
- Household Water Treatment
 - Network, 302
- one billion without access, 301
- pathogens
 - ill effects, 301
- unsafe water and sanitation, 300
- untreated human waste, 302
- water scarcity and pollution, 302

durability, 535

- dematerialization, 530

dust storms and desertification, 147**Earth Summit, 21, 194, 305****Eastern Europe, 262****ecosystem services, 3, 4, 6, 8, 253, 511, *see nature's services*****Egypt**

- right-to-know, 44

electricity production

- biomass, 399–400
- coal
 - LCA, 386
- coal versus nuclear, 393
- coal, oil, gas, 385–388
- dams, 403
- geothermal, 401
 - heat mining, 401
- hydrogen fuel cells
 - stationary, 401
- micropower
 - off central grid, 404
- natural gas
 - nitrogen oxides, 387
- nuclear fusion, 394
- nuclear power, 392–394
 - France, 393
 - LCA, 394
 - safety, 393
 - waste disposal, 393
- ocean energy
 - thermal energy conversion, 403
- tidal, 402
- wave, 402
- pollution
 - reducing, 388–392**
- pollution burning coal, 386
- renewable sources, 395–404
- renewables
 - dependence on sun, 395
- smart grid, 406
- solar, 395–398
 - photovoltaic, 395–397
 - large operations, 397
 - LCA, 396
 - medium operations, 396
 - polysilicon pollution, 396

- small operations, 395
 - storing energy, 397
- solar, concentrated, 397
- wind machines
 - storing energy, 398
- Emergency Planning and Community Right-to-Know Act (EPCRA)**, *see* **laws, US**
- emissions trading**, 110
- endocrine disrupter**, *see* **hormones, environmental**
- end-of-pipe**, 39, 45
 - definition, 39
- endosulfan**, 469
- energy use, world**, 374–377
 - coal, 375
 - conservation
 - in industry, 390–392
 - in the home, 388–389
 - conservation and efficiency, 388–392
 - conservation, promoting, 403
 - energy intensity, 407
 - fossil fuels, 375
 - future possibilities, 407
 - increased demand, 374
 - associated pollution, 374
 - industry
 - cogeneration, recycled energy, 391
 - district heating, 390
 - electric motors, 390
 - energy audit, 391
 - manufacturing, 390
 - reducing
 - clean coal technology, 391
 - cleaner fuels, 391
 - reducing use, 392
 - steam generation, 390
 - waste energy, 391
 - Japan as a model, 407
 - rural poor, 405
 - wood and other biofuels, 375
- England**, 107
- environmental health, poverty**, 21
- environmental hormones**
 - potential human impact, 86
- environmental issues**
 - high risk global issues, 36
 - US trends
 - US EPA, 512
- environmental justice**, 110
- Environmental Performance Index**, 535
 - good governance, 536
- environmentally benign manufacturing**, 532
- environmentally preferable products**, 318
- epidemics**
 - cancer, 83
 - water-borne, 290
- epidemiology**, 93–97
 - benzene, 94
 - biological plausibility, 96
 - birth defects, 96
 - chimney sweeps, 94
 - cluster, 95
 - community studies, 95
 - confounding factors, 94
 - definition, 93
 - electromagnetic fields, 96
 - exposure evaluation, 94
 - judging studies, 95–96
 - limits of, 96
 - occupational exposures, 94
 - PCBs, 418
 - radon, 94
 - risk factor, 96
 - scrotal cancer, 94
- EPR**, 325, 331, 333, 368, 521, 522
 - ethanol**, 400
 - from cellulosic material, 383
 - from corn, 383
- ethanol and aflatoxins**, 78
- Ethiopia**, 480
- EU**, 44, 403, 407, 420, 422, *see also* **European Union**
- Europe**, 23, 24, 27, 28, 76, 78, 101, 112, 121, 134, 141, 143, 147, 150, 151, 152, 156, 165, 166, 168, 174, 190, 202, 223, 263, 264, 269, 270, 272, 278, 279, 297, 298, 299, 365, 369, 370, 385, 390, 397, 399, 408, 426, 431, 435, 446, 522, 532, 533, 536
 - air pollutants, 141
 - energy production
 - coal, 385
- European Pollutant Emission Register**, *see* **laws, EU**
- European Union**, 44, 85, 111, 134, 151, 152, 165, 194, 195, 324, 342, 365
 - Producer Pays Program, 325
- exotic**, 1, 278, 475
 - control agents, danger, 475
- exposure to chemicals**, *see* **chemical exposure**
- extended producer responsibility (EPR)**, 325
- Exxon Valdez oil spill**, 246, 444
- FDA**, *see* **agencies: US Food and Drug Administration**
- Federal Insecticide, Fungicide, and Rodenticide Act**, *see* **laws**
- fire retardants**
 - PBDEs, 414, *see* **PBDEs**
- fishable and swimmable**, 39, 236, 255
- Florida**, 7, 79, 82, 83, 86, 144, 441, 461, 463
- fluorine**, 543, 544
- formaldehyde**
 - ill effects, 139
- France**, 14, 74, 331, 371, 392, 459, 536
- Freedom Car**, 382

frogs, 82, 114, 158, 244, 274, 469

fuel cells, 381

furans, *see* **dioxins**

gasoline

combustion, 11

general circulation models, *see* **global warming**

genetically engineered organism (GEO)

why develop, 461

Geneva, 299

GEOs, 461, 476 *see* **genetically engineered organisms**

geothermal

electricity production, 401

space heating, 401

Germany, 14, 24, 151, 158, 166, 201, 232, 297, 331, 332, 333, 337, 396, 397, 399, 452, 494, 536

recycling, 322

Ghana, 265

Giardia lamblia, 289, 290

global dimming, 23, 143

global distillation, *See* **grasshopper effect**

global warming

a warming earth, 176–178

assessing, 182–185

GCMs, 182–184

IPCC report, 184, 206

background, 170

feedback loop, 186

heat island, 176

how seen, 64–68

future, 206–208

melting ice, 178

permafrost, 180

sea levels, 182

warming earth, 176

warming oceans, 178

ice core studies, 173–175

ice-core bubbles, 542

mitigation, 203–205

natural?, 183

external forcings, 183

human signature, 183

sun's radiation, 183

reducing

carbon dioxide, 196

CFCs, 198

economics of, 206

fluorochemicals, 198

how, 196–198

International Energy Agency, 208

Kyoto, 194–196

Kyoto, beyond, 208

less-developed countries, 209

methane, 198

Montreal Protocol, 198

nitrous oxide, 199

political entities, 199–203

soot, 199

global warming, greenhouse gases

carbon dioxide, 187–188

sinks, 187

sources, 187

carbon dioxide equivalent, 185

CFCs and others, 192

levels of, 173

livestock emissions, 192

methane, 189–190

fate, 190

sources, 189

nitrous oxide, 191

ocean acidification, 188

ozone

fate, 191

soot, 192

water vapor, 186

Gobi desert, 144

grasshopper effect, 15–16, 413

Great Lakes, 67, 255, 256, 284, 410, 417, 418, 419, 420, 423, 433, 466

green chemistry

designing chemicals, 415

what it is, 523

Green Revolution, 480

Greenland, 449

growth regulators, 472

Gulf of Mexico, 250, 276, 277, 278, 279

Haber-Bosch, 273, 275

fertilizer, 273

population growth, 273

Hawaii, 435

hazard

definition, 35

variety of meanings, 99

Hazard and risk, 34

hazardous air pollutants, *see* **air pollutants, HAPs, air pollutants, hazardous**

hazardous products, 500–502

alternatives, 504

characteristic

corrosive

examples, 501

flammable

examples, 502

more than one hazard, 502

reactive, 502

examples, 502

toxic, 501

characteristics

labels, 501

corrosive

ill effects, 501

HHW

- antifreeze, 507
- collection programs, 507
- paint, oil-based, 507
- pesticides, 507
- reducing amounts, 508
- used oil, 507
- household hazardous waste (HHW), 506
 - labels, 491, 502–504
 - caution, 503
 - labels
 - required information, 503
 - nontoxic, 504
 - reducing exposure, 504
 - reducing HHW, 506
 - safe use, 504
 - toxic
 - labels, 501
 - TUR, 504
 - ventilation, 504

hazardous waste

- characteristics, 348
 - corrosive, 349
 - flammable, 349
 - reactive, 349
 - toxic, 348
- generators, 352
- hazard or risk, 349
- reducing generation, 365
- tracking cradle to grave, 356
- why important, 348
- WMH**, 353–355
 - disposal, 354
 - pollution prevention, 353
 - recycling and reuse, 353
 - sources, 352
 - treatment, 355, 363
 - bioremediation, 354
 - purposes of, 354

hazardous waste generators

- industry categories, 349

hazardous waste sites, 350, 351

- brownfields, 361
- cleanup
 - bioremediation, 363
 - genetically modified organisms, 363
 - metal contamination, 362
 - phytoremediation, 363
 - site specific standards, 361
- cleanup methods**, 361–363
 - definition, 356
 - evaluating, 356
 - old, 350
- reducing risk**, 360–361
 - cleanup, 360–361
 - imminent hazard, 360
- Superfund, 356

hazardous waste sites, Superfund, 71

- Coeur d'Alene megasite, 351
- Love Canal, 350
 - cleanup, 350
 - dioxins, 351
- mining megasites, 351
- National Priority List, 356
- Smuggler Mountain, 71

hazardous waste, household, 349

- composition, 352

hazardous waste, international transport, 364–365**Basel Convention**

- Control of Transboundary Movements of Hazardous Wastes, 364–365
- electronic waste, 370
- electronics
 - illegal movement, 366
- ships**, old, 370–371

hazards

- old buildings
 - asbestos, 505

heat island, *see* **global warming****heavy metal**, 304, 362, 370

- definition, 427

helium, 545**hemoglobin**, 60, 120, 293, 549**hexachlorobenzene**, 415

- as PBT, 415

hexazinone, 470**Hong Kong**, 343**hormones**, 80

- cortisol, 295
- estrogen, 62
- hormone receptor, 62
- pharmaceutical
 - androgens, 86
- pharmaceutical estrogens, 83

hormones, environmental,

- 80–86
- alligators, 82
- BPA, 83
- dioxins, DDT and PCBs, 413
- estrogen mimic
 - DDT, 82
- Lake Apopka, 82
- mimics, 62
- phthalates, 85
 - infant males, 101
- phytoestrogens, 81, 86
- pollutant, 62

Houston, 25, 123

- air pollution, 118

Hudson River, 417**Human Domination**, 1, 33, 512**Hungary**, 14**hydrocarbons**, 133, 489

- hydrochloric acid**, 556
- hydrogen**
 - fuel cell, 381
- Iceland**, 401, 402
- incomplete products of combustion**
 - examples, 555
- India**, 12, 22, 149, 265, 302, 371, 407, 536
 - coal reserves, 386
 - energy use, 387
 - economic activity, 535
 - energy use per capita, 375
 - Kerala, 25
 - power plants emission controls, 392
 - steel, 370
- individuals**
 - consequences of actions, 334
 - personal actions, 319
 - pollution prevention examples, 48
 - recycling and reuse
 - examples, 49
- Indonesia**, 452, 479
- indoor air pollutants**, 487–491
 - auto exhaust, 488
 - benzene
 - description, 490
 - ill effects, 490
 - sources, 490
 - biological
 - description, 493
 - carbon monoxide
 - sources, 487
 - formaldehyde
 - description, 489
 - ill effects, 490
 - from carpets, 494
 - from combustion appliances, 487
 - from consumer products
 - advice, 491
 - reducing exposure, 486
 - from stoves, fireplaces, 488
 - moisture
 - mold, 492
 - reducing, 492
 - mold
 - reducing, 486
 - sources, 486
 - nitrogen oxides
 - combustion appliances, 487
 - other chemicals, 491
 - PAHs
 - benzo(a)pyrene, 489
 - description, 489
 - sources, 489
 - paradichlorobenzene
 - sources, 491
 - particulates
 - combustion appliances, 487
 - description, 494
 - sources, 494
 - PERC
 - sources, 490
 - radon**
 - action level, 494, 498
 - how generated, 494
 - ill effects, uncertainty, 498
 - lung cancer, 498
 - polonium-218 and -214, 497
 - reducing levels, 497
 - smoking, 497, 498
 - sources, 494
 - testing for, 497
 - well water, 497
 - tobacco smoke, 487
 - ubiquitous chemicals, 488
 - VOCs
 - sources, 488
- indoor air pollution**, 77
 - background, 483
 - ill effects, 485–486
 - chronic, 486
 - examples, 485
 - temporary, 486
 - reducing, 493
 - ventilation, 486
 - sources, 483
- indoor air pollution, less-developed countries**, 499–500
 - carbon monoxide, 499
 - China, 500
 - indoor air pollution
 - ill effects, 499
 - reducing
 - alternative fuels, 500
 - efficient stoves, 500
 - reducing exposure, 500
 - smoke, 499
 - exposure, 499
 - fuels used, 499
- industrial ecology**, 51–54, 513–515, 513–516
 - phosphorus, 271
 - ultimate goal, 514
 - wastewater, 263
- industrial symbiosis**, 51–54
- integrated pest management**, 268, 474, *See* **IPM**
- Inuit**, 15, 413, 416, 442
- ionizing radiation**, *see also* **indoor air pollutants: radon**
 - alpha, beta, gamma particles, 497
 - carbon-14, 495
 - cosmic rays, 495
 - exposure sources, 496

- isotopes
 - nuclear fission, 394
 - radioisotopes, 495
- potassium-40, 495
- radioisotopes, 175
 - half-life, 497
 - radon, 497
 - tritium, 542
 - uranium, thorium, 393
- radon, 497
 - background, 495
- terrestrial sources, 495
- thorium-232, 495
- uranium-238, 495
- X-rays, 496
- Iowa**, 399
- IPCC**, *see* **global warming**
- iron**, *see* **metals**
- isopropyl alcohol**, 504
- Israel**, 264, 420
- Istanbul**
 - air pollution, 118
- Italy**, 203, 331, 351, 382, 524
- Japan**, 15, 23, 24, 28, 36, 70, 145, 146, 147, 165, 167, 209, 326, 331, 333, 334, 336, 343, 368, 374, 375, 380, 382, 392, 394, 407, 418, 420, 431, 444, 466, 516, 521, 524, 532, 533, 534, 535, 536, 537
 - DfE, 368
 - minimizing energy use, 534
 - Waste Electrical and Electronic Equipment Directive, 368
- Java**, 447
- jelly comb**, 278
- Kabul**, 343
- kaizen**, 533
- Kalundborg**, 51, 390, 515
- Kauai**, 435
- Kentucky**, 29, 300
- Kenya**, 344, 499, 500
- Korea**, 24, 145, 146, 165, 167, 370
- Kyoto Protocol**, *see* **global warming**
- lakes**
 - Lake Chad, 147
 - Lake Erie, 147
 - Lake Ontario, 420
- Latin America**, 15, 147, 265, 308, 464, 475, 477, 480
- laws**
 - EU
 - take back, 325
 - EU Registration, Evaluation and Authorization of Chemicals, 111
 - EU Waste Electrical and Electronic Equipment Directive, 324
- one size fits all, 42
- unintended consequences, 42
- US Clean Air Act, 38, 39, 43, 118, 124, 137, 138, 154, 156, 162, 164, 168, 169, 413, 445
 - air quality standards, 118
 - grandfathering, 392
- US Clean Air Act Amendments, 138, 140, 158, 162, 164, 379, 433
- US Clean Water Act, 38, 39, 236–249, 261, 263
- US Comprehensive Environmental Response, Compensation and Liability Act, 38, *see also* US Superfund
- US Emergency Planning and Community Right-to-Know Act, 43
- US Energy Policy Act, 381
- US Federal Food Drug and Cosmetics Act, 102
- US Federal Insecticide, Fungicide, and Rodenticide Act, 38, 471, 504
- US Hazardous Substances Labeling Act, 502
- US Oil Pollution Act, 258
- US Poison Prevention Act, 503
- US Pollution Prevention Act, 46
- US Resource Conservation and Recovery Act, 38, 315, 354
- US Safe Drinking Water Act, 38, 236, 287–293
- US Superfund, 38, 71, 350, 351, 352, 354, 356, 357, 360, 361, 364, 372, 373, 417
- US Toxic Substances Control Act, 38, 111, 249
- US Toxics Release Inventory, 43–44, 352
- LCA**, 331, 517–519
 - coal, 386
 - computers, 370
 - definition, 30
 - environmentally preferable products, 519
 - four stages of, 517
 - metal products, 428
 - refrigerators, autos, 370
- lead**, *see* **metals**, **lead and PBT metal**, **lead, metals**
- Legionella bacteria**, 289
- life cycle assessment**, *See* **LCA**
- Lima**, 308
- lime**, *see* **metals**, **calcium oxide**
- livestock**
 - CAFOs, 279
 - greenhouse gas emissions, 51, 192
- Los Angeles**, 24, 25, 53, 109, 123, 132, 144, 148, 149, 256, 396
- Louisville**, 300
- lye**, 502
- Maine**, 369, 390, 402, 443, 470
- malaria**, 471
- Manila**, 344
- marine organisms**, 327
- Maritime Provinces**, 441
- Maryland**, 270, 369

- Massachusetts**, 319, 366, 457
- McDonough, William**, 10, 311, 515
- megacities**, 27, 149, 257
- mercury**, 140
- metal pollutants**
 - agricultural soils, 431
 - Arctic haze, 426
 - characteristics, 425–427
 - exposure
 - food, drinking water, 427
 - how exposed, 431
 - fresh and marine waters, 431
 - hazardous waste sites, 431
 - mining
 - ancient practices, 431
 - sulfur and acid, 428
 - wastes, 428
 - particulates, 426
 - reducing levels, 432
 - pollution prevention, 433
 - soil and sediment, 426
 - sources, 428–431
 - fossil fuel burning, 429
 - mining, 428
 - mining, overburden, 312, 428
 - smaller sources, 430
 - transport in water, 426
 - transport with wind, 426
- metals**, 70, 363, 427, *see also* **hazardous waste sites and chemical toxicity**
 - aluminum
 - bauxite mining, 322
 - recycling, 322
 - and coal burning, 453
 - arsenic, 430, 451–453
 - as pesticide, 457
 - sources, 453
 - sources, natural, 453
 - arsenic, cadmium, lead, 145
 - cadmium, 70, 427
 - Arctic, 449
 - mining, 448
 - natural sources, 449
 - NiCad batteries, 448, 450
 - takeup into plants, 449
 - uses, 448
 - zinc mining, 450
 - calcium oxide, 426
 - characteristics, 425–427
 - copper, 448
 - copper arsenate
 - as pesticide, 457
 - hazardous, 427
 - heavy, 262
 - definition, 427
 - in coal, 386
 - iron, 331, 336
 - iron (steel), 322, 324, 378
 - manufacture, 320, 322, 387, 407
 - mills, 361
 - recycling, 370, 452
 - usage, 452
 - iron oxide, 426
 - lead
 - ancient mining, 431
 - clean up, 362
 - dispersive emissions, 412
 - old leaded paint, 71
 - properties and uses, 434
 - remaining uses, 437
 - smelting, 351
 - Superfund sites, 351
 - tetraethyl, 426
 - lead, *see also* PBT metal, lead
 - lead, 448
 - lead arsenate
 - as pesticide, 457
 - lithium, 432
 - mercury, *see also* PBT metal
 - artisanal mining, 439
 - as pesticide, 457
 - cinnabar, 439
 - cycling in environment, 440
 - hot spots, 443
 - isotopes, 441
 - mercuric oxide, 440
 - products containing, 439
 - properties, 140
 - sources, 439
 - vapor, 440
 - metal oxides, 426
 - mining, 71, 427
 - ancient practices, 431
 - natural, 427
 - nickel, 381
 - nutrient metals, 427
 - plant hyperaccumulation, 363
 - plutonium, 363
 - poisoning with, 432
 - problematic, 428
 - radioactive, 386
 - recoverable, 320
 - recovering metals from electronics, 369
 - selenium
 - wildlife poisoning, 432
 - shipbreaking, 370
 - strontium
 - bioaccumulation in bones, 67
 - thallium, 430
 - therapeutic uses, 432
 - bismuth, 432
 - folk remedies, 432
 - gold, 432
 - lithium, 432

- tin, 433
 - antifouling paint, 433
 - organotin toxicity, 433
- tin, tributyl- (TBT), 433
- toxicity
 - nutrition, 432
- uranium and thorium, 393
- zinc
 - in cadmium mining, 448
- methane**, 387, 545, 548
- methanol**, 501
- methyl bromide**, *see* stratospheric ozone depleting chemicals
- methyl chloride**, *see* stratospheric ozone depleting chemicals
- methyl isocyanate (MIC)**, 18, 43, 525
- methylene chloride**, 136, 504
- Mexico**, 147, 149, 464
 - reducing lead's risk, 438
 - right-to-know, 44
- Mexico City**, 27, 109, 150, 151
 - air pollution, 118
- Michigan**, 361
- Millennium Development Goals**, 21, 302
- Millennium Ecosystem Assessment**, 3, 7
- Milwaukee**, 290, 300
- Minamata**, 444
- mining**, 14, 28, 29, 45, 48, 119, 189, 199, 240, 245,
 - 303, 311, 312, 322, 339, 341, 347, 349, 351, 356, 360, 362, 372, 375, 385, 386, 401, 421, 426, 427, 428, 431, 433, 434, 435, 439, 440, 446, 448, 453, 454, 513, 534
- coal, 9, 386
- Minnesota**, 318, 319, 399, 441, 445, 531
- Mississippi River**, 464, 512
- mixtures, toxicity of**, *see* toxicity: mixtures
- mole**, 552
- Molina, Mario**, *see* stratospheric ozone, depletion
- Mongolia**, 144, 145, 146, 167
- monocrotophos**, 469
- motor vehicle fuels**
 - biodiesel, 383
 - biofuels, 383
 - flexibly fueled vehicles, 381
- motor vehicles**
 - electric, 381
 - fossil fuel use, 377–384
 - gasoline use, 378
 - history, 377
 - pollution from, 377–378
 - reducing**, 378–381
 - biomass fuels, 384
 - energy efficiency, 384
 - flexibly fueled vehicles, 381
 - hybrids, 380
 - hydrogen fuel cell, 381
 - increasing fuel economy, 380–381
 - maintenance, 380
 - reducing, how to, 379
- Mt. Pinatubo**, 127, 184, 193, 224
- Nairobi**, 344
- nanotechnology**, 516
- NAPAP**, *see* acid deposition
- NASA**, *see* US Aeronautics and Space
 - Administration, agencies: US National Aeronautics and Space Administration
- natural gas**, 387
- Natural Resources Defense Council**, 256, 299
- nature's services**, 2, 7, 38 *see also* ecosystem services
 - Table 1.1 3
- neon**, 543
- Nepal**, 400
- nerve gases, organophosphates**, 467
- Netherlands**, 74, 107, 203, 207, 276, 399, 536
- New Delhi**, 22, 148, 150
- New Hampshire**, 152
- New Jersey**, 332, 345
- New York**, 2, 6, 13, 32, 33, 53, 87, 109, 132, 149, 159, 164, 165, 345, 400, 417, 418
- New York City**, 3, 7, 256, 291, 292, 300, 317, 322, 339, 377
- Niagara Falls**, 350
 - Love Canal, 350
- Nicaragua**, 480
- nicotine**
 - cotinine metabolite, 91
- nicotine sulfate**, 457
- NIMBY**, 325
- nitric acid**, 557
- nitric oxide**, 59
- nitrogen fixation**, 1 *see* bioavailable nitrogen
- nitrogen glut.**, *See* water pollution, nitrogen glut
- nitrogen oxides**, *See* air pollutants, criteria
- nitrogen, bioavailable**, 272
- nitrogen, reactive**, 272
- nitroglycerine**, 59
- North Carolina**, 131, 247, 276
- Northern Ireland**, 402
- Norway**, 420, 447
- nutrition**, 294, 449
 - Arctic ponds, 16
 - arsenic poisoning, 294, 432
 - cadmium, 450
 - liver cancer, 74
 - malnutrition, 74, 480
 - metals, 432
 - xenobiotics, 70
- nylon**, 529
- ocean acidification**, *see* Box 7.5
- OECD**, 36, 281, 343, 375, 387, 404
- Ogallala aquifer**, 5

- oil spill**, 8, 246, 283, 362, 444
 - Exxon Valdez, 246
 - Gulf war, 246
- Ontario**, 300, 421
- ore**
 - bauxite, 322
 - cinnabar, 439
 - copper, 431
 - gold, 29
 - iron, 370
 - lead, 29, 431
 - metal, 245, 311, 429
- Oregon**, 399
- oxalic acid**, 501
- ozone hole**, *see* **stratospheric ozone depletion**
- ozone, ground level**, *see* **air pollutants, criteria**
- ozone, stratospheric**, *see* **stratospheric ozone**
- Pacific Garbage Patch**, 325–328
- Pacific Ocean**, 24, 144, 178, 326, 422
- packaging**
 - functions of, 324
- PAHs**, *see* **air pollutants, criteria: particulates**
 - bioavailability, 66
- PAHs (polycyclic aromatic hydrocarbons)**, *see* **criteria air pollutants (particulates) and indoor air pollutants**
- Pakistan**, 370
- Paracelsus**, 57
- parathion**, 467
- Paris**, 109
- pathogens**, 300–302
 - wells, where site, 297
- PBDEs**, 419–420
 - blood of house cats, 420
 - Canadian Arctic, 420
 - fire retardants, 414, 419
 - in breast milk, 420
 - in foods, 420
 - outgassing, 419
 - reducing, 420
 - toxicity, 420
- PBT metal, cadmium**
 - bioaccumulation, 67, 449, 453
 - exposure
 - limits, 453
 - study of, 450
 - vegetarians, smokers, 449
 - why in food, 448
 - exposure sources
 - food, 449
 - ill effects, 70, 449–450
 - calcium metabolism, 450
 - carcinogen, 450
 - epidemiologic study, 450
 - itai itai, 70
 - occupational exposure, 449
 - target organs, 449
- levels in environment, 448
- reducing levels
 - Australia, 450
 - batteries, 450
 - regulations, 451
- sources, 448
- transport, 449
- PBT metal, lead**, 434–438
 - bioaccumulation, 67
 - blood levels, 436
 - prehistoric, 438
 - exposure sources
 - children, 435
 - home and workplace, 435
 - ill effects, 435
 - IQ and memory, 436
 - Zambian children, 87
 - lead from earlier emissions, 434
 - reducing risk
 - from gasoline, 436
 - from paint, 436
 - lead safe, 437
 - old lead, 437
 - removing from soil, 362
 - sources, 434
 - natural, 438
 - storage in bones, teeth, 435
 - transport, 435
- PBT metal, mercury**, 415, 438–448
 - Arctic animals, 416
 - biomagnification, 67, 442, 444, 448
 - fish, 441
 - blood levels, 447
 - exposure
 - dental amalgams, 446
 - fish, 103, 442
 - fish-eating animals, 442
 - Inuit, 442
 - prenatal, 442
 - wildlife, 443
 - workplace, 443
 - fish advisories, 444
 - commercial fish, 444
 - ill effects, 444
 - humans, 444
 - mad hatter, 438
 - poisoning, Minamata, 444
 - mercury to methylmercury, 403, 431, 439, 442
 - reducing deposition, 445
 - reducing risk, 446
 - changing industrial processes, 446
 - combustion, 445
 - dental amalgams, 447
 - eliminating products, 446
 - international reductions, 446

- regulations, 445
- workplace, 445
- risk
 - guidelines, 447
 - prenatal, 447
 - selling mercury, 448
- sediment, 426
- sources, 440
 - mining, 440
 - power plants, 440
- transport, 441
 - atmospheric lifetime, 440
 - identifying sources, 441
- transport and accumulation, 440
- PBTs, metals**, 434
 - multiple problems, 412
- PBTs, organic**
 - “dirty dozen” polychlorinated, 415
 - Arctic animals, 413
 - bodies of Inuit, 413
 - characteristics, 411–413
 - characteristics
 - bioaccumulation, 411
 - biomagnification, 412
 - persistence, 411
 - toxic, 413
 - transport, 413
 - volatility, 413
 - DDT, 466
 - decreases in Arctic animals, 416
 - emissions
 - dispersive, 412
 - fire retardants, 414
 - multiple problems, 412
 - names of “dirty dozen”, 415
 - number of, 410
 - PBT examples, 414
 - PCBs, 548–549
 - PDBEs
 - reducing risk, 420
 - PFOSs, 421–422
 - polybrominated fire retardants (PBDEs), 414, 419–420
 - polyhalogenated, 411
 - POPs, 411
 - reducing, 413–416
 - screening for, 414
- PCBs**, 11, 15, 17, 38, 67, 68, 72, 73, 75, 90, 92, 103, 107, 156, 219, 243, 249, 262, 288, 357, 363, 369, 370, 410, 412, 415, 416, 417, 418, 420, 421, 422, 423, 424, 444, 448
 - bioaccumulation, 67, 412
 - bioavailability, 66
 - chloracne, 417
 - cooking oil contamination, 418
 - cycling in environment, 417
 - epidemiological studies, 418
 - exposure today, 417
 - family, 417–419
 - fish exposure, 418
 - Great Lakes fish, 419
 - Hudson River**
 - contamination and cleanup, 417–418
 - Superfund site
 - dredge sediment, 418
 - obvious toxicity, 418
 - sediment concentration, 417
 - subtle toxicity, 419
 - toxicity, 417, 418, 419
 - ubiquitous contaminant, 417
 - uses, 417
 - where still found, 416
- Pennsylvania**, 332, 495
- persistent organic pollutants (POPs)**
 - see also* **PBTs**
- persistent, bioaccumulative, and toxic**, *see* **PBTs**
- Peru**, 308, 477
- pest populations**
 - pest resurgence, 470
 - resistance
 - development of, 470
 - increasing problem, 471
 - secondary pest, 470
- pesticidal chemicals**, 65
 - atrazine, 464
 - DDT
 - broad spectrum insecticide, 459
 - history of, 457
 - fumigant examples, 459
 - hydrogen cyanide, 457, 459
 - methyl bromide, 459
 - neem tree extract, 460
 - nicotine sulfate, 457
 - pheromone, 461
 - pyrethrum, 457
 - rotenone, 467
- pesticide pollution**
 - crops and food, 465
 - exposure, 464–466
 - farming
 - conventional, 473
 - IPM, 474
 - organic, 473
 - ill effects, 466–469
 - amphibians, 469
 - birds, 468
 - fish, 469
 - humans, 469
 - insecticides
 - carbamates, 467
 - organophosphate poisoning, 467
 - organophosphates, 466
 - polychlorinated, 466
 - nontarget species, 468–469

pesticide pollution (cont.)

- on pollinating insects, 468
- soil organic material, 470
- organophosphates
 - fate, 467
- pest resistance, 470–471
- POPs fate, 466
- POPs, persistence and climate, 464

reducing risk, 471–476

- biocontrol, 475
- changing farming methods, 473–475
- crop protectant, 472
- ecologically appropriate regions, 477
- educating farmers, 476
- green chemistry, 472
- organic farming, 473
- pheromones and growth regulators, 472
- reducing pesticide use, 474
- regulations, 471
- sustainable farming, 476
- techniques, 474–475

residues

- monitoring imported food, 466
- monitoring produce, 465

sources of, 463–466**transport**, 463

- POPs, 464

where detected, 464**pesticides**

- “dirty dozen”, 415
- alternatives to, 460
- arsenic
 - chickens, 452
- biopesticides, 461
 - botanicals, 460
 - classes of, 460
 - genetically engineered, 461
 - microbials, 461
- broad spectrum, 459
- categories, 457
- definition of, 456
- desirable characteristics, 473
- disinfectants, 459
- exposing insects, 467
- exposure
 - farmers’ children, 77
- flower growing, 78
- fumigants, 459
- herbicides, 468
- household hazardous waste, 457
- ingredients
 - active and inert, 471
- insecticides
 - organochlorine, 466
 - persistence, 466
 - polychlorinated examples, 466

introduction to, 456–458

- organophosphate metabolites, 91
- organophosphate, parathion, 467
- organophosphates, 60
- pest resistance, 458
- polychlorinated
 - POPs, 466
 - solubility, 466
- POPs
 - why banned, 466
- quantities used, 463
- registration process, 465
- school use, 78
- selective (narrow spectrum), 459
- testing in humans, 115
- tolerances, 465
 - what they are, 113
- types of, 459–461
- water solubility, 464
- who uses
 - almost everyone, 463
- why use, 456, 463
 - aesthetic reasons, 462, 463
 - grow in more places, 462
 - long storage time, 462
 - longer season, 461
 - monocultures, 462
 - public health reasons, 462
- wood preservative, 451

pesticides, less-developed countries,

477–480

- Cambodia, 478
- China, 478
- dangerous pesticides, 478
- Ethiopia, 480
- ill effects
 - poisoning, 477
- Indonesia, 479
- Nicaragua, 480
- obsolete pesticides, 478
- prior informed consent, 478
- reducing pesticide use, 479
- reducing risk
 - Farmer Field Schools, 479

petroleum distillates, 504**PFOSs**

- Arctic wildlife, 422
- bioaccumulative, 421
- fluorine chemicals, 421
- persistence, 421
- reducing levels, 422
- toxicity, 421

pH, see water pollutants, conventional**pH, ocean**, 558**phenol**, 459**pheromone**, 472**Philadelphia**, 332, 380

- Philippines**, 27, 184, 344
- phthalates**, 85
 - metabolites, 92
 - plasticizers, 414
- Plant-Incorporated-Protectants**, 461
- plasticizers**, 414
- Poland**, 151
- pollutant**
 - concentrations
 - described, 9
 - definition, 8
 - oxidation, 17
 - sources, 12
 - transport
 - air, 14
 - chemical signature, 23
 - grasshopper, 15
 - transboundary, 23
 - water, 14
- pollutant, anthropogenic**, 10
- pollutants**
 - anthropogenic, 10
 - barely detectable, 19
 - buried, 16
 - fate, 16
 - fate and transport, 13
 - inorganic, 17
 - mineralization, 17
 - natural, 10
 - organic
 - degradation, 16
 - fate, 16
- pollution**
 - actions at a distance, 29
 - drivers
 - affluence, 28
 - individuals, 29, 30, 31
 - population growth, 26
 - technology, 28
 - electronic waste, 370
 - less-developed countries, 21
 - obvious, 8
 - why it happens, 10
- pollution indoor air**, 77
- pollution prevention**
 - examples, 46
 - industry, 47
 - housekeeping practices, 46
- pollution prevention (P²)**, 46–48
 - definition, 45
- polyacrylates**, 524
- polyethylene terephthalate**, 306, 323
- polysilicon**, 396
- polyvinyl chloride**, 532
- POPs**, *see also* **PBTs, organic**
 - three families, 416
- population growth**, 8, 12, 26, 27, 36, 171, 197, 260, 264, 286, 305, 470
 - poverty and efficient resource use, 515
- Portugal**, 402
- Potomac River**, 243
- precautionary principle**, 85, 89, 112, 114, 447
- product stewardship**, 521
- propane**, 381
- pyrethrins**, 460
- pyrethrum**, 457
- Quebec**, 413
- radon**, 11, 107, 484, 485, 494–499, 545
 - in mines, 498
- radon-222**, 497
- recycling**
 - problems, 49
- recycling and reuse**, 48–49
 - examples, 49
- red tide**, 274
- Re-power America**
 - carbon-free energy, 406
- reuse**, 48
- Reykjavík**, 402
- right-to-know**
 - Europe, *see* **laws, EU**
- Rio de Janeiro**, 305
- risk**
 - defined, 98
 - definition, 35
- risk assessment**
 - chemical, *see also* chemical risk assessment
 - comparative, *see also* comparative risk assessment
 - comparative, 37
 - individual activities, 334
- risk management**, *see also* **chemical risk management**
 - children, 113
 - greater protection, 113
 - pesticides, 113
 - Europe, North America, 112
 - non-regulatory tools, 111
 - pesticide tolerance, 113
 - precautionary principle, 111, 112
- river**
 - Big Sandy, 29
 - Coeur Alene, 351
 - Cuyahoga, 8
 - Danube, 14, 278
 - Emory, 430
 - Hai, 23
 - Hudson, 351, 417, 418
 - Mississippi, 158, 250, 276, 277, 464, 512
 - New River, 276
 - Potomac, 83, 243
 - Rhine, 14, 240, 280, 403, 418

- river** (cont.)
 - Songhua, 24
 - Tisza, 14
 - Yangtze, 3, 146, 280
 - Yellow, 146, 280
- Romania**, 14
- Rowland, F. Sherwood** *see* **stratospheric ozone, depletion**
- Russia**, 375, 394, 435
- rust**, 426
-
- Safe Drinking Water Act**, *see* **laws**
- San Diego**, 218
- San Francisco**, 144, 254, 299, 321, 322, 337, 345, 377, 446
- sand storms**, *see* **air pollution**
- sanitation**
 - greatest medical milestone, 301
- Scotchgard™**, 421
- Scotland**, 402
- Seattle**, 270, 533
- selenium**, 432
- Seoul**, 145
- septic systems**, *see* **wastewater treatment**
- servicizing**, 522–523
 - chemicals
 - how it works, 522
- sewage**, 300–308
- shellfish**, 139, 236, 247, 255, 258, 259, 274
- shipbreaking**, 370–371
- silicon tetrachloride**, 396
- silicosis**, 69
- silver**, *see* **metals, silver**
- Singapore**, 264, 337, 343
- sludge**, *see* **wastewater treatment**
- smog, history of word**, 122
- smokers**, 63, 133, 295, 431, 487, 488, 490, 497, 498
- sodium hydroxide**, 557
- sodium hypochlorite**, 459
- solanine**, 62
- solar energy**, 395–398
 - passive, 398
- solid waste**
 - China, 344
 - combustion of, 336
 - slums, 343
 - sources, 311
 - types, 311
- solid waste, developed countries**
 - management, 343
- solid waste, less-developed countries**
 - in slums, 343
 - problems, 343–345
 - recovering value
 - Bangladesh, 344
 - Curitiba, 345
 - scavengers, 344
- solid waste, municipal**, 317
 - components, 313
 - composting, 329
 - design for the environment (DfE) *see* **design for the environment**
 - disposal, irresponsible, 326
 - environmentally preferable products, questions, 519
 - ill effects, 313
 - impact on oceans**, 325–328
 - junked cars, 331
 - landfills, 341
 - bioreactor, 340
 - leachate, 339
 - methane, 339
 - mining resources, 341
 - sanitary, 339
 - Pacific Garbage Patch, land origin of, 326
 - plastic bags, 345
 - banning, 345
 - pollution prevention**, 316
 - design for recycling, 369
 - examples, 316
 - reducing food waste, 317
 - reducing toxicity, 317
 - reducing volume, 316
 - quantities generated, US, 314
 - recycling**, 321–325
 - appliances, 324
 - common materials, 322
 - electronics, 324, 366, 368
 - packaging, 324
 - paper, 322
 - plastics, 323
 - challenges, 323
 - problems, 325
 - promoting, 322, 331, 333
 - used oil, 324
 - why do, 321
 - recycling examples, 337
 - reducing**
 - environmentally preferable products, 317–318
 - preferable products, 317
 - guidelines, 318
 - take back, 334
 - source reduction
 - reuse, 48
 - treatment
 - incineration, 335–339
 - Japan, 334
 - pro and con, 336
 - regulation of, 338
 - two purposes, 335
 - waste management hierarchy, 315, 335
- solid waste, social issues**
 - Europe
 - Green Dot, 325

- landfills
 - NIMBY, 340
 - siting, 340
 - take back, 325
 - Europe, Japan, 333
- source reduction**, *see* **pollution prevention**
- reuse, 48
- Soviet Union**, 208, 278
- Spain**, 396, 397, 420
- Stabilization Wedges**
 - stabilizing atmospheric carbon dioxide, 406
- steel**, 452
- Stockholm Convention**, 420, 422 *see* **Stockholm Convention on Persistent Organic Pollutants**
 - banning the “dirty dozen”, 415
- stoichiometry**, 552
- stratospheric ozone**
 - CFCs
 - Freon, 218, 219, 220
 - properties, 218
 - generating ozone, 215–216
 - making and remaking, 215
 - protective effect, 215
 - questions and answers, 215
 - ultraviolet radiation, 215
 - measurements, 217
- stratospheric ozone depleting chemicals**
 - catalytic action, 221
 - CFCs, properties, 219
 - depleting potential, 220
 - fate
 - CFCs and halons, 220
 - halons, properties, 219, 220
 - ill effects
 - greenhouse gases, 228
 - natural depleters, 220
 - reducing
 - alternatives, 230–232
 - smuggling, 230
 - water soluble chemicals, 221
- stratospheric ozone depletion**
 - future, 230
 - history, 218
 - ill effects**, 224–227
 - ocean life, 226
 - ozone hole, 218, 224, 230, 232
 - particle sources, 224
 - reducing**, 228–233
 - less-developed countries, 229
 - the future, 232
 - UV index, 225
 - volcanic eruptions, 224
 - where observed, 221–223
 - Antarctica, 221
 - Arctic, 222
 - other regions, 222
 - stratospheric ozone depletion**
 - reducing depleters, 228
 - sub-Saharan Africa**, 27, 201, 265, 305, 536
 - sulfonamides**, 102
 - sulfur dioxide**, *see* **air pollutants, criteria**
 - sulfuric acid**, 558
 - Superfund**, *see* **laws**
 - Surround**, 472
 - Sweden**, 304, 331, 447, 452
 - Switzerland**, 278, 299
 - table salt**, 221, 249, 546
 - Taiwan**, 345, 364, 370
 - take back**, 111, 318, 368, 369, 370, 521 *see* **extended producer responsibility**
 - electronics, 521
 - Japan, European Union, 534
 - stimulating DfE, 522
 - Tanzania**
 - Environmental Performance Index, 536
 - TCDD**, 105
 - Tennessee**, 430
 - teratogens**, 75
 - thalidomide**, 59, 76
 - Tijuana**, 438
 - toilets**, 303–305
 - Tokyo**, 109, 149, 407, 444
 - toluene**, 527
 - Toronto**, 421
 - toxaphene**, 416
 - toxic effects**
 - children and in utero, 75
 - Toxic Equivalency Potential**, 44
 - Toxic Substances Control Act**, *see* **laws**
 - toxicant**, *see* **individual chemicals**
 - toxicity, chemical toxicity and epidemiology**
 - acute and chronic, 58
 - aspirin, 61
 - body organ
 - immune system, 72
 - kidney, 72
 - liver, 71, 74
 - lung, 73
 - nervous system, 72, 466
 - skin, 73
 - children’s sensitivity, 76
 - DDT, 413
 - definitions, 58
 - dose per time, 61
 - dose–response, 60
 - factors affecting, 70–71
 - examples, 70
 - gender, age, nutrition, 70
 - individual and species variation, 69
 - poverty, 74, 77
 - hormones, environmental, 62

toxicity, chemical toxicity and**epidemiology (cont.)**

- ill effect
 - nervous system, 466
- immune system, 72, 226
- irritant
 - skin, lungs, 73
- LD50, 60
- local, 63
- mixtures**, 20, 63, 248, 469, 489, 491
- nutrient toxicity, 60
- obvious
 - PCBs, 418
- PBDEs, 420
- PCBs, 418, 419
- solanine, 62
- subtle
 - PCBs, 418
- systemic, 63
- whole effluent, 63

Toxics Release Inventory (TRI), *see* laws, US: right to know**Toxics Use Reduction, 48****Toxics Use Reduction (TUR), 504****transboundary**

- intensifying dust storms, 146
- particulate matter, 144
- pathogens, 144
- pollutant travel**, 142–144
- reducing
 - treaties, 152
- sand, 145
- tracing travel, 143, 152

treaties

- Basel Convention, 364, 368, 478
- Convention on Long-Range Transboundary Air Pollution, 152
- International Convention for the Prevention of Pollution from Ships (MARPOL), 328
- Montreal Protocol, 152, 198, 209, 213, 222, 228, 229, 230, 231, 233, 234
- Rotterdam Convention on Pesticides, 478
- Stockholm Convention on Persistent Organic Pollutants
 - showing results, 416

treatment

- reasons to treat waste**, 50

TRI, *see* Toxics Release Inventory**triclocarban**, 86**Turkey**, 12**Tyvek**, 323**UK**, 177, 333, 397, 399, 402, 444**ultraviolet radiation, *see also* stratospheric ozone**

- A, B, and C, 218

UN Environment Program, 480**UN Food and Agriculture Organization**, 192, 280, 478, 479**UN International Maritime Organization**, 433**UN World Meteorological Organization**, 172

- UNEP**, 1, 8, 36, 152, 153, 233, 234, 257, 258, 284, 285, 302, 308, 309, 326, 327, 349, 352, 364, 370, 372, 415, 423, 428, 434, 438, 440, 446, 448, 479

UNICEF, 293**United Arab Emirates**, 536**United Kingdom**, 297, 397, 524, *see also* **UK****United Nations Environmental Program, *see* UNEP****urban sprawl**, 260**US Emergency Planning and Community Right-to-Know Act (EPCRA), *see* laws****US Environmental Protection Agency, *see* agencies****US EPA****US Food Quality Protection Act**, 102, 104, 113, 465**US Hazardous Substances Labeling Act, *see* laws****Utah**, 433**Velpar**, 470**Vibrio cholera**, 308**Vietnam**, 265, 452, 536

- arsenic, 293

vinyl chloride, 80, 94, 119, 357, 439**Virginia**, 42, 264**virus, hepatitis B**, 74**vitamin A**, 59, 76**VOCs, *see* air pollutants, VOCs****volatile organic chemicals (VOCs)**, 136**volcano**, 10, 127, 193, 224, 401**warfarin**, 59**Washington**, 327, 369, 533**waste, *see also* solid waste**

- definition, 9

waste and emissions

- complexity, 512
- quantities produced, 513
- straining the environment, 512

waste management hierarchy (WMH), 45, 46, 321

- disposal, 50, 335
- pollution prevention, 45
- recycling, 321
- recycling and reuse, 48
- treatment
 - why treat, 50

wastewater

- gray water, 265
- municipal treatment, 108, 140, 242, 263, 277
- reclamation, 265
- reducing volume, 265
- reuse (recycling), 264
- reusing
 - less-developed countries, 265
- treatment
 - alternatives, 266–267
 - on site, 266

- small facilities, 266
- wetlands, 267
- wastewater treatment**
 - improved, 263
 - industrial, 263
 - land spreading sludge, 262
 - nutrient removal, 263
 - sludge, 262
 - biosolids, 262
 - metal content, 262
- water pollutants**
 - banned, 249
 - from storm drains, 256
 - metals, 243
 - PCBs, 243
 - pollution prevention, 264
 - reducing
 - best management practices, 240
- sewage**, 255–257
 - combined sewer overflow, 255
 - fecal bacteria, 256
 - sewer terminology, 255
 - shellfish, 255
 - stormwater, 255
- VOCs, 252
- water pollutants, conventional**, 241–248
 - biochemical oxygen demand**, 241
 - how generated, 244
 - definition, 241
 - nutrients**, 242
 - algal blooms, 274
 - background, 272
 - Black Sea, 278
 - dissolved oxygen, 276
 - excess, 276, 279
 - Haber-Bosch, 273
 - harmful algal blooms, 274
 - ill effects, 273–274
 - ill effects**
 - eutrophication, 273
 - nitrogen glut
 - reducing, 279
 - reducing**, 277–278
 - reducing, 271
 - sources, 275–276
 - CAFO, 275
 - oil and grease**, 246
 - oil spills, 245
 - pathogens**, 247–248
 - sources, 247
 - pH**, 244
 - suspended solids**, 245
 - viruses and bacteria, 247
- water pollutants, dead zone**, 272–279
- water pollutants, drinking water**
 - VOCs, 253
- water pollutants, nonconventional and nontoxic**, 249
- water pollutants, nonpoint sources**
 - reducing, 267–272
 - agricultural runoff, 268–269
 - atmospheric deposition, 272
 - best management practices, 268
 - urban runoff, 269
 - water use, 272
- water pollutants, point sources**
 - nutrients
 - reducing, 271
 - reducing, 260–265
 - wastewater
 - sources, 260
 - wastewater treatment, 261
- water pollutants, priority**, 248
 - overlap with HAPs, 248
 - pesticides, 248
- water pollutants, toxic**, *see* **water pollutants, priority**
- water pollution**
 - “nitrogen glut”, 272–279
 - atmospheric deposition, 242
 - complicated picture, 512
 - dead zone, 244
 - decreasing, *see also* wastewater
 - eutrophication, 243
 - hypoxia, 242
 - mining, 245, 428
 - nonpoint sources, 239–241
 - scarcity, due to, 302
 - sewage, 303
- water pollution, conventional**
 - nutrients
 - hypoxia, 274
- water pollution, nonpoint sources**
 - runoff, seriousness, 240
- water pollution, NPS**, *see also* **water pollution, nonpoint sources**
- water pollution, point sources**, 239
- water pollution, water body type**, 250–260
 - coastal, 254
 - land-based pollution of, 254
 - megacities, 257
 - non-plastic pollutants, 258
 - plastics, 257
 - population growth, 254
 - reducing BMPs, 258
 - sewage, 257
 - estuary, 254
 - groundwater, 250–252
 - river, 250
 - wetlands, 253
 - wetlands, services, 253
- watershed, definition**, 240
- West Bengal**
 - arsenic, 293
- WHO**, *see also* **World Health Organization**
- whole effluent toxicity**, 20, 63

Wisconsin, 266, 269, 290, 300, 507, 509

World Health Organization, 22, 36, 81,
110, 148, 293, 300, 302, 307, 310, 368,
417, 477

World Summit, 334

World War II, 394

xenobiotics, 64, 71

foreign chemicals, 63

xero waste

examples, 531

Yokohama, 534

Yorktown, 42

Yugoslavia, 14

zero emissions, 529

zero waste, 369, 511, 531

cities committing to, 533

how progress toward, 529

individual level, 535

New Zealand, 534

sustainability, 531