

## 18.1 SURFACE FRESHWATER RESOURCES

Freshwater is a scarce and valuable resource—one that can easily be contaminated. Once contaminated to the extent it can be considered “polluted,” freshwater quality is difficult and expensive to restore. Thus, the study of surface water pollution has focused primarily on streams and lakes, and most of the scientific tools developed by such regulatory agencies as the U.S. Environmental Protection Agency have been applied to protecting water quality in this segment of earth’s surface waters. The amount and distribution of fresh surface water was illustrated in Chapter 3.

The water stored in reservoirs and lakes, together with the water that flows perennially in streams, is subject to heavy stress, and because it is used for water supplies, agriculture, industry, and recreation, this water can easily be contaminated.

## 18.2 MARINE WATER RESOURCES

Oceans contain most of the water of the planet. Yet even with the phenomenal volume of water in which contaminants may be dispersed, marine resources can be polluted. Using various biological and physical parameters, we usually classify the ocean environment as three components: the coastal zone, the upper mixed layer, and the abyssal ocean. Several regulatory agencies and international organizations share different responsibilities for those components. The coastal zone, which is most susceptible to the day-to-day kinds of contamination found in freshwater lakes and rivers, is often the province of water quality regulatory agencies established by individual nation states. International organizations have traditionally dealt with pollution concerns of the open ocean and its seabed, which includes the other two components. In addition to these physically described components of the sea, there are legally defined (and disputed) zones, sometimes overlapping, that influence regulatory practices, as indicated in Figure 18.1.

### 18.2.1 The Coastal Zone

The **coastal zone** extends from the low-tide line to the 200-meter depth contour, tending to match the geophysical demarcation of the continental shelf. The coastal zone can be as wide as 1400 km along some coasts and less than a kilometer along others. The average width of the zone worldwide is about 50 kilometers, comprising about 8% of the surface of the ocean. (The coastal zone of Alaska is larger than that of the rest of the United States.) Within the coastal zone definition, the difference between estuaries and the open coast is important in considering the disposal of wastewater and the potential for pollution problems.

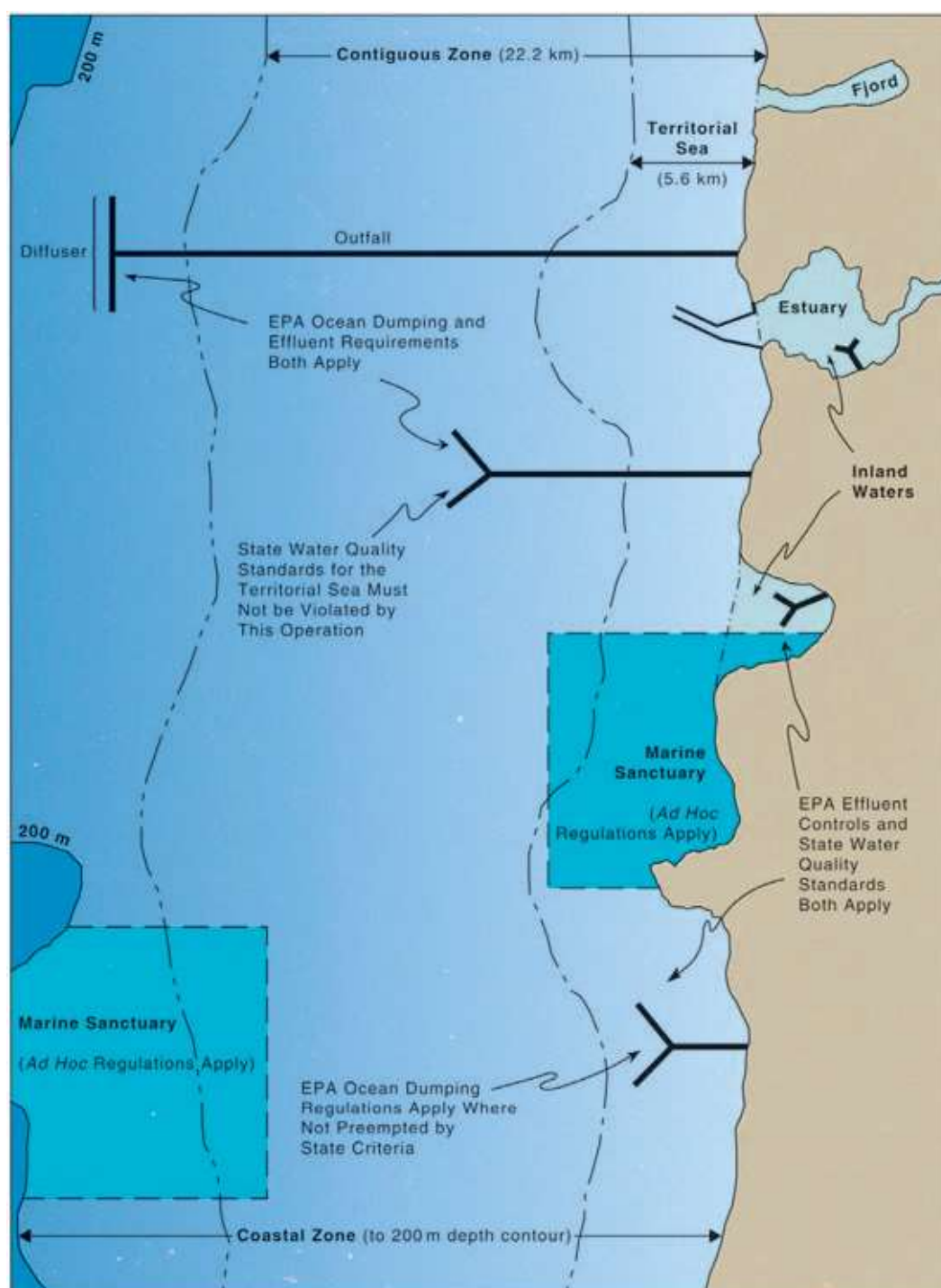
Almost all of the water-carried wastes of a continent enter the coastal zone through an estuary. **Estuaries** are bodies of water with a free connection to the sea whose salinity is measurably diluted with fresh water, as from a river. Because estuaries provide critical and limited habitat for marine organisms to rear and feed their young, water quality is of special concern. Species that inhabit the coastal zone, and especially the estuaries, have to be very resilient to such natural environmental stresses as wide daily variations in salinity, turbidity, temperature, and UV radiation. Owing to this natural resiliency, coastal organisms may be able to tolerate contaminants associated with industrial and municipal wastes better than residents of the continental shelf, where the natural environment is quite stable. The estuarine habitat must be maintained primarily because of its limited extent, as distinguished from the shelf habitat, which is enormous. For this reason, treated wastewater effluents are usually discharged offshore rather than into estuaries in coastal regions. A large pipeline or tunnel, called an **outfall**, is used to transport the effluent to the disposal site.

In disposing of treated wastes offshore, we also need to take the physical features of the coastal zone into account. For example, continental headlands that protrude into the sea can impede both circulation of water and exchange of nearshore water with open ocean water. Outfalls are therefore best located far offshore rather than inside the region of headland influence. Similarly, outfalls should not be located close to shore in the vicinity of estuaries or bays because tidal incursions can carry diluted wastes into the estuary, thereby eroding one of the advantages offered by offshore disposal.

### 18.2.2 Open Ocean Waters

A variety of the majority of circumstances can contribute to the contamination of the open ocean waters beyond the coastal zone, including atmospheric fallout, oil spills, and dumping of hazardous wastes and sewage sludge as practiced by some countries of the world. Floatable and soluble materials tend to stay in the **upper mixed layer** of the ocean, where they may be decomposed. This upper layer is also the most active photosynthetic zone of the ocean, where the majority of plant—and hence animal—life can thrive. The depth of this layer, which varies between 100 and 1,000 meters, changes with season and geographic location. Although mixing between the upper and deeper layers of the ocean is impeded by strong density gradients, particles formed in the upper mixed layer, or discharged there, may eventually settle so far that they can no longer be resuspended by surface-generated turbulence and thus become part of the detrital sediment load of the deep ocean waters.

Because the quality of the water in the upper mixed layer can significantly affect all life there, it is important to take precautions with waste disposal operations. When ocean disposal of certain materials is justified, we can use technologies to avoid contamination of the upper mixed layer and facilitate transit and long-term retention of the



**Figure 18.1** Water pollution regulations in the coastal zone. The outfalls depicted (both T- and Y-shaped) all use diffusers. From *Pollution Science* © 1996, Academic Press, San Diego, CA.

material in the deep waters of the open ocean, that is, the **abyssal ocean**. For example, containers have been proposed for disposal of such materials as xenobiotic chemicals or radioactive wastes. Pipelines can also be used to carry liquid carbon dioxide to the seabed, where it can be retained for a long time—conceivably long enough to help reduce the rate of global warming.

### 18.3 SOURCES OF SURFACE WATER POLLUTION

Water pollution is a qualitative term that describes the situation when the level of contaminants impedes an intended water use. It takes just a small amount of contaminant to pollute

a waterbody intended for a drinking water supply. But the same water might not be considered polluted if the water were to be used, for example, for agriculture. Nor is pollution restricted to chemical contaminants. Physical factors of the environment can also contribute to pollution. For example, heated water discharged from a power plant can change the temperature of an aquatic environment. It might not be a problem in a lake or a river during the winter, but it can certainly be a problem in the summertime. Moreover, heated water or water containing some contaminant may not be a problem at any time of the year, provided it is rapidly mixed with the surface water, and the diluted material doesn't accumulate over time. There are also many kinds of contaminants that can usually be accommodated by the natural environment without resulting in pollution, but in many situations, these same contaminants (sometimes in conjunction with other contaminants) can cause pollution even in well-mixed water bodies.

Major sources of surface water contamination are construction, municipalities, agriculture, and industry, however, the water delivered to earth in the form of precipitation is not necessarily pure to begin with. Near the coast, it may contain particulate and dissolved sea salts, and farther inland, it may contain organic compounds and acids scrubbed from contaminants added to the atmosphere both by natural processes and by anthropogenic (human) activities. Gases from plant growth and decay, and gases from geological activity are examples of naturally derived atmospheric contaminants that can be returned to earth via precipitation. The acid rain problem of the New England states is a classic example of anthropogenically derived atmospheric contaminants that contribute to surface water pollution (see Chapter 22).

#### 18.4 SEDIMENTS AS SURFACE WATER CONTAMINANTS

The properties of particulates or sediments in water are described in Chapter 9. Soil water erosion and its control are described in Chapter 16. The ability of rivers to carry sediment over large distances has resulted in the landscape of continents. Certainly, some background level of sediment load in rivers is considered natural and desirable. Problems ensue when anthropogenic activities in a river's watershed increase, or in some cases decrease, sediment load. Running water, wind, and ice are the major factors responsible for the detachment, entrainment, and transport of particulate matter. Geologic erosion is highest in areas with relatively steep gradients such as low- to intermediate-order streams in mountainous areas. Historically, natural erosion has been the largest source of sediment supplied to rivers. As human land use activities increase in watersheds around the globe, anthropogenic effects now are major contributors to both increased sediment supplied to rivers as well as the blocking and impoundment of this sediment behind dams. Both impoundment and increased erosional processes in watersheds

can have profound biological, physical, and chemical impacts on rivers and streams.

Almost any kind of human activity in watersheds can result in an increase of suspended sediment in rivers. A few classic examples of anthropogenic activity known to increase sedimentation are:

**Logging, deforestation, wildfire.** Specific types of logging activity can increase sediment yield by two orders of magnitude for short periods. Fire suppression and drought can combine to create catastrophic wildfires, which can have devastating impacts on receiving waters from these areas.

**Overgrazing by domestic animals.** Sedimentation can increase not only due to decreased vegetative interception of precipitation-enhancing erosion, but also through direct trampling of the streambed and channel.

**Urbanization and road construction.** Road construction commonly results in a 5–20 fold increase in suspended sediment yield. Impervious materials such as pavement, parking lots, or rooftops can increase the velocity of storm water runoff, which will increase erosion once this water comes in contact with soil.

**Mining operations.** Mines, particularly strip mines, can lead to extraordinarily high levels of erosion and subsequent sedimentation in rivers. An example is the coal strip mines in Kentucky.

On a global scale, rivers discharge roughly 40,000,000 m<sup>3</sup> into the world's oceans annually. For every cubic meter of water reaching the ocean, there is (on average) an accompanying 0.5 kilogram of sediment carried away from the continents.

Suspended sediment is also a major carrier of pollution. While rivers may be transporters of pollution, suspended sediment is the “package” these pollutants are carried in. Heavy metals, organic pollutants, pathogens, and nutrients responsible for eutrophication can all be found attached to sediments in flowing water. The “quality” or overall pollutant load of suspended sediment depends on the degree of pollution in the watershed.

Transport of sediments in water is dependent on many factors, including sediment particle size and water flow rate (see Chapter 9). The quantification and predicted rates of transport of sediment are based upon the assumption that for any given flow and sediment, there is a unique transport rate. Estimates of sediment transport rates are based upon measures of flow (including velocity, depth, shear velocity, viscosity, and fluid density) and both sediment size and density. There are different classification terminologies, based upon the mode of sediment transport in a stream. **Bed load** refers to the sediments moving predominantly in contact with or close to the streambed. In contrast, **suspended load** refers to sediments that move primarily suspended in fluid flow, but that may also interact with bed load. Suspended load has a continual exchange between sediment in fluid flow and on the bed as it is constantly being entrained from the bed and suspended, while heavier particles settle out from the flow to the bed. **Solute load** refers to the total amount of dissolved



material (ions) carried in suspension and can only be quantified by laboratory analytical techniques. **Total load** is the total amount of sediment in motion and is the sum of bed load plus suspended load. It is important to remember that these classifications are somewhat artificial. The sediment load carrying capacity of a stream or river constantly changes both spatially and temporally as flow changes. Flow in any river or stream is never homogenous, so the resulting sediment movement in any section of stream or river varies greatly.

Particles that are too heavy to be fully suspended may roll or slide along the bed (**traction load**) or hop as they rebound on impact with the bed. In the latter case, ballistic trajectories occur, and the particle is said to move by **saltation**. **Stream competence** refers to the heaviest particles that a stream can carry. Stream competence depends on stream velocity; the faster the current, the heavier the particle that can be carried. **Stream capacity** refers to the maximum amount of total load (bed and suspended) a stream can carry. It depends on both discharge and velocity, since velocity affects the competence and therefore the range of particle sizes that can be transported. Note that as stream volume and discharge increase, so do competence and capacity. This is not a linear relationship, and doubling the discharge and velocity does not automatically double the competence and capacity. Stream competence varies as approximately the sixth power of velocity. For example, doubling velocity usually results in a 64 times increase in competence. For most streams, capacity varies as a range of squared to cubed values. For example, tripling the discharge usually results in a 9–27 times increase in capacity. Most of the work of streams is accomplished during floods, when stream velocity and discharge (and therefore competence and capacity) are many times their level compared to periods of quiescent flow. This work is in the form of bed scouring (erosion), sediment transport (bed and suspended loads), and sediment deposition.

#### 18.4.1 Suspended Solids and Turbidity

It has been stated that **total suspended solids (TSS)** in water are the most important pollutant. Erosion happens constantly around the planet, and some rivers and streams have naturally high TSS levels without any human intervention. The Yangtze River in China and the Colorado and Mississippi Rivers in the U.S. are examples of rivers that have historically entrained large amounts of sediment due to local topography, geology, and climate (Figure 18.2).

Total suspended solids are defined as all solids suspended in water that will not pass through a 2.0  $\mu\text{m}$  glass-fiber filter (dissolved solids would be the fraction that does pass through the same size filter). The filter is then dried in an oven between 103 and 105°C, and weighed. The increase in weight of the filter represents the amount of TSS.

Problems with TSS arise when excess erosion occurs in a watershed due to human land use practices. Excess levels of TSS can come from either point (municipal and industrial wastewater) or nonpoint (*e.g.*, agriculture, timber harvesting,



**Figure 18.2** Flooding in the Santa Cruz River, Arizona. Arid regions are especially prone to increases in suspended sediment concentrations during flood events. Source: <http://az.water.usgs.gov/>.

mining, and construction) sources. Generally, water with less than 20 mg/L is considered relatively “clear”; levels between 40 and 80 mg/L tend to be “cloudy”; while levels over 150 mg/L would be classified as “dirty” or “muddy.” Point sources generally require treatment, usually through settling or flocculation, prior to being released into a river or stream. Nonpoint sources are much more difficult to manage due to several sources acting synergistically. No-till farming, sedimentation basins, and silt fences are common practices to reduce run off from agriculture or construction areas. Stormwater retention ponds and regular street sweeping can reduce the impact of stormwater runoff from urban areas.

Increasing levels of TSS often result in a waterbody being unable to support a diversity of aquatic life. Sedimentation of the stream bed as velocity decreases often results in the suffocation of many aquatic macroinvertebrates and the eggs of fish. Where TSS is deposited results in increased **embeddedness** (the percentage of any piece of substrate covered in sediment) of cobble, rocks, and boulders within the stream. Several species of macroinvertebrates use the bottom of rocks as refuge from predators or from fast-flowing water, and as embeddedness increases, this vital habitat is diminished or completely lost. Additionally, TSS absorbs heat and can increase the temperature of a waterbody. In lakes and reservoirs, this can exacerbate thermal stratification as heat accumulates close to the surface. Suspended solids can also decrease the amount of dissolved oxygen due to consumption of organic matter by respiring bacteria. In lakes or reservoirs with a large algal biomass, sudden inputs of water containing suspended sediments have been known to deplete the oxygen of water and cause massive fish kills. The once-photosynthesizing algae switch to respiration as light for photosynthesis was reduced or eliminated.

Besides the relatively direct effects of suspended solids on water bodies, perhaps the greatest indirect effect are the pollutants that may be attached to suspended sediment.

Examples of pollutants known to sorb to sediment particles are nutrients, metals, organic compounds such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCBs), and a wide assortment of herbicides and pesticides. All of these contaminants have differing solubilities and therefore differing fates once they enter a river, stream, or lake. Sediment-associated pesticides in water are an emerging problem in agricultural areas.

Turbidity is related to, but not a proxy for, suspended sediments. Specifically, turbidity is the quantification of the light that is scattered or absorbed rather than transmitted through a water sample. Turbidity is another measure of water clarity but is not a measure of dissolved substances that can add color to water. Particulates are what add turbidity to water and can include such things as silt, clay, organic matter, algae and other microorganisms, and any other particulate matter that can scatter or absorb light. The amount of light scattered or absorbed is proportional to the concentration of particulates in the sample. The exact amount and wavelength of light scattered by a particle is dependent on the particle's shape, size, and refractive index, which makes any correlation between turbidity and suspended solids difficult and impractical. However, turbidity is directly related to the level of particulates and is an excellent general indicator of water quality in its own right. Units of measure for turbidity are in **nephelometric turbidity units (NTUs)** and are measured on a nephelometer (often called a turbidimeter). Turbidimeters operate by shining an intense beam of light up through the bottom of a glass tube containing the sample. Light scattered by particulates in the sample is detected by a sensitive photomultiplier tube at a 90-degree angle from the incident beam of light. The amount of light reaching the photomultiplier tube is proportional to the level of turbidity in the sample. The photomultiplier tube converts the light energy into an electrical signal, which is amplified and displayed on the instrument meter.

## 18.5 METALS AS SURFACE WATER CONTAMINANTS

Metals that can be toxic to humans and wildlife are often found in industrial, municipal, and urban runoff and in atmospheric deposition from coal-burning plants and smelters and from natural weathering of rocks and soils. Levels of harmful metals in water have risen globally with increasing urbanization and industrialization. Currently, there are over 50 heavy metals that can be toxic to humans. Of these, 17 are considered very toxic and simultaneously readily accessible.

Common heavy metals known to be toxic to humans include arsenic, cadmium, chromium, copper, lead, mercury, and zinc. Interestingly, chromium, copper, and zinc are essential micronutrients required by the human body for growth, and toxicity depends upon enhanced dose.

Heavy metals are also environmentally persistent, which exacerbates any potentially toxic exposure because these metals often accumulate under certain environmental conditions.

### 18.5.1 Mercury

Mercury in the environment is one of the most widely recognized and publicized pollutants. Under certain environmental conditions, elemental mercury complexes to form methylmercury, which is especially mobile in the environment and toxic to humans and wildlife. Use of mercury in the tanning industry and for making hats was the first time that it was widely recognized as a toxic substance affecting the brain; hence the term “mad as a hatter” (see also Chapter 13). Today, release of mercury in smokestack emissions from coal-burning power plants is the primary source of contamination. Bioaccumulation of methylmercury in long-lived predatory fish from cold freshwater lakes (pikes and walleyes) and in coldwater marine species (swordfish, sharks, and some tunas) has led to public warnings for pregnant and nursing women to limit consumption of shark and swordfish and for all of the public to limit consumption of fish from certain lakes in parts of the United States and Western Europe.

The cycling of mercury through the environment is complex and depends on several physical, chemical, and, most importantly, biological aspects of the system in question. The manner in which mercury cycles through any given area or ecosystem determines its relative toxicity and subsequent bioaccumulation rate upward through the food chain. The term **bioaccumulation** refers to the net accumulation, over time, of pollutants within an organism from both biotic and abiotic factors. The term **biomagnification** refers to the progressive accumulation of persistent toxicants by successive trophic levels. Biomagnification relates to the concentration ratio in a tissue of predator organisms as compared to that in its prey. Mercury exists in several forms in the environment: elemental mercury ( $\text{Hg}^0$ ), inorganic mercury compounds ( $\text{Hg}^{+1}$  or  $\text{Hg}^{+2}$ ), and organic mercury compounds ( $\text{HgCH}_3$  or  $\text{Hg}(\text{CH}_3)_2$ ), which include both methyl- and dimethylmercury (Figure 18.3).

There are numerous pathways by which mercury can make its way into water bodies. Inorganic and methylmercury can enter water directly from atmospheric deposition, methylmercury and  $\text{Hg}^{+2}$  can be bound to organic substances in runoff, and surface water flow in upper soil layers can transport  $\text{Hg}^{+2}$  and methylmercury to water bodies. There has been a global increase of mercury released into the atmosphere since the beginning of the Industrial Age, so that atmospheric deposition onto watersheds and surface water often plays as large a role as runoff from natural sources.

Once in an aquatic ecosystem, mercury goes through several complexation and transformation processes. While most forms of mercury are bioavailable, methylmercury (MeHg) is the form most readily absorbed and bioaccumulated. The methylation of mercury in aquatic systems not only requires a certain range of physicochemical factors, but also the presence of a group of bacteria known as **sulfate-reducing bacteria (SRBs)**. There are several species of SRBs, but some of the most common include strains of *Desulfovibrio* and *Desulfobacter*. The majority of methylation that occurs in lakes and



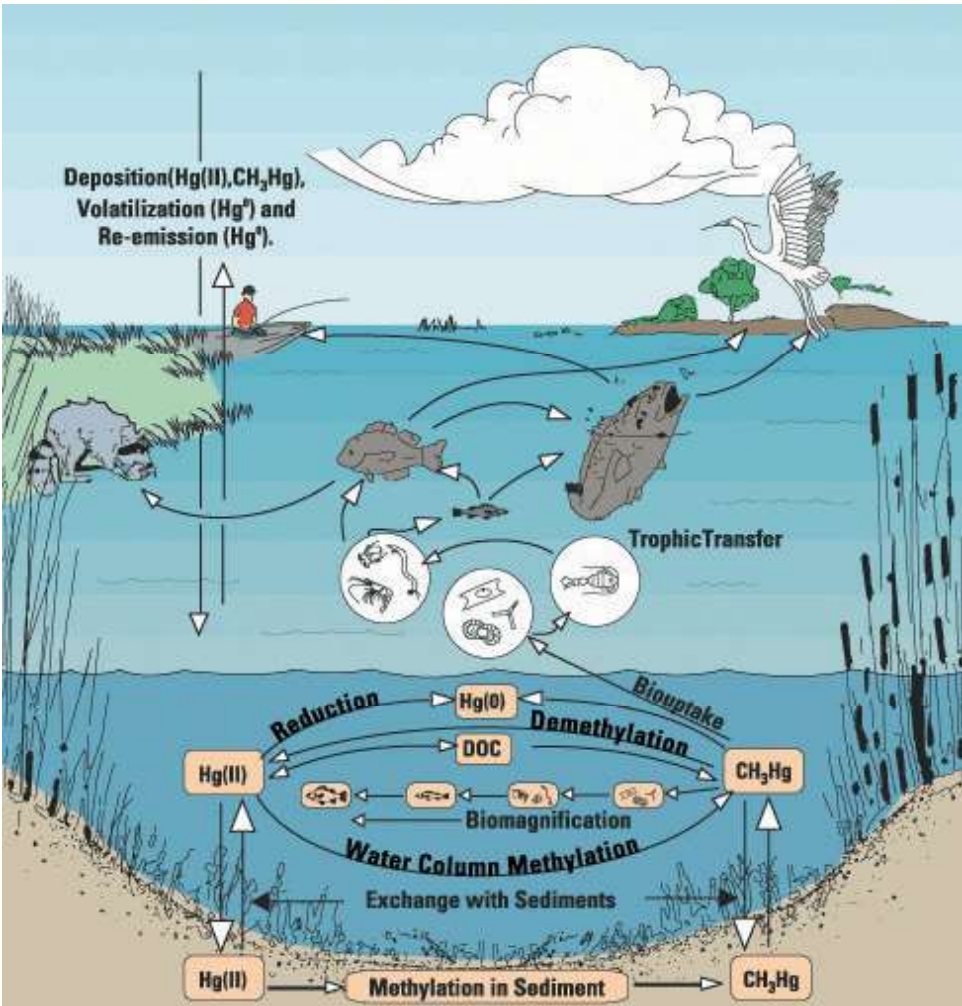


Figure 18.3 Common transformations of mercury in aquatic ecosystems.

TABLE 18.1 Factors influencing the methylation of mercury in aquatic ecosystems.

PHYSICAL OR CHEMICAL CONDITION	INFLUENCE ON METHYLATION
Low dissolved oxygen	Enhanced methylation
Decreased pH	Enhanced methylation within the water column
Decreased pH	Decreased methylation in sediment
Increased dissolved organic carbon	Enhanced methylation within sediment
Increased dissolved organic carbon	Decreased methylation within water column
Increased salinity	Decreased methylation
Increased nutrient concentrations	Enhanced methylation
Increased temperature	Enhanced methylation
Increased sulfate concentrations	Enhanced methylation

reservoirs is within anaerobic sediments. Factors affecting the methylation of mercury are outlined in Table 18.1, while common transformations of mercury are given in Figure 18.4.

Mercury in all forms is a potent toxin that can cause developmental effects in the fetus as well as toxic effects on the liver and kidneys of adults and children. Sublethal effects of mercury toxicity can affect the ability to learn, speak, feel, see, taste and move. Children under the age of 15 are most vulnerable, because their central nervous system is still developing. Mercury is easily passed from pregnant mother to fetus, and even extremely small trace amounts of mercury can have devastating effects to a developing central nervous system. Mercury toxicity can occur through skin contact, in-

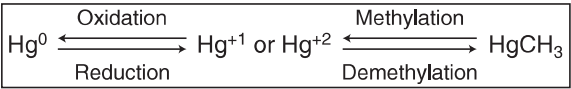


Figure 18.4 Common transformations of mercury.

halation, or ingestion. Due to biomagnification, the most common route of exposure to humans is through consumption of contaminated fish. Approximately 60,000 babies are born in the U.S. each year with some degree of mercury toxicity.

The methylation, biomagnification, bioaccumulation, and toxicity of mercury are often linked to the problem of increasing eutrophication. Increases in most of the factors that cause eutrophication within a waterbody, including increased sulfate content, also increases the rate of methylation and subsequent toxicity to humans and wildlife. Humans have not only increased the availability of mercury deposited into aquatic systems, we have, through cultural eutrophication, also increased the bioavailability and subsequent toxicity of mercury in these systems.

### 18.5.2 Arsenic

Arsenic is an element widely distributed throughout the earth's crust. As such, it is often introduced into water through the dissolution of minerals and ores and may concentrate in groundwater. Arsenic is also used in industry and agriculture and is a byproduct of copper smelting, mining, and coal burning. One form of arsenic, chromated copper arsenate, is the most common wood preservative in the U.S. and contains 22% arsenic.

Inorganic arsenic occurs in several different forms in the environment, but in natural waters it is most commonly found as trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Most of the organic species of arsenic, usually at very high levels in seafood, are less toxic and are readily eliminated by normal body functions.

Symptoms from arsenic exposure include vomiting, esophageal and abdominal pain, and bloody diarrhea. Long-term exposure can cause cancers of the skin, lungs, urinary bladder, and kidney as well as other skin changes, such as pigmentation changes and thickening.

One of the largest mass poisonings in the world recently occurred in Bangladesh, where 53 out of a total of 64 districts had groundwater contaminated with arsenic. The cause of arsenic contamination was related to the onset of intense agriculture in the region where irrigation resulted in large-scale withdrawal of groundwater via wells (see Chapter 10).

### 18.5.3 Chromium

Chromium is found in natural deposits as ores containing other elements. Additionally, chromium is an important industrial metal, where it is used in alloys such as stainless steel, protective coatings on other metals and magnetic tapes, pigments for paints, cement, paper, rubber, and floor coverings. Chromium has several oxidation states, but the most common are  $+2$ ,  $+3$  and  $+6$ , with  $+3$  being the most stable. Oxidation states of  $+4$  and  $+5$  are relatively rare.

Toxicity of chromium depends on oxidation state. Chromium(III) is an essential nutrient, while the hexavalent form, chromium(VI), is believed to be carcinogenic in

humans. Evidence to date indicates that the carcinogenicity is site-specific, limited to the lung and sinonasal cavity, and dependent on high exposures.

### 18.5.4 Selenium

Selenium occurs naturally in the environment as selenide and is often combined with sulfide, copper, lead, nickel, or silver. Like chromium, selenium is a micronutrient needed in very small quantities in humans and wildlife to produce the amino acid selenocysteine. However, it can be toxic at higher doses. The relatively narrow range between selenium acting as a beneficial nutrient ( $50 \mu\text{g/day}$ ) and the initiation of toxicity ( $400 \mu\text{g/day}$ ) in humans means that it needs to be closely monitored in the environment, especially in areas with alkaline soils, because this is where selenium is often found in its most oxidized and toxic form. As with several other naturally occurring heavy metals, problems may arise due to increased availability of selenium in aquatic systems primarily due to irrigation and farming practices. Symptoms of short-term selenium toxicity include hair and fingernail changes, damage to the peripheral nervous system, and irritability. Long-term symptoms include damage to liver and kidney tissue and nervous and circulatory systems (Figure 18.5).

Selenium is a bioaccumulative pollutant; however, unlike mercury, selenium concentrations do not increase upward through the food chain, *i.e.*, it does not biomagnify. Selenium toxicity can have devastating effects on both terrestrial and aquatic wildlife. Selenium can affect the growth and survival of juvenile fish as well as the offspring of adult fish exposed to sublethal levels. Birds that have eaten fish suffering from selenium toxicity either succumb to the acutely toxic effects of selenium or produce offspring, often stillborn, with gross skeletal deformities. Due to selenium uptake in terrestrial plants, both domestic and wildlife species foraging on these plants can be affected.

## 18.6 NUTRIENTS AND EUTROPHICATION OF SURFACE WATERS

On a global scale, eutrophication has often been cited as the number one cause of impairment to surface water resources. Eutrophication is the gradual accumulation of nutrients, and organic material subsequently utilizing these nutrients as an energy source, within a body of water. While eutrophication is often cited as an example of anthropogenic pollution of inland waters such as lakes and streams; coastal areas, estuaries, and salt marshes are also commonly affected. Eutrophication often results in increases in algal biomass, and therefore some discussion of what these nutrients are, and what specific ratios cause eutrophication, are in order.

Justus Von Liebig, a German analytical chemist and professor of chemistry at the University of Giessen, made great contributions to the science of plant nutrition and soil fertility in the mid-1800s. Liebig's **Law of the Minimum**

## CASE STUDY 18.1

### SELENIUM TOXICITY IN KESTERSON RESERVOIR, CALIFORNIA

California's Kesterson Reservoir in the San Joaquin Valley is a classic example of one of the most dramatic cases of heavy metal toxicity known to date. Kesterson Reservoir was built in the late 1960s to address the issue of California's decreasing wetland habitat by using agricultural drainage for the creation of wetlands solely for the purpose of attracting and harboring native wildlife species. Due to its perceived benefit to wildlife, Kesterson was made into a National Wildlife Refuge under the auspices of the U.S. Fish and Wildlife Service.

Mountains forming the western boundary of the San Joaquin Valley consist of shale enriched with selenium. The San Joaquin Valley is an area of poorly drained soils where intensely irrigated agriculture in the otherwise arid valley resulted in selenium becoming highly concentrated in agricultural drainage. By 1981, almost all of the water entering Kesterson Reservoir was agricultural drainage from poorly drained soils.

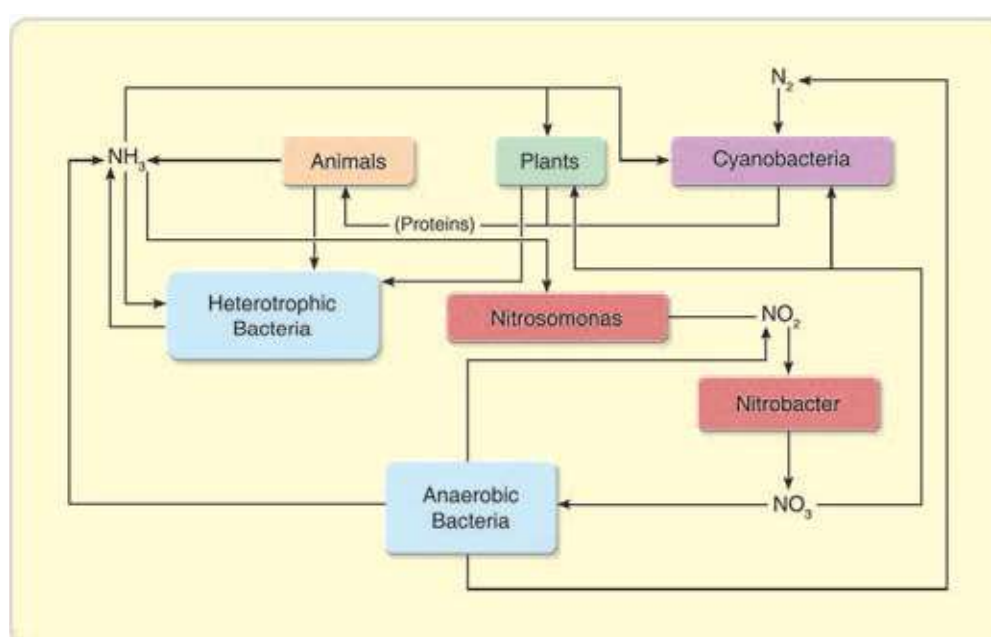
Mosquitofish collected by the U.S. Fish and Wildlife Service in the early 1980s from Kesterson Reservoir contained levels of selenium approximately 100 times higher than mosquitofish found in neighboring wetlands not receiving agricultural effluent. Several studies were implemented during the 1980s to determine whether selenium or other toxicants were present at levels that could harm wildlife.

Agricultural drainage entering Kesterson Reservoir had an average selenium concentration of 0.3 ppm,

seemingly low levels at first glance. The greatest damage, however, rested in the bioaccumulative nature of selenium. Algae had average selenium concentrations of 69 ppm, aquatic plants had 73 ppm, aquatic insects more than 100 ppm, and mosquitofish 170 ppm, which was more than 500 times the concentration of the aquatic habitat in which these mosquitofish lived. All of these levels were much higher than those found in neighboring wetlands not receiving agricultural drainage.

Numerous birds feeding on aquatic organisms in Kesterson Reservoir suffered and died due to selenium toxicity. Symptoms included emaciation, feather loss, degeneration of live tissue, and muscle atrophy. Adult birds that did not immediately succumb to the toxic effects of selenium produced offspring, usually stillborn, that had abnormal or missing eyes, beaks, legs, wings, and feet. The area created to enhance and preserve wildlife, especially migrating and native waterfowl, now appeared to be a death trap to their survival.

Millions of dollars have been spent studying the effects of selenium toxicity at Kesterson Reservoir and millions more have been spent on cleanup efforts. The circumstances that caused the devastating effects to wildlife at Kesterson Reservoir emphasizes the need to find viable solutions to disposing of contaminant-laden waters emanating from agricultural drainage in arid regions.



**Figure 18.5** The nitrogen cycle in aquatic systems. Source: <http://www.marietta.edu/~mcshaffd/aquatic/sextant/chemistry.htm>.



states that yield is proportional to the amount of the most limiting nutrient, whichever nutrient it may be. From this, it may be inferred that if the deficient nutrient is supplied, yields may be improved to the point that some other nutrient is needed in greater quantity than the soil can provide, and the Law of the Minimum would apply in turn to that nutrient. This same law can be applied to aquatic systems. The nutrients that most often limit primary production in aquatic systems are forms of carbon, nitrogen, and phosphorous. The specific ratio of limitation (on a molar basis) is 106C:16N:1P. **Carbon** is ubiquitous in the environment and atmosphere, but can become limiting during intense photosynthesis by algae or aquatic plants. Since carbon dioxide is utilized during photosynthesis, it is possible for this carbon nutrient to be temporarily depleted during daylight hours. This situation would be reversed during the evening, when respiration would exceed photosynthesis, and the carbon dioxide utilized during the day would be released back into the water. Generally, it is uncommon for carbon to be a limiting nutrient.

The idea of nutrient limitation based upon the ratio between C:N:P in aquatic systems only works when one of these essential nutrients is, indeed, “limiting” the growth of primary producers such as algae. In eutrophic or hypereutrophic systems, ratios may indicate that a nutrient is “limiting” in the traditional sense, however, if *all* nutrients are orders of magnitude higher than what it takes to limit primary production than, in this case, ratios can be misleading and nothing is truly limiting growth. Often, in hypereutrophic systems, algal biomass can become so large that the only limiting factor is available light for photosynthesis, as algal cells near the surface shade those at depth.

**Nitrogen** is an essential plant nutrient used in the synthesis of organic molecules such as amino acids, proteins, and nucleic acids. Nitrogen (mostly as  $N_2$  or “dinitrogen” gas) comprises 78% of the Earth’s atmosphere. Most of the abundant nitrogen found in the atmosphere is not yet bioavailable. Nitrogen must be “fixed” into nitrate ( $NO_3^-$ ), ammonia ( $NH_3$ ), or ammonium ( $NH_4^+$ ) before it can be used by organisms incapable of fixation. Organisms capable of nitrogen fixation include certain species of bacteria, actinomycetes, and cyanobacteria. In aquatic systems, cyanobacteria perform the majority of nitrogen fixation. In aquatic systems, the forms of nitrogen of greatest interest are (in order of decreasing oxidation state):

- Nitrate ( $NO_3^-$ )
- Nitrite ( $NO_2^-$ )
- Ammonia ( $NH_3$ )
- Ammonium ( $NH_4^+$ )
- Organic-N (amino groups)

Total oxidized nitrogen is the sum of  $NO_3^- + NO_2^-$ . Organic nitrogen is the organically bound fraction and includes such natural materials as proteins and peptides, nucleic acids and urea, and numerous synthetic organic materials. Analytically, organic nitrogen and ammonia can be

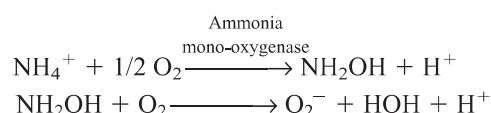
determined together and referred to as “Kjeldahl nitrogen”, a term that reflects the technique used in their determination. Total Kjeldahl nitrogen (TKN) is not synonymous with total nitrogen. If TKN and  $NH_3$  are determined individually, “organic nitrogen” can be estimated by the difference.

$$TKN + NO_3^- + NO_2^- = \text{Total Nitrogen}$$

All forms of nitrogen (organic and inorganic) are interconvertible. The nitrogen cycle is an important component of overall biogeochemical cycling in aquatic systems.

**Ammonification** is an important process in the nitrogen cycle and is, basically, the process of decomposition with production of ammonia or ammonium compounds, especially by the action of bacteria on organic matter. Aquatic animals commonly excrete  $NH_3$  as a waste product of metabolism. The excreted or mineralized  $NH_3/NH_4$  is then available for direct uptake and utilization by other organisms, or it may be converted to more oxidized forms of nitrogen for incorporation into cells. In some nitrogen-poor lakes or reservoirs, the excretory contribution (*e.g.*, ammonification) from zooplankton can provide up to 90% of the nitrogen required by primary producers. Ammonification is difficult to quantify because of the rapid uptake of  $NH_3$  and  $NH_4$  by primary producers. Ammonification is the opposite of assimilation and protein synthesis. Both aerobic and anaerobic bacteria play vital roles in ammonification.

**Nitrification** is the biological oxidation of  $NH_4^+$  and  $NH_3$  to  $NO_2^-$  and then  $NO_3^-$ . Nitrification is important because  $NH_4^+$  and  $NH_3$  are toxic to species of aquatic vertebrates. Nitrification is performed by bacteria that gain energy from oxidizing reduced forms of nitrogen. The aerobic chemototrophs involved in nitrification are species of *Nitrosomonas* and *Nitrobacter*. Nitrification consumes and simultaneously requires oxygen, and is a two-part process.



This process requires 66 Kcal of energy/gram atom of ammonium oxidized.

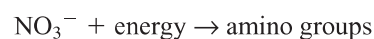
Under anaerobic conditions:



Ammonium oxidation has important ecological significance in aquatic systems. The microbes that perform nitrification are relatively inefficient autotrophs that use the energy gained from oxidizing ammonia to fix carbon. Thus, these bacteria have a dual ecological role: they are involved in recycling nitrogen and in fixing carbon into organics. The microbes that perform nitrification are fragile. These organisms are acid-sensitive even though they produce acid. If a large source of nitrogen is added into the environment, these organisms can potentially kill themselves by metabolizing it to nitric acid. Since they are also strict aerobes, they can be killed if introduction of wastes leads to excessive growth of other species that deplete oxygen (*i.e.*, eutrophication).

**Denitrification** is the reduction of nitrate ( $\text{NO}_3^-$ ) to nitrogen gas or to organic nitrogen compounds and can be a significant pathway for the loss of nitrogen from aquatic systems. There are two types of denitrification, assimilatory and dissimilatory.

**Assimilatory nitrate reduction.** Many organisms can only acquire nitrogen in the form of nitrate and must reduce nitrate to form the amino groups needed for metabolism.



The “energy” in the above equation is usually supplied by enzymatic activity (nitrogenase).

**Dissimilatory nitrate reduction.** Dissimilatory nitrate reduction is performed by anaerobic bacteria that use nitrate as the terminal electron acceptor in the absence of oxygen. The overall equation is:



The individual steps of dissimilatory nitrate reduction are:

1. Reduction of nitrate to nitrite  
 $2\text{HNO}_3^- \rightarrow 2\text{HNO}_2^- + 4\text{e}^-$   
 Enzyme: dissimilatory nitrate reductase
2. Reduction of nitrite to nitric oxide  
 $2\text{HNO}_2^- \rightarrow 2\text{NO} + 2\text{e}^-$   
 Enzyme: dissimilatory nitrite reductase
3. Reduction of nitric oxide to nitrous oxide  
 $2\text{NO} \rightarrow \text{N}_2\text{O} + 2\text{e}^-$   
 Enzyme: dissimilatory nitric oxide reductase
4. Reduction of nitrous oxide to dinitrogen  
 $\text{N}_2\text{O} \rightarrow \text{N}_2 + 2\text{e}^-$   
 Enzyme: dissimilatory nitrous oxide reductase.

Since reductions are energy yielding, 24 ATPs are generated per mole of nitrate reduced.

Although denitrification requires anoxic conditions, it has been observed in aerated lake sediments and can form relatively thin biofilms on rocks in streams. Evidently, denitrification can occur in microzones of anoxia within sediments and biofilms. Oxygen produced through photosynthesis by benthic algae may inhibit denitrification. Denitrification requires an organic carbon source and proceeds faster where more carbon is available in the water and sediments. Denitrification may contribute a significant portion of the oxidative metabolism in water bodies where nitrate levels are high. Within any given waterbody, denitrification can occur simultaneously with nitrification. Denitrification occurs due to microorganisms, usually facultative anaerobes and predominantly two genera: *Pseudomonas* and *Bacillus*. Dissimilatory denitrification is used in sewage treatment and bioremediation where denitrifying bacteria aid in converting organic nitrogen to nitrogen gas that escapes to the atmosphere.

As explained by the previous processes, all forms of nitrogen are interconvertible. While there are losses of

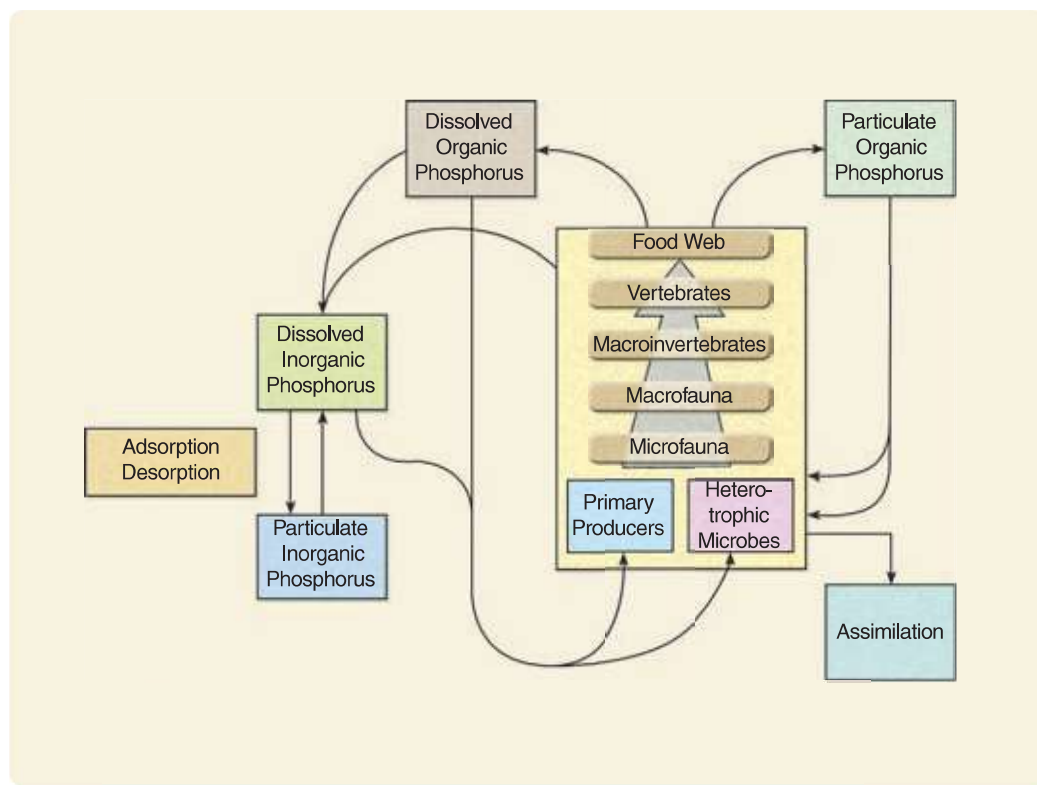
nitrogen within any aquatic system, there are simultaneous gains from the atmosphere and from recycling within any given region. Problems with eutrophication arise when humans contribute to loading of nitrogen to a waterbody from either point or nonpoint sources of pollution.

Since the 1940s, the amount of nitrogen available for uptake in aquatic systems at any given time has more than doubled (see also Chapter 16). Human activities now contribute more to the global supply of fixed nitrogen each year than natural processes. Anthropogenic nitrogen totals about 210 million metric tons per year, while natural processes contribute about 140 million metric tons. This influx of extra nitrogen has caused serious distortion of natural nutrient cycling in aquatic systems. Excess nitrogen can wreak havoc with aquatic ecosystem structure affecting the number and kind of species found.

**Phosphorous**, like nitrogen, is essential to all life. Phosphorous functions in the storage and transfer of a cell's energy and in genetic systems. Cells use adenosine triphosphate (ATP) as an energy carrier that drives a number of biological processes, including photosynthesis, muscle contraction, and the synthesis of proteins. Phosphate groups are also found in nucleotides and therefore nucleic acids. Phosphorous is usually more scarce environmentally than other principle atoms of living organisms including carbon, hydrogen, oxygen, nitrogen, and sulfur.

Phosphorous occurs naturally in rocks and other mineral deposits. During weathering, the rocks gradually release the phosphorus as phosphate ions, which are soluble in water, and the mineralized phosphate compounds breakdown. The phosphorus cycle in aquatic systems is shown in Figure 18.6. Phosphorous exists primarily as phosphates in two forms: orthophosphate and organically bound phosphate. These forms of phosphate occur in living and decaying plant and animal remains as free ions, chemically bonded, or mineralized and chemically bonded in sediments. Analytically, phosphorous in water is usually categorized as being either dissolved or particulate, depending on whether or not it can pass through a 0.45- $\mu\text{m}$  filter. The “dissolved” fraction can have a substantial colloidal component. Within the dissolved fraction, inorganic P (dissolved inorganic phosphorus) occurs as orthophosphate ( $\text{PO}_4$ ). Dissolved inorganic phosphorous is sometimes referred to as **soluble reactive phosphorous (SRP)**. **Total phosphorous (TP)** is determined on a nonfiltered sample by heat and acid digestion, which converts the sample to SRP for measurement.

In unpolluted rivers, SRP averages about 0.01 mg/L on a worldwide basis and total phosphorous averages about 0.025 mg/L (Maybeck, 1982). Agricultural activities may increase SRP levels to 0.05–0.1 mg/L, and municipal effluents may increase SRP concentrations to 1.0 mg/L or much higher. Particulate phosphorous includes P incorporated into mineral structures, adsorbed onto clays, and incorporated into organic matter. Worldwide averages of particulate phosphorous concentrations are about 0.5 mg/L. This level can be much higher depending upon land use and erodibility of the watershed.



**Figure 18.6** The phosphorus cycle in aquatic systems. From Calow P. and Petts G.E. (1992). *The Rivers Handbook*. Vol. 1. Reprinted with permission of Blackwell Publishing.

Phosphorous is often the limiting macronutrient with regard to primary production in aquatic systems. Because of this, and its relative scarcity, it is quickly removed from its dissolved state and incorporated into living biomass. Bacteria and algae are both responsible for turnover rates as fast as 1–8 minutes (Rigler, 1973). Turnover rates usually follow the order of (in order of decreasing turnover times): Bacteria → algae → zooplankton → vertebrates.

It's been estimated that in freshwater lakes, zooplankton excrete about 20% of the phosphorous required by phytoplankton, whereas bacteria can excrete up to 80%. Therefore, food web dynamics play a large role in either the sequestration or the recycling of phosphorous in aquatic systems. The speed at which phosphorous is moved between biotic and abiotic compartments makes interpretation of different forms difficult. It's impossible to distinguish between zooplankton-P, bacterial-P, algae-P, and sometimes even inorganic-P. The best way to quantify phosphorous in a body of water is by analysis of total phosphorous.

Eutrophication, besides increasing algal biomass, often results in depletion of dissolved oxygen, increases in pathogenic bacteria and viruses, increases in potentially toxic species of algae, fish kills, and loss of biodiversity. Remediation efforts of even a small lake are usually cost-prohibitive, and it is very difficult, if not often impossible, to return a lake or reservoir back to an earlier trophic state. The best approach is a proactive, watershed-based one that attempts to protect waterbodies from cultural eutrophication.

This usually requires collaboration among several resource agencies, in addition to municipalities and individual landowners in the watershed.

### 18.6.1 Harmful Algal Blooms

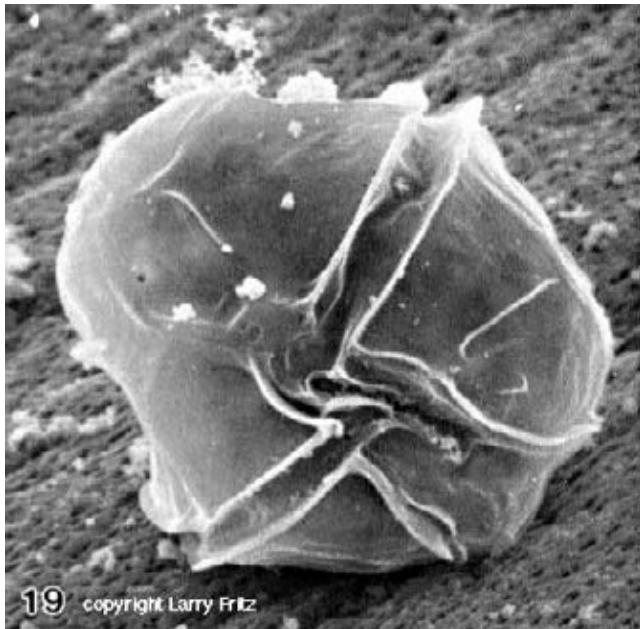
Planktonic (*i.e.*, free-floating algae) are vitally important components of all marine and freshwater systems on the planet. They form the base of the food chain in all aquatic systems. Of the thousands of known species, a few hundred have the potential to produce a wide variety of toxins under certain environmental conditions. Eutrophication greatly exacerbates the growth and prevalence of potentially toxic species.

#### 18.6.1.1 Harmful algal blooms in marine systems

Most **harmful algal blooms (HABs)** occur in coastal areas where terrestrial runoff of nutrients causes the growth and proliferation of sometimes monospecific blooms of toxic algae. Dinoflagellates (Division Dinoflagellata) are marine phytoplankton often associated with toxic blooms.

Dinoflagellates are microscopic, unicellular, flagellated protists that can be either autotrophic (photosynthetic) or heterotrophic (consuming other organisms). Heterotrophic forms often have life history patterns more akin to an animal than a plant. Additionally, dinoflagellates are routinely





**Figure 18.7** Scanning electron micrograph of *Alexandrium tamarense*, a typical dinoflagellate associated with paralytic shellfish poisoning. Source: <http://www.whoi.edu/redtide/species/species.html>.

found in freshwater and often produce some of the same toxins found in marine systems.

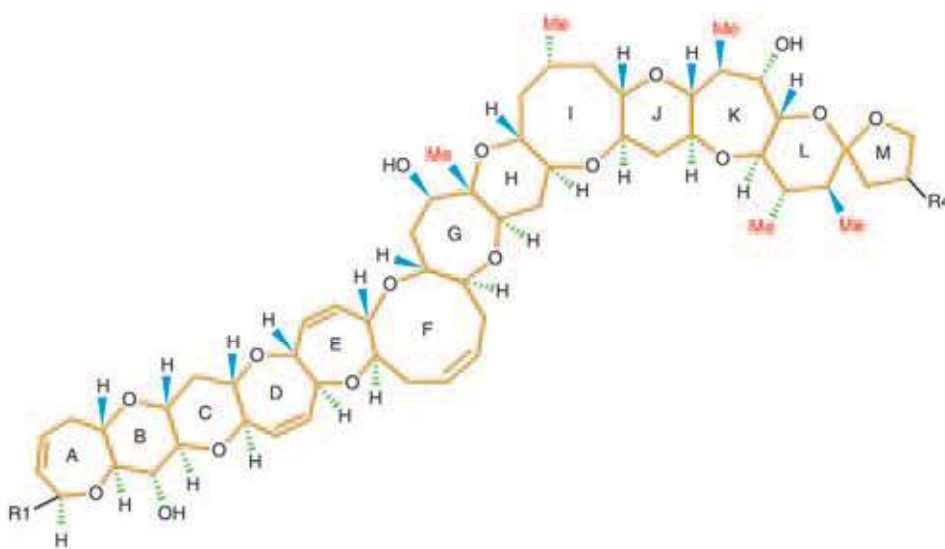
Dinoflagellates have the potential to produce a variety of toxins that can be harmful to humans and wildlife. Some affect humans following the ingestion of shellfish or fish that have consumed toxic dinoflagellate species (Figure 18.7).

Ciguatera poisoning is the most commonly reported disease associated with consumption of seafood. Ciguatera is

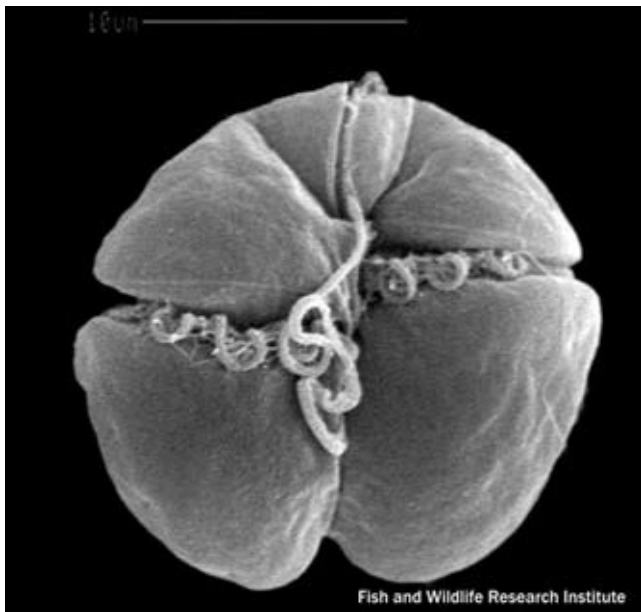
a lipid-soluble toxin that can affect a variety of fish species and can be very toxic to humans after ingestion of these fish. Tropical and subtropical fish species, including barracuda, grouper, and snapper, are commonly affected. The dinoflagellate species most often associated with ciguatera poisoning is *Gambierdiscus toxicus* but other species including *Prorocentrum mexicanum*, *P. concavum*, *P. lima*, and *Ostreopsis lenticularis* have also been implicated (Figure 18.8). Ciguatera exhibits both gastrointestinal and neurological symptoms, with the time to onset usually less than 24 hours. Gastrointestinal symptoms include diarrhea, abdominal pain, nausea and vomiting. The most common neurological symptoms include abnormal or impaired skin sensations, vertigo, lack of muscle coordination, cold-to-hot sensory reversal, myalgia (muscular pain), and itching. Neurological symptoms may recur intermittently, with gradually diminishing severity for as long as six months. No deaths have been reported from ciguatera in the U.S., although worldwide, the mortality rate is 7–20% of people infected.

Brevetoxin is a large, lipophilic, polyether toxin primarily produced by the dinoflagellate *Karenia brevis* (Figures 18.9 and 18.10). Brevetoxin poisoning occurs with the most frequency in the Gulf of Mexico and has caused sporadic fish kills for decades. These toxins also affect shellfish, which can in turn poison humans who ingest contaminated shellfish. This syndrome is referred to as **neurotoxic shellfish poisoning (NSP)** and produces similar symptoms similar to ciguatera poisoning. There have been no reported fatalities from NSP, although it has been known to kill laboratory mammals.

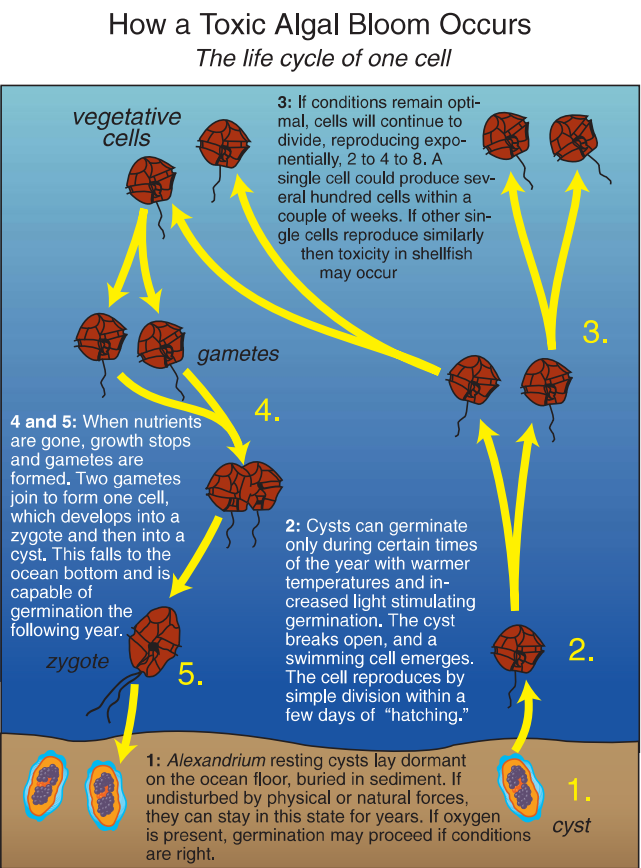
Under certain environmental conditions, dinoflagellates can rapidly multiply in numbers and form “tides.” Usually, tides are identified by the color of the dinoflagellate causing the bloom. “Red” tides (Figure 18.11) are often associated with species of *Alexandrium* and “brown” tides with species of *Aureococcus*.



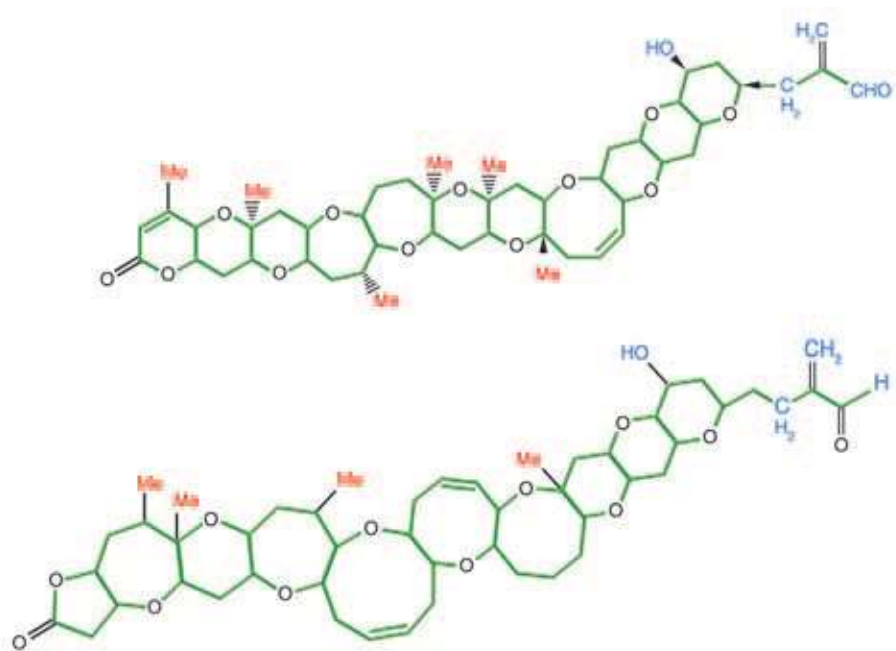
**Figure 18.8** Structure of ciguatoxin Type I. Source: <http://www.aims.gov.au/arnat/arnat-0004.htm>.



**Figure 18.9** Scanning electron micrograph of *Karenia brevis*. Source: Florida Fish and Wildlife Conservation Commission (<http://www.csc.noaa.gov/crs/habf/proceedings/intro.html>).



**Figure 18.11** Red tide formation. Source: Jack Cook, Woods Hole Oceanographic Institution (<http://www.whoi.edu/redtide/whathabs/whathabs.html>).



**Figure 18.10** Structure of brevetoxin-A and brevetoxin-B respectively. Source: <http://www.aims.gov.au/arnat/arnat-0003.htm>.

The initiation of either red or brown tides is complex due to the complex life cycles of dinoflagellates but usually involves warm, nutrient-enriched water.

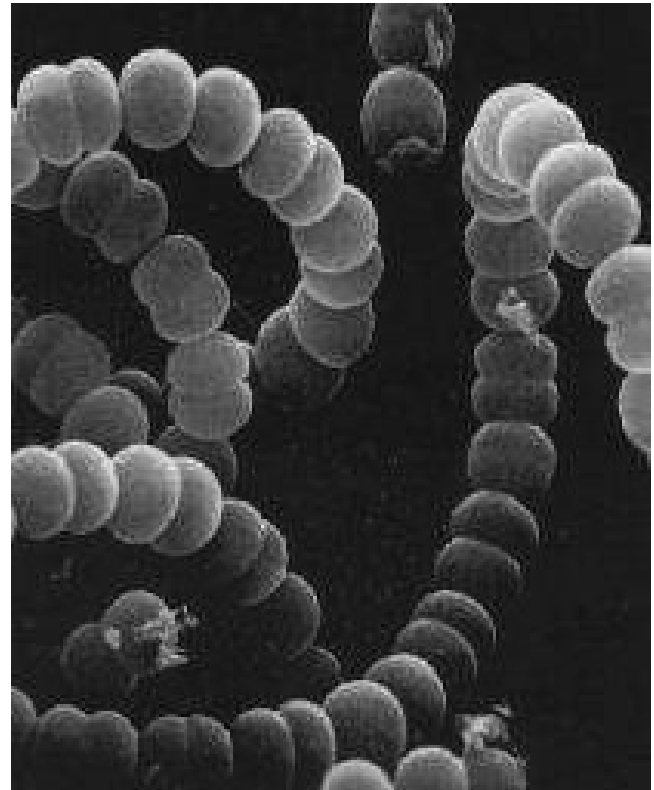
#### 18.6.1.2 Harmful algal blooms in freshwater systems

While freshwaters often contain many of the same dinoflagellate species found in marine systems, and sometimes the same toxins, the majority of freshwater toxins are caused by several different species of cyanobacteria. Cyanobacteria, like dinoflagellates in marine systems, greatly increase in number in eutrophic waters and occur on a global scale (Figure 18.12). Cyanobacterial toxins (“cyanotoxins”) can affect both humans and wildlife. Humans are usually affected from ingesting water containing cyanotoxins, and the disease is categorized based upon the type of toxin in the water. Toxins produced by cyanobacteria can be either hepatotoxic or neurotoxic.

One of the ubiquitous cyanotoxins is microcystin, which can be produced by species of *Anabaena* (Figure 18.13), *Nodularia*, *Nostoc*, *Oscillatoria*, and *Microcystis* (Figure 18.14). There are over 50 different analogues of microcystin (Figure 18.15). These toxins mediate toxicity by



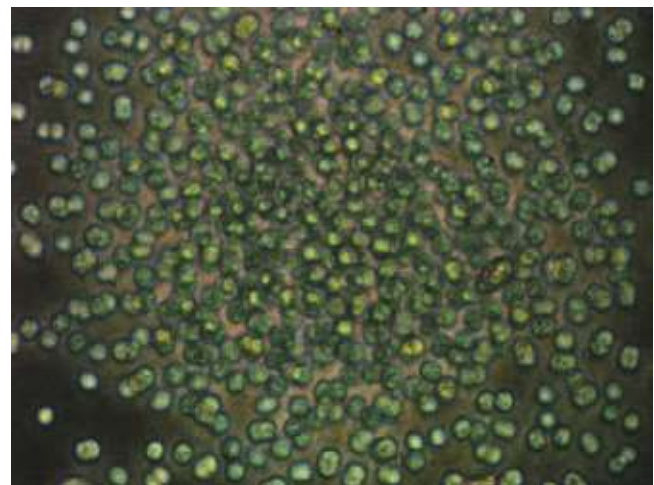
**Figure 18.12** The curtain divides the two halves of the lake. The area of the lake in the lower half of the picture had phosphorus, a limiting nutrient, experimentally added to it and now contains a massive bloom of cyanobacteria. Source: <http://www.umanitoba.ca/institutes/fisheries/eutro.html>.



**Figure 18.13** Scanning electron micrograph of *Anabaena flos-aquae*. Courtesy Dr. Wayne Carmichael ([http://www.nps.gov/romo/resources/plantsandanimals/names/checklists/other\\_algae/bluegreens/anabaena\\_f-a.html](http://www.nps.gov/romo/resources/plantsandanimals/names/checklists/other_algae/bluegreens/anabaena_f-a.html)).

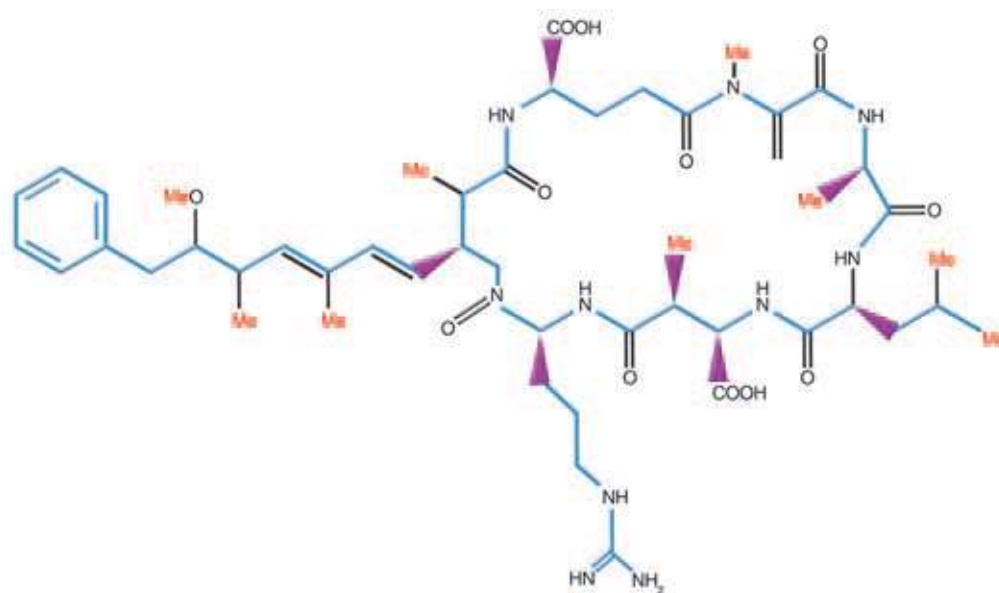
inhibiting liver function (*i.e.*, hepatotoxic) and can often be found at high levels in drinking water reservoirs.

Anatoxin-a is a small, low-molecular-weight neurotoxic alkaloid produced by species of *Anabaena*, *Aphanizomenon*, *Cylindrospermum*, *Microcystis*, and *Oscillatoria*. Anatoxin-a is a powerful, depolarizing, neuromuscular blocking agent that strongly binds to the nicotinic acetylcholine receptor



**Figure 18.14** Image of *Microcystis* sp. Photo courtesy David Walker.





**Figure 18.15** Structure of microcystin. Source: <http://www.aims.gov.au/arnat/arnat-0002.htm>.

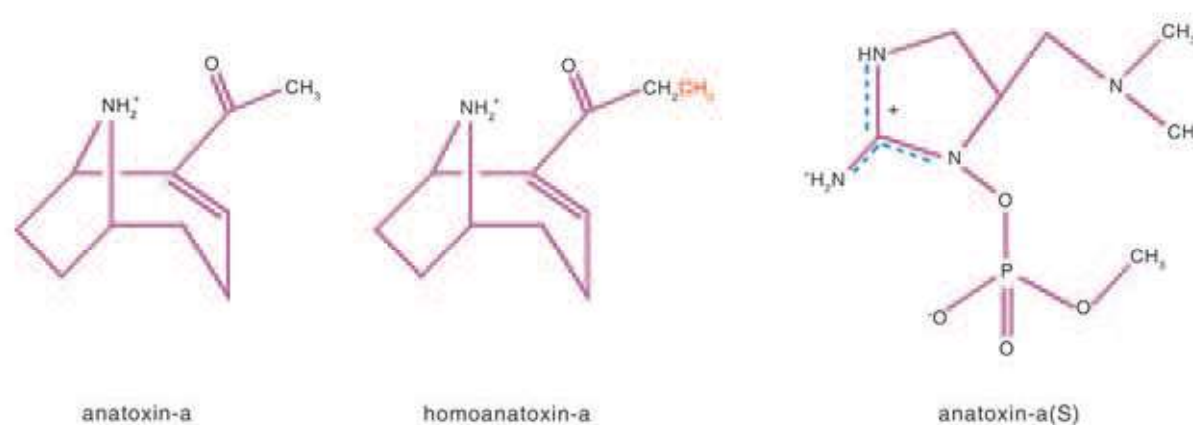
(Figure 18.16). This is a potent neurotoxin that can cause rapid death in mammals through respiratory arrest.

Cylindrospermopsin, while having many of the properties of hepatotoxin, also resembles neurotoxin. It is produced primarily by *Cylindrospermopsis raciborskii*, but has also been found in *Umezakia natans* and *Aphanizomenon ovalisporum*. Cylindrospermopsin has poisoned at least 149 people, many of them children requiring hospitalization, in Palm Island, Queensland, Australia. At one time believed to be strictly a tropical to subtropical species, *C. raciborskii* has been found in waters in the north temperate U.S. recently. Like most cyanotoxins, cylindrospermopsin can often be found in drinking water reservoirs.

## 18.7 ORGANIC COMPOUNDS IN WATER

### 18.7.1 Persistent, Bioaccumulative Organic Compounds

Certain organic compounds, due to their physicochemical properties (Chapter 7), are very persistent in the environment. These compounds are referred to as persistent, bioaccumulative, toxic (PBTs) contaminants (Chapter 10). These compounds are the most important organic contaminants in aquatic systems. These compounds bioaccumulate and biomagnify within the aquatic ecosystem, and they often accumulate in the sediments of surface water bodies.



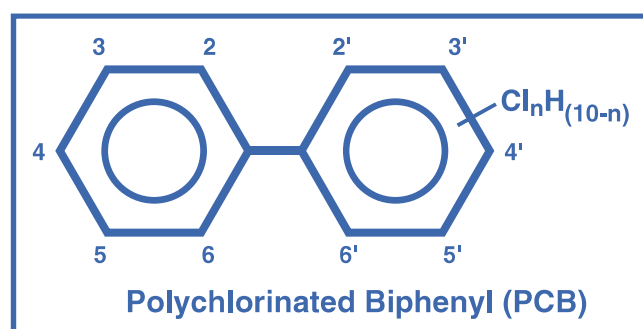
**Figure 18.16** Structure of anatoxin-a and the homologue homoanatoxin-a and anatoxin-a(s). Source: <http://www.aims.gov.au/arnat/arnat-0002.htm>.

**Dichlorodiphenyltrichloroethane (DDT)** is an organochlorine pesticide that was in widespread use from the 1940s to the early 1970s, when it was used primarily for agricultural crops or vector-pest control (the control of insects known to carry malaria and typhus).

When DDT is released into the environment, it begins to degrade into several different metabolites. Once bound to sediment particles, DDT and its degradation products can persist for up to 15 years depending upon environmental conditions. Water is the main route of exposure of DDT and its metabolites to humans and wildlife. Ingestion of foodstuffs and in particular consumption of fish is how humans ingest the largest amounts of DDT, primarily due to bioaccumulation. In fish and other wildlife, especially predatory birds feeding on fish, even if acute toxicity and death does not occur, reproductive failure often results.

The use of DDT in the US has been banned since 1972, however, the need to protect agricultural crops and humans from insect-borne vectors of disease still exists. Most organochlorine pesticides, including DDT, have been replaced with less environmentally persistent compounds such as organophosphate, carbamate, and synthetic pyrethroid pesticides. While these compounds are degraded in the environment at a much faster rate than DDT, they are also more acutely toxic. Even though DDT was banned over 30 years ago, due to its persistence, we still feel its toxic effects in the U.S. Twenty years after the ban of DDT, the U.S. EPA reported that out of 388 sites throughout the nation sampled between 1986 and 1989, total DDT and PCBs (discussed later), were detected at 98 and 90% of all sites respectively. Fish still remain vulnerable to the effects of DDT. A study by Munn and Gruber in 1997 showed total DDT was detected in 94% of whole-fish samples collected in streams of eastern Washington State.

**Polychlorinated biphenyls (PCBs)** are a group of organic compounds with similar physical structure and chemistry, ranging from oily liquids to waxy solids (Figure 18.17). All PCBs are formed from the addition of chlorine (Cl) to biphenyl (C<sub>12</sub>H<sub>10</sub>), which is a dual-ring structure



**Figure 18.17** Basic structure of a polychlorinated biphenyl.

Source: <http://www.epa.gov/toxteam/pcb/defs.htm>.

consisting of two 6-carbon benzene rings linked by a single carbon-carbon bond. The presence of a benzene ring allows a single attachment to each carbon, meaning that there are 10 possible positions for chlorine to replace the hydrogens in the original biphenyl.

Any unique compound in the PCB category is referred to as a “congener” whose individual name is dependent upon the total number and position of each chlorine substitute. There are 209 PCB congeners.

Due to the chemical stability and high boiling point of PCBs, they were used in hundreds of industrial applications, including electrical insulation, hydraulic equipment, and plasticizers in paints, plastics, and rubber products. Prior to their ban in 1977, total production of PCBs in the U.S. was more than 1.5 billion pounds. Because of the vast amount of possible congeners, PCBs were sold as many different trade names but one of the most prevalent was Arachlor®.

Similar to DDT, PCBs are environmentally persistent and adhere strongly to particulates in water, meaning that they can remain intact in sediments of lakes and rivers for extended periods. Because of PCBs’ strong adherence to sediments and suspended particles in water, actual contamination of a waterbody may be several times higher than the actual solubility of a particular PCB. Also like DDT, all PCBs are extremely lipophilic, meaning that they can bioaccumulate and biomagnify in aquatic environments. First detected in the 1960s, PCBs were found to be contaminants on a global scale, occupying virtually every component of the environment including air, water, soil, fish, wildlife, and human blood.

Uptake of PCBs by microorganisms is very rapid and extremely high bioconcentration factors are often seen. Uptake by microorganisms is by true absorption into cells rather than adsorption onto the cell.

Fish are especially susceptible to the accumulation and concentration of PCBs, and all life stages of almost every species readily absorb PCBs from the water. PCB congeners with higher chlorination levels are taken up most rapidly by fish. Due to the fact that PCBs are usually at higher levels in sediments, fish such as bottom feeders are most susceptible; however, route of exposure in fish can occur through water, sediment, or prey. Due to rapid uptake of PCBs in fish tissue, birds, especially those that eat fish, are also vulnerable. Egg-laying females can transfer substantial amounts of PCB to eggs with subsequent reproductive failure.

Route of exposure to humans, like DDT, is generally much greater for aqueous environments (through either direct ingestion of water or through eating contaminated fish) than terrestrial. PCBs are probable carcinogens in humans and are known to be carcinogenic to laboratory animals. The risks associated with consuming fish contaminated with PCBs are more than 1,000 times greater than the 1-in-a-million cancer risk used to regulate most hazardous wastes.

### 18.8 ENTERIC PATHOGENS AS SURFACE WATER CONTAMINANTS

Almost all animals are capable of excreting disease-causing intestinal microorganisms (enteric pathogens) in their feces (see Chapter 11). Sources of pathogens into surface waters include:

- Urban storm water
- Combined sewer and sanitary sewer overflows
- Animal feeding operations
- Sewage treatment plants
- Septic tanks (onsite systems)

Pathogens can remain infectious for prolonged periods of times in surface waters presenting health risks to recreational users shellfish harvesting, and drinking water treatment plants. While drinking water treatment plants are required to treat water from surface sources, the more pathogens that are present in the raw water, the more treatment is required. Also, after periods of heavy rains, when the amount of suspended matter and pathogens often increases, it is difficult to remove all pathogens. For example, it has been shown that waterborne disease outbreaks in the United States are related to the intensity of rainfall events (Curriero et al., 2001).

Forty percent of rivers and estuaries that fail to meet ambient water quality standards fail because of pathogens,

## CASE STUDY 18.2

### “SILENT SPRING” AND “OUR STOLEN FUTURE”

Rachel Carson (1907–1964) was a scientist, author, and ecologist who spent most of her adult life working for the U.S. Fish and Wildlife Service. She received a letter from a friend in Massachusetts in the summer of 1957 stating that an airplane had flown back and forth over the friends’ property spraying DDT to control mosquitoes. The following day, there were numerous dead birds in her yard. She contacted Carson to see what could be done to prevent further spraying. While doing preliminary research on the problem, Carson was shocked at how prevalent the use of pesticides, and DDT in particular, had become. From 1958 to 1962, Rachel Carson performed research for the book that would become *Silent Spring*. To many, this book would become the seminal work exposing the ecological effects of pesticide use in addition to laying the foundation for the modern environmental movement.

*Silent Spring* opens with a fable of a rural town that suddenly suffers sickness and death, with its citizens realizing they had unwittingly been poisoning themselves with pesticides. Next, Carson explained the science, in easily understandable prose, that this scenario was happening all over the country. She explained how stronger pests survived poisoning so that increasingly stronger pesticides were needed to have the same efficacy over time. Rachel Carson was one of the first to explain about bioaccumulation and biomagnification, and how DDT, at low levels in the water, becomes concentrated as it works its way up the food chain. Her message was that humans could never fully control nature without harmful side effects.

This book was not well received by many, especially companies that manufactured pesticides and were a very powerful and influential group of lobbyists. One company threatened a lawsuit before the book went to press.

The lawsuit never manifested, and the company was later found to be one of the worst offenders with respect to the manufacturing and use of toxic chemicals.

In 1996, Dr. Theodora Colborn wrote *Our Stolen Future*. Dr. Colborn is a senior scientist with the World Wildlife Fund and one of the world’s leading experts on endocrine-disrupting chemicals in the environment. This book does not examine the acutely toxic properties of certain synthetic organic compounds, but rather their long-term chronic effects. The endocrine-disrupting effects (see Chapter 31) of a plethora of chemicals are the most insidious and difficult to quantify, but, due to their ubiquity, are perhaps the most devastating on a global scale over the long term. Some endocrine-disrupting chemicals alter sexual development, while others affect intelligence and behavior. Sometimes the effects exerted by these chemicals are not realized until a child reaches puberty or sometime thereafter, even though the effects were brought about in the womb. This book explains that typical dose–response curves do not work with endocrine-disrupting compounds, and that high-dose studies often miss important low-dose biological effects. The author explains that the way we, as a society, use chemicals today is like performing a vast experiment, not in the laboratory, but in the real world. Dr. Colborn was recently awarded the Rachel Carson Award for Integrity in Science by the Center for Science in the Public Interest (CSPI).

What both Rachel Carson and Theodora Colborn epitomize is that it is not enough to elucidate and evaluate scientific problems, but rather that it is of equal importance to communicate the implications of scientific research to nonscientific audiences.



usually measured by fecal coliform bacteria (see Chapter 11) (Smith and Perdek, 2004).

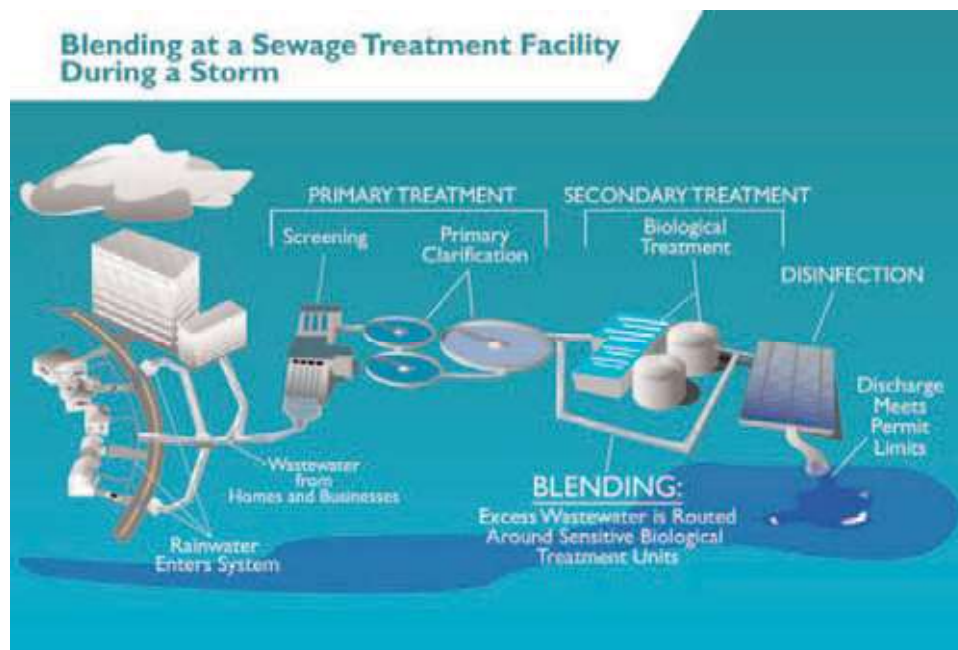
Stormwater can contain a wide variety of pathogens that originate from the feces of wild and domestic animals. Besides pets, other animal sources in urban areas include pigeons, geese, rats, and raccoons. Animal feces accumulate on the ground, and following a storm event are flushed into nearby streams and lakes. This results in a rapid increase in the concentration of enteric organisms, sometimes exceeding that found in raw sewage. In some cities, sewers that collect domestic sewage are combined with stormwater drains or collection systems. These flows are then transported to a sewage treatment plant for treatment. Unfortunately, after periods of heavy rainfall, this combined flow is greater than the sewage plant can treat, requiring the sewage plant to discharge untreated combined sewage and stormwater. These events are referred to as **combined sewer overflows** or **CSOs**. CSOs generally occur in older parts of the country, involving approximately 900 cities. To reduce the impacts of CSOs, cities may blend the untreated wastewater with treated wastewater (Figure 18.18) or may construct large holding reservoirs where the combined flows can be stored until they can be treated later (see Case Study 18.1).

In the United States, there are 238,000 animal feeding operations, or AFOs (sometimes called confined animal feeding operations, or CAFOs) that produce 350 million tons of manure annually. This figure does not include manure from grazing animals. These operations generate approximately 100 times as much manure as municipal wastewater

treatment plants produce sewage sludge (biosolids) in the United States. The Clean Water Act (see Chapter 15) requires operations having more than 1,000 animals to have a discharge permit. Runoff from AFOs and farmland can contribute significant levels of pathogens that can infect humans, such as *Cryptosporidium* and *Escherichia coli* O157:H7 (see Chapter 11).

Septic tanks (also referred to as **decentralized** or **onsite wastewater treatment systems**) collect, treat, and release about 4 billion gallons of treated effluent per day from an estimated 26 million homes, business, and recreational facilities in the United States (see Chapter 27). Poorly treated wastewater from improperly operating or overloaded systems can contain enteric pathogens that by transport through the soil can make their way to nearby streams and lakes. Overflows from failing onsite systems can result in the sewage reaching the surface. The discharge of partially treated sewage from malfunctioning onsite systems was identified as a principal or contributing source of degradation in 32% of all harvest-limited shellfish growing areas in the United States. Problems with surface water contamination by onsite systems are most likely to occur in areas with shallow groundwater tables (e.g., within a few feet of the surface).

In the United States it is required that sewage discharges be disinfected to reduce the level of pathogens (see Chapter 26). While very effective in eliminating most enteric bacterial pathogens, significant levels of enteric virus and protozoan parasites may remain.



**Figure 18.18** Blending at a sewage treatment facility. Source: [www.epa.gov](http://www.epa.gov).

# CASE STUDY 18.3

## TUNNEL AND RESERVOIR PLAN (TARP) TO CONTROL EXCESS STORMWATER

Chicago and 51 older municipalities in Cook County, Illinois, have combined sewer systems. This means when rain falls, stormwater runoff drains into a combined sewer, where it mixes with the sewage flow from homes and industry. The net result is one massive quantity of dirty water! A system that

was designed to treat 2 billion gallons of wastewater per day may be inundated with more than 5 billion gallons of stormwater runoff (about 1" of rain) during a single rainstorm. When the urban area grew and treatment plants were at capacity, there was no alternative but to allow the excess

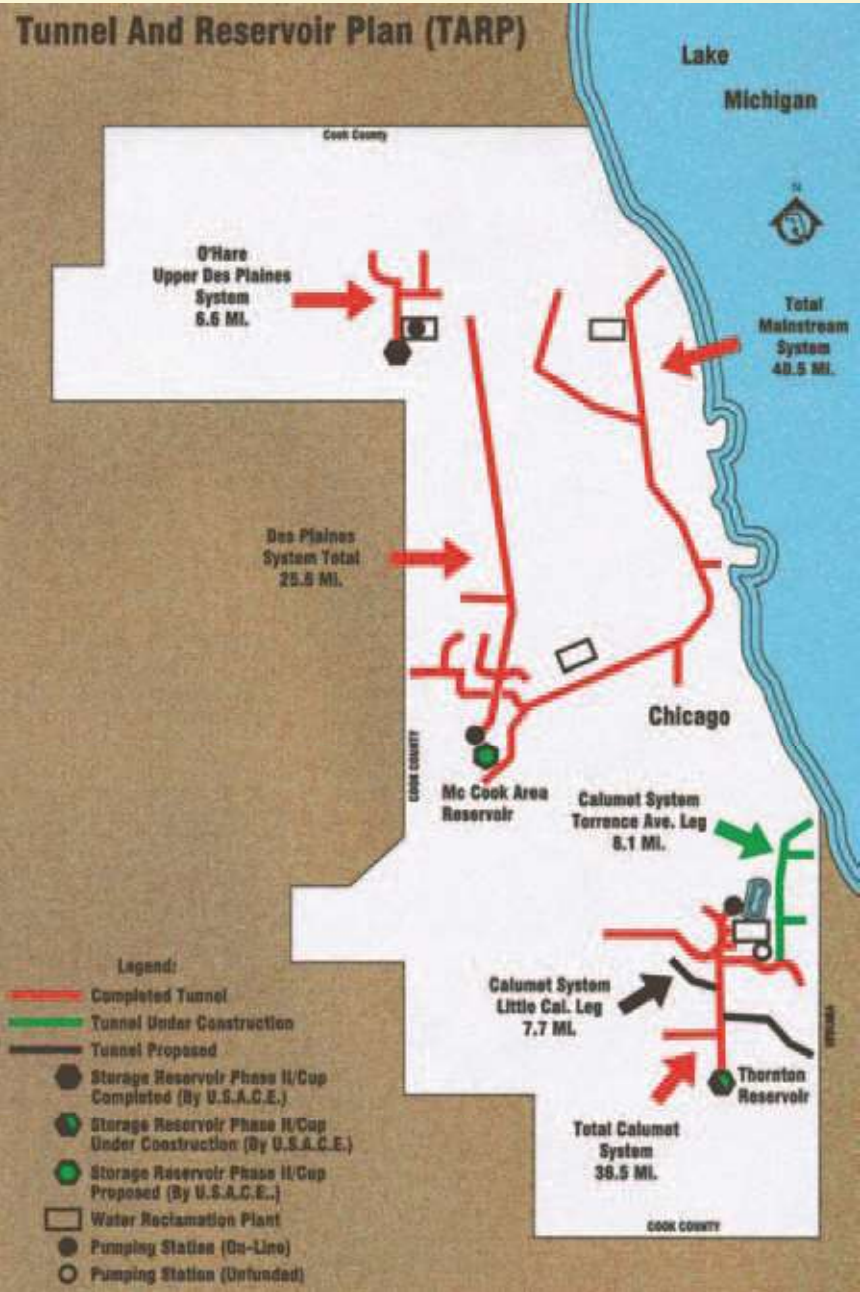


Figure 18.19 Tunnel and reservoir plan (TARP). Photo courtesy C.P. Gerba.

mixture of raw sewage and stormwater to spill directly into the rivers and canals as combined sewer overflow or CSO. This meant that much untreated sewage, diluted with storm runoff, was bypassing treatment plants and polluting lakes, rivers, and streams, and also causing street and basement flooding. A better solution had to be found.

In the 1970s, a team of engineers from the City of Chicago, Cook County, and state agencies considered various plans to solve the problem of flooding and water pollution. The hybrid plan selected as best and most cost-effective was the **Tunnel and Reservoir Plan** or **TARP** (Figure 18.19). Under this plan, 109 miles of huge underground tunnels would be burrowed under the city to intercept combined sewer overflow and convey it to large storage reservoirs. After the storm had subsided, the overflow could then be conveyed to treatment plants for cleaning before going to a waterway.

The Mainstream tunnel is 35 feet in diameter, bored in limestone rock 240 to 350 feet below ground, and holds 1 billion gallons of water (Figure 18.20). Mainstream is one of the largest rock tunnel bores on record. Since tunnel contractors would be working beneath homes, businesses, and streets, excavation by extensive blasting was ruled out. Boring by huge tunnel-boring machines (TBMs) was selected instead, to cause less rock disturbance, noise, and vibration.

Nearly 15 years later, the success of this project is evident by the dramatic improvements in the water quality of the Chicago River, the Calumet River, and other waterways. Game fish have returned, marinas and riverside restaurants abound, and river recreation and tourism has improved. <http://www.mwrdgc.dst.il.us/plants/tarp.htm>



**Figure 18.20** The Mainstream tunnel. Photo courtesy C.P. Gerba.



**INFORMATION BOX 18.1****Microbial Source Tracking**

Fecal contamination of surface waters can result from numerous sources, including human sewage, manure from livestock operations, indigenous wildlife, and urban runoff. Effective watershed management requires identification of, and targeting mitigative action towards, the dominant source of fecal contamination in the watershed. Several **microbiological source tracking (MST)** methods have been developed to fill this need. MST methods are intended to discriminate between human and nonhuman sources of fecal contamination, and some methods are designed to differentiate between fecal contaminations originating from individual animal species.

MST methods involve the isolation of fecal bacteria (*Escherichia coli*, enterococci) or viruses (human or bacterial) from a watershed. Subsequently molecular analyses of DNA or RNA, or patterns of sensitivity to different antibiotics, are performed to “fingerprint” the organisms. Samples of potential sources of the fecal bacteria are then collected in the watershed (e.g., from cattle, ducks, pigeons, dogs, sewage treatment plants, and urban runoff), and a “fingerprint” of these bacteria is obtained. By matching the fingerprints, the major sources of fecal bacteria in a watershed or waterbody can be identified. Identification of human enteric viruses (see Chapter 11) is an indication of human sewage as a source. Certain bacteriophages are only found in humans and others only in animals; hence, this is another approach that can be used.

**18.9 TOTAL MAXIMUM DAILY LOADS (TMDL)**

A **total maximum daily load (TMDL)** is the maximum amount of pollution that a waterbody can assimilate without violating water quality standards. A TMDL is the sum of the allowable loads of a single pollutant from all contributing point and nonpoint sources, so that a waterbody can meet a designated use, such as swimming or fishing. Under the Clean Water Act of 1972, states are required to identify surface waters not meeting water quality standards and develop a TMDL for each pollutant for each listed waterbody. The processes of TMDL development and implementation are shown in Figure 18.21. Once the impaired body of water is identified, a study is usually conducted to identify the sources and concentration of pollutants. From this, an informational plan is developed to reduce the most significant source(s) so that water quality standards can be met.

TMDL = point sources of waste allocations (e.g., sewage treatment plant discharge) + non-point source load allocations (urban runoff) + natural sources (mineral deposits, wild

animals) + growth factor (growth of enteric bacteria) + a margin of safety (to compensate for uncertainties about the link between pollutant loads and impairments)

A load allocation is the part of a TMDL/water quality restoration plan that assigns reductions to meet identified water quality targets. For example, in a given watershed it was found that cattle were the major source of fecal coliform bacteria in the streams. To reduce fecal coliform loading, fences were placed to limit direct access of the cattle to the stream.

Fecal coliform bacteria and temperature (largely thermal waters from power plants) are the major contaminants that cause most waterbodies to not meet water quality standards for intended uses in the United States (Figure 18.22).

**18.10 QUANTIFICATION OF SURFACE WATER POLLUTION**

Even as treatment methods were being developed, methods were simultaneously developed to quantify and assess both the disease threat and the dissolved oxygen problem posed by the discharge of municipal wastes into waterbodies. Quantitative methods are also used to calculate the degree of treatment needed. Such methods are based on an understanding of the physical and biochemical processes controlling the decay of microbes and chemicals over time.

**18.10.1 Die-Off of Indicator Organisms**

Early in the development of quantitative assessment methods, scientists realized that the many different microorganisms that exist in human wastes could not be effectively cultured and counted. Consequently, they settled on the coliform group of organisms to serve as an indicator of fecal pollution because they could be cultured and counted easily. Known to exist in large numbers in the gut of all warm-blooded animals, the coliform group provides a good indication of fecal pollution; however, it is not very specific, so other indicators such as fecal coliforms and streptococci may also serve as indicators of the sanitary quality of water.

Tests have shown that 99.99% of the indicator bacteria can be removed by wastewater treatment. But the residual 0.01% remains a problem raising concerns about the quality of water for recreational use, for example. The fact is that the number of bacteria in sewage is tremendous (500 million to 2 billion per 100 milliliters), so that, in assessing quality, the percentage of removal is not as useful as is the actual remaining concentration. The microorganism concentrations allowed for various uses of water are relatively small. For drinking purposes, the concentration of fecal coliforms should, of course, be 0, but a concentration of less than 1 per 100 mL may be allowed; for bathing, a concentration of 1000 per 100 mL is frequently accepted. If, for purposes of

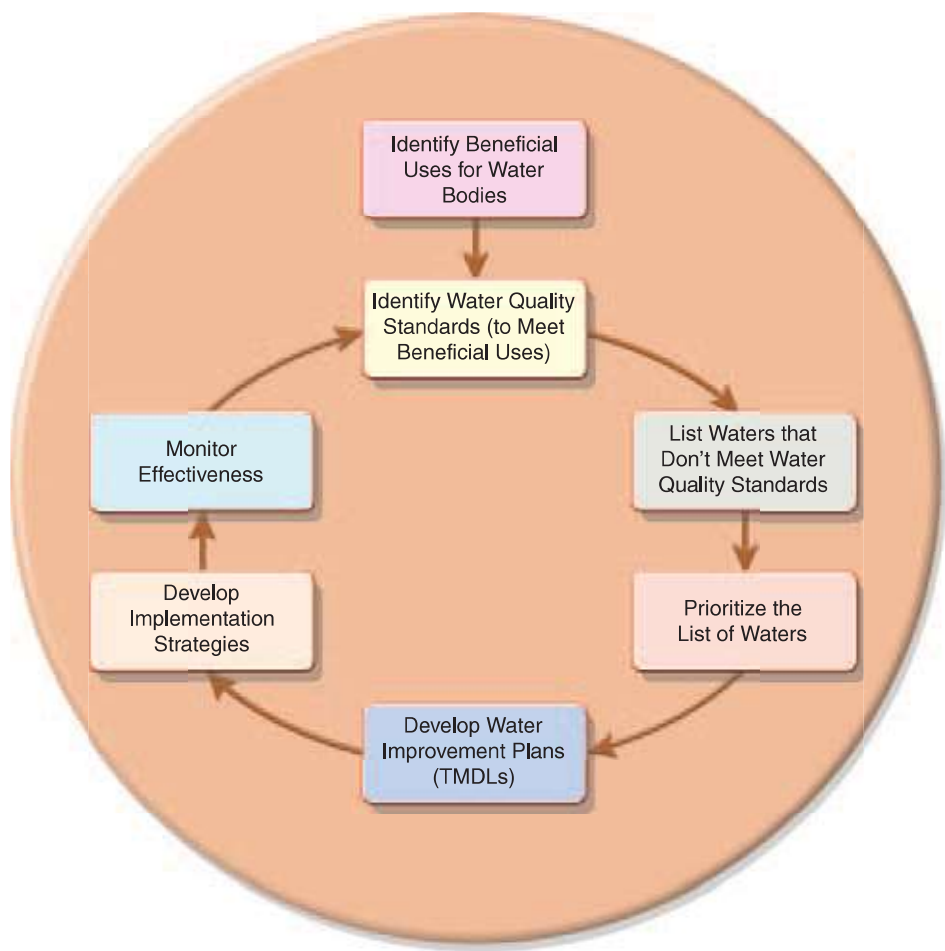


Figure 18.21 TMDL development and implementation.

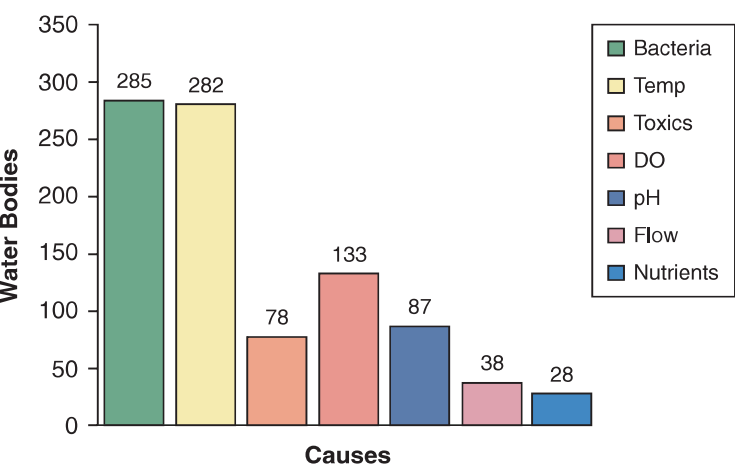


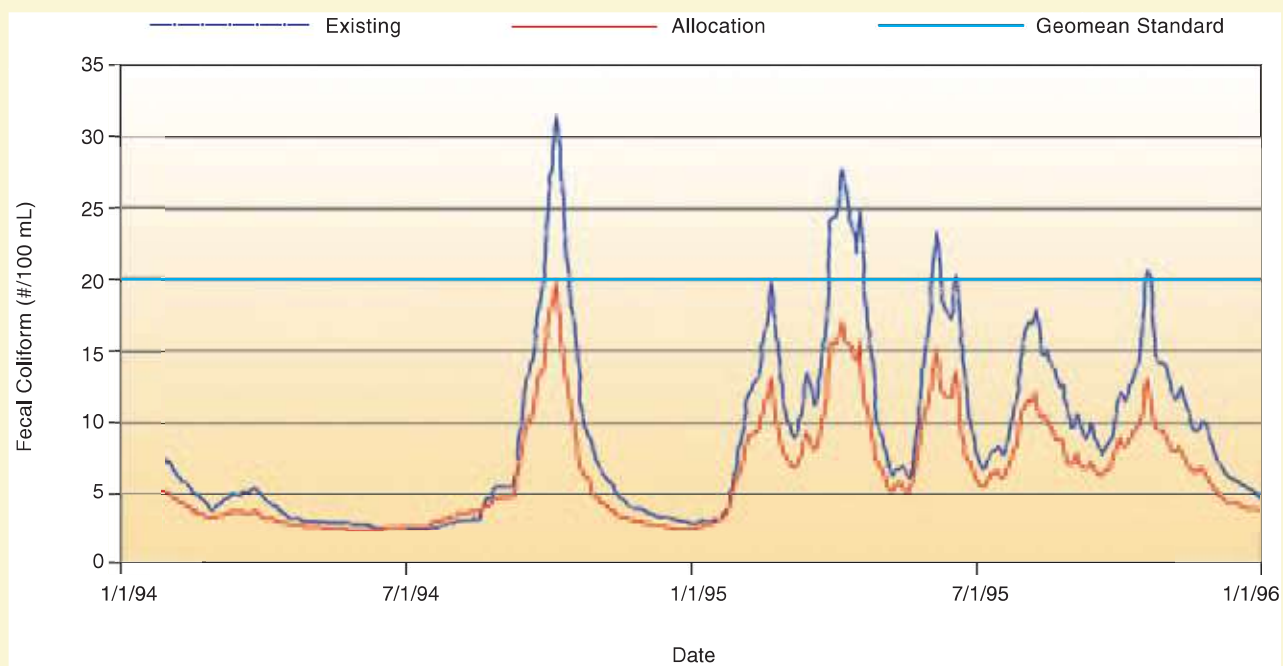
Figure 18.22 Major causes for water bodies that fail to meet water quality standards. Source: [www.epa.gov](http://www.epa.gov).

## CASE STUDY 18.4

### TOTAL MAXIMUM DAILY LOAD (TMDL) FOR FECAL COLIFORM BACTERIA IN THE WATERS OF DUCK CREEK IN MENDENHALL VALLEY, ALASKA

Duck Creek is on the list of impaired waters in Alaska because of fecal coliform bacteria. The primary sources of fecal coliform bacteria in the creek were found to be urban runoff and animal waste. As the watershed became more developed, urban runoff and pet populations increased. This increased the level of fecal coliforms entering Duck Creek. Duck Creek is used as a source of drinking water, and the State of Alaska standard for such water bodies is a geometric average of 20 fecal coliforms per 100 mL. This standard was usually exceeded several

times per year (Figure 18.23). Based on the water quality standards for fecal coliform bacteria and the hydrologic conditions of Duck Creek, the loading capacity for fecal coliform bacteria was established at  $2.23 \times 10^{11}$  fecal coliforms per year. To meet these objectives it was recommended that wetlands be constructed to retain stormwater flows, greenbelts be developed to serve as buffers to overland flow, and eroding banks be stabilized. In addition, pet owners were encouraged to clean up and properly dispose of pet waste.



**Figure 18.23** Existing fecal coliform concentrations in Duck Creek and allocation to meet standards as a drinking water source water body. Source: [www.epa.gov/owow/tmdl](http://www.epa.gov/owow/tmdl).

demonstration, we assume that raw sewage has a population of one billion ( $10^9$ ) per 100 mL, a removal efficiency of 99.99% would still leave 100,000 per 100 mL. The good news is that the concentration of organisms decreases with time and distance downstream of the discharge point owing to natural processes. Depending on the location and proximity of uses, the point of discharge and method of discharge can be designed to optimize the rate of natural purification, further reducing downstream pollution problems. The bad news is that we have only a partial understanding of all the processes that affect die-off.

The concentration  $C$  of bacterial indicators of fecal contamination has been observed to decrease with time  $t$  according to a first-order reaction, the equation of which is

$$\frac{dC}{dt} = -KC \quad (\text{Eq. 18.1})$$

where  $K$  is the **die-off rate constant**. One parameter frequently employed in water pollution analyses obtained by solution of the first-order reaction equation is  $t_{90}$ , which is the time required for 90% die-off of the bacteria. This parameter is analogous to the half-life ( $t_{50}$ ) used in radioactiv-



ity studies and is calculated in the same fashion. Thus, given the value of  $K$

$$t_{90} = \frac{2.3}{K} \quad (\text{Eq. 18.2})$$

The general solution of Equation 18.1 is used to find the concentration at any time  $C_t$ , after the initial concentration  $C_i$  is determined:

$$C_t = C_i e^{-Kt} \quad (\text{Eq. 18.3})$$

This information can be used to calculate freshwater or marine die-off. To find the concentration of bacteria after effluent has traveled in the river for, say, 8 hours, it is necessary to determine the value of  $K$  for the specific situation being studied. Results of many studies in lakes and streams have shown that  $K$  varies widely, depending on the temperature of the water, the amount of sunlight, and the depth at which the plume travels. An average value for fresh water is about  $K = 0.038$  per hour; however, values from 0.02 to 0.12 per hour have been measured. Using Equation 18.3 and  $K = 0.038$  per hour, the initial concentration  $C_0 = 100,000$  per 100 mL would be reduced to about 74,000 per 100 mL in  $t = 8$  hours due to die-off alone. In many cases, it is preferable to predict the concentration at a given distance downstream, rather than at time increments. Most U.S. rivers have a remarkably uniform low-flow current of 1.5 to 2 km per hour, which can be used to convert low-flow travel time to distance. In our example, this travel distance would be between 12 and 16 km. Travel times for other flow conditions vary from river to river, so field measurements may be needed to relate bacterial concentrations to specific locations downstream.

In analyzing coliform die-off cases in the marine environment, we often use an average value of 1.2 per hour for  $K$ , which is nearly 30 times greater than that of freshwater. This rapid die-off rate is usually attributed to the salinity of the marine environment, although it may also be related to a greater concentration of predatory animals. In addition, the natural flocculation and sedimentation of particles that occurs in estuaries could account for removal of bacteria from the water column. There are, however, other factors that can reduce the die-off rate. For example, when an effluent is discharged at a great depth, the die-off can slow down considerably because sunlight cannot penetrate deeply enough.

Calculating seawater die-off is similar to freshwater die-off. The value of  $K$  for marine waters usually ranges from 0.3 to 3.8 per hour. Recently, however,  $K$  values as low as 0.02 per hour have been found where an effluent plume is transported in a layer far below the surface, say, 40 meters, suggesting that die-off is reduced because of the low penetration of UV radiation to that depth. What difference would this low  $K$  value make in the concentration?

Using the average value of  $K = 1.2$  per hour, the original concentration,  $C_0 = 100,000$  per 100 mL, would die off to  $C_1 = 6.7$  per 100 mL in  $t = 8$  hours using Equation 18.3. But using  $K = 0.02$  per hour instead of 1.2 per hour, we get 85,000 per 100 mL. Thus, for a 60-fold reduction in  $K$ , the

concentration is increased by a factor of  $85,000/6.7 = 13,000$ ! It is evident from this example how important it is to have accurate values for  $K$  and how widely the results can vary with equally good, but different, estimates for  $K$ .

Variations in the rates of indicator bacterial die-off are not the only problem we have to contend with. Noncoliform pathogenic microorganisms may decay at rates different from those of our coliform indicators. Therefore, as water-analysis techniques become more sophisticated, we will need to conduct many field observations to establish values that can be used to predict die-off rates for specific pathogens.

In addition to the decrease of bacterial concentrations due to die-off in either fresh or marine surface waters, bacterial concentrations are decreased as the water is diluted with upstream ambient water at the point of effluent discharge and further diluted as it flows downstream. The effect of dilution may or may not be important in meeting water quality criteria, depending on the initial mixing, the nature of the subsequent flow patterns, and the distance to water use areas. But before discussing the mechanics of the dilution process, observe how the same first-order decay process used for assessing indicator bacteria die-off can be applied to the analysis of the fate of biodegradable organics.

### 18.10.2 Organic Matter and Dissolved Oxygen

Biodegradable organic compounds are decomposed by bacteria and other organisms that live in surface waters. While some organics are mineralized to carbon dioxide and oxides of nitrogen, others are synthesized into more microbial biomass, most of which is subsequently decomposed as well. All this decomposition consumes dissolved oxygen (DO), upon which many desirable species of fish, other aquatic organisms, and wildlife depend. Thus depressed dissolved oxygen concentrations adversely affect these life forms. For example, some fish can survive at concentrations near  $1 \text{ mg L}^{-1}$ , most are adversely affected at DO concentrations below  $4 \text{ mg L}^{-1}$ . The maximum amount of oxygen that pure surface water can hold is a function of salinity, temperature, and atmospheric pressure; compared to the maxima of many other substances, however, it is remarkably low. Note that solubility of  $\text{O}_2$  decreases with increasing temperature, which is the opposite of the temperature-solubility relationship observed for most substances in water.

Domestic sewage can contain about 300 to 400  $\text{mg L}^{-1}$  of organic compounds, 60% of which is readily degradable by bacteria commonly found in nature. Readily degradable implies that most of the material will be decomposed within about a week in a stream or other body of water that is sufficiently large. The change in the concentration of the organic matter with time is conveniently described by the first-order decay equation used to describe bacterial die-off. However, the value of this  $K$  depends on the specific organic compounds in the sewage. For domestic sewage, an average value is about  $K = 0.4$  per day, ranging from 0.1 to 0.7 per day. As more industrial wastes

are contributed to the sewer system, the rate constant may increase or decrease. The amount of organic material discharged to a surface water depends on the population served by the municipal sewer system and treatment technology employed. Each person contributes about 90 grams per day of organics; thus, if the population is 100,000 people, the mass emission rate is 9 metric tons per day. The concentration of organics in the sewage depends on the amount of water added by the individual households and that added by other water uses in the community. If the average water use is 300 liters per person per day, the concentration is  $300 \text{ mg L}^{-1}$ .

### 18.10.3 Measurement of Potential Oxygen Demand of Organics in Sewage

#### 18.10.3.1 COD

A parameter frequently used for industrial wastes, particularly where industrial wastes contribute heavily to the sewer system, is the **chemical oxygen demand (COD)**, which is a measure of the amount of oxygen required to oxidize the organic matter—and possibly some inorganic materials—in a sample. Note that the method employed to obtain this parameter, which involves reflux of a sample in a strong acid with an excess of potassium dichromate, does not specifically measure the organic content in the sample, but rather the amount of oxygen required for oxidation. This approach therefore provides a direct measure of the potential impact of oxygen consumption on the oxygen content of the waterbody.

#### 18.10.3.2 BOD

The **biochemical oxygen demand (BOD)**—is the most commonly used parameter in the analysis of oxygen resources in water. The BOD is the amount of oxygen con-

sumed over time, usually 5 to 20 days, as the organic matter is oxidized both microbially and chemically.

### 18.11 DETERMINING BOD

The laboratory method used to determine BOD has changed very little since it was initiated in the 1930s. We begin by setting up many sample bottles to contain a sample of waste, mixed in water either from the disposal site or from a standard laboratory supply. Then we use standard methods to find the initial concentration of DO, after which the bottles are incubated in a dark water bath at a given temperature, usually  $20^\circ\text{C}$ . Every day for five or more days, we open a few of the bottles and measure the remaining DO. The difference between the initial value and the value at each time period, that is, the **demand**, is plotted as the BOD for the series of days.

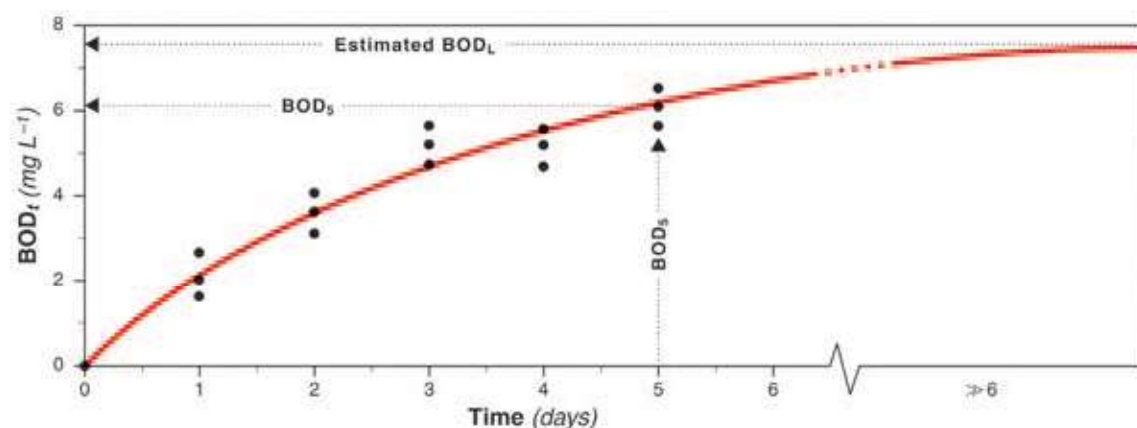
From the data obtained in the laboratory, we construct a smooth curve that lets us calculate the reaction rate coefficient  $K$  by graphical or analytical methods. The curve we construct, whose equation is

$$\text{BOD}_t = \text{BOD}_L(1 - e^{-Kt}) \quad (\text{Eq. 18.4})$$

becomes more and more horizontal as time progresses (Figure 18.24). By extrapolating the curve to horizontal, we can make an estimate of the ultimate value, called the **limiting value of BOD**, or **BOD<sub>L</sub>**.

We can use the curve in this example to compute the value of  $K$  for the wastewater sample in this laboratory test. First, by extrapolating this curve to horizontal, we see that the estimated value of  $\text{BOD}_L$  would be about  $7.6 \text{ mg L}^{-1}$ . Next, by substituting the value read from the curve for day five ( $6.1 \text{ mg L}^{-1}$ ), so that  $\text{BOD}_t = \text{BOD}_5 = 6.1$  and  $t = 5$ , we can find  $K$  from Equation 18.4:

$$\begin{aligned} \text{BOD}_5 &= \text{BOD}_L(1 - e^{-5K}) \\ 6.1 &= 7.6(1 - e^{-5K}) \end{aligned}$$



**Figure 18.24** Typical biochemical oxygen demand test results illustrating the graphical method for determining  $\text{BOD}_L$  and  $\text{BOD}_5$  for use in solving Eq. 18.4 to find  $K$  as described in the text. Note that, in actuality, the extrapolated curve is asymptotic to  $y = \text{BOD}_L$ . From *Pollution Science* ©1996, Academic Press, San Diego, CA.

so that

$$1 - \frac{6.1}{7.6} = e^{-5K} \text{ or } \ln 0.197 = -5K$$

Thus

$$K = \frac{-1.62}{-5} = 0.32 \text{ per day}$$

### 18.11.1 Impact of BOD on Dissolved Oxygen of Receiving Waters

Typically, municipal sewage is treated to some degree to remove organics, and hence to reduce BOD, before discharge to surface waters in developed countries of the world. The amount of BOD remaining after treatment can range from 10 to 70% of the amount originally in the sewage. The impact on receiving waters depends on many environmental and waste characteristics, most of which are briefly mentioned later in this chapter. After the BOD parameters already explained, the next most important considerations are the amount of DO in the waterbody before the sewage is added, called the **initial DO (DO<sub>i</sub>)**, and the rate at which additional oxygen is transferred from the atmosphere to the receiving water.

Many rivers and streams have depressed DO concentrations, that is, a **DO deficit**, because of wastewater added by cities upstream. The saturation value of DO is 100% with the quantification in mg/L depending upon temperature, salinity, atmospheric pressure. The local deficit—the difference between the saturation value and the observed initial value at the location of waste discharge—must be included in the computation of the downstream DO deficit caused by a new effluent discharged to the stream. Before presenting an example calculation, let's first examine how nature deals with the DO deficit.

Deficits tend to be redressed by oxygen gas derived from the atmosphere. Such replenishment occurs by a process of gas–liquid mass transfer at the surface and subsequent mixing throughout the depth of water. This overall process can be described in an approximate manner by a first order-equation, the solution of which is

$$D_t = D_i e^{-Rt} \quad (\text{Eq. 18.5})$$

where:

$D_t$  is the deficit at time  $t$

$D_i$  is the initial deficit (*i.e.*,  $\text{DO}_s - \text{DO}_i$ )

$R$  is the reaeration coefficient

Note that the larger the magnitude of  $R$ , the quicker a given deficit is removed. The value of  $R$  depends on the degree of vertical mixing in a waterbody, as well as its overall depth. It varies from 0.1 per day in small ponds to above 1 in rapidly moving streams.

Most DO problem situations require that we determine the oxygen deficit resulting from the simultaneous effects of the oxygen demand of a waste and the competing restoration of oxygen from atmospheric reaeration. The

combined result is termed the **self-purification capacity** of the waterbody. The deficit shown graphically as a function of time (or distance) is known as the **oxygen sag curve** because of its characteristic spoon shape. The equation for the curve is

$$D_t = \left[ \frac{K(\text{BOD}_L)}{R-K} \right] (e^{-Kt} - e^{-Rt}) + D_i e^{-Rt} \quad (\text{Eq. 18.6})$$

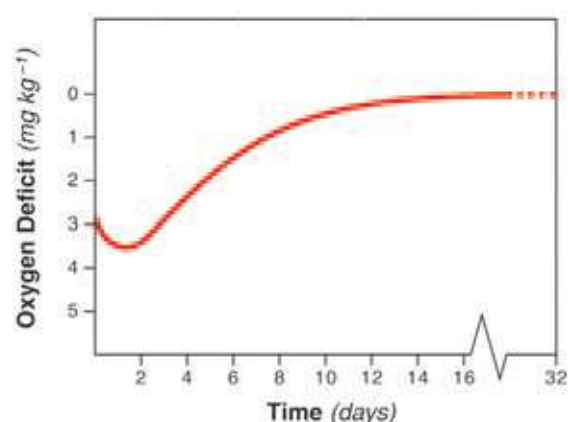
where the terms are as defined above.

An example of the curve produced by the equation is shown in Figure 18.25. The values of  $K$  and  $\text{BOD}_L$  are taken from Figure 18.24; the value for  $D_i$ , the initial deficit, was 3 mg L<sup>-1</sup> due to upstream discharges; and a reaeration coefficient  $R$  of 0.5 per day was chosen for a large, slow-flowing stream. This example might represent a case of highly treated sewage, a typical effluent plume after an initial dilution of 4, or poorly treated sewage dispersed from a diffuser that provides an initial dilution factor of 25.

One interesting result from the solution of the oxygen sag equation is that the deficit, irrespective of the saturation value of DO, is the same as long as the initial deficit is the same. Sometimes, water quality standards impose limits both on the amount of deficit *per se* and on the resulting DO value itself. For example, a regulation could require that a waste discharge must neither increase the deficit by more than 10% nor depress resulting DO concentration below 5 mg L<sup>-1</sup>.

When water systems are heavily used or highly valued water uses are threatened, additional factors require consideration:

1. The diurnal demands and supplies of oxygen from photosynthesizing organisms.
2. The oxygen demand of organic materials deposited in the sediment layer.



**Figure 18.25** Dissolved oxygen sag curve determined using values of  $\text{BOD}_L$  and  $K$  from Figure 18.24. The equation for this curve is given in Eq. 18.6. From *Pollution Science* ©1996, Academic Press, San Diego, CA.



3. The oxygen demand of nitrogen compounds discharged in the effluent.
4. Variations in the reaeration coefficient  $R$  with travel time due to flow conditions in the waterbody.
5. The wide range of sewage flows encountered over the lifetime of a river.

Comprehensive computer programs are available to describe the concentration of oxygen in large watersheds consisting of dozens of interconnecting streams and dozens of wastewater inputs; however, data on plume travel,  $K$  values, and  $R$  values still have to be obtained with time-consuming laboratory studies and physically demanding field studies. Dilution of wastes is one of the most important factors to consider in assessing impacts. The methods used to assess effects on the dissolved oxygen resource of a waterbody and bacterial contamination are applicable to a wide variety of toxic chemical problems.

## 18.12 DILUTION OF EFFLUENTS

Dilution can be—but is not necessarily—an effective way to prevent pollution of surface waters. Environmental scientists do not categorically embrace the old saw, “Dilution is the solution to pollution.” Instead, we recognize through the analytical process of risk assessment that certain principles underlie the utility of dilution in managing waste discharges. The first principle concerns the concentration dependence of the pollutant response mechanism. Here, we want to know if the effect of the contaminant is directly related to its concentration. That is, we ask if the concentration is reduced sufficiently, will the degree of effect be directly reduced?

Further, once the contaminant concentration is reduced, can it subsequently become more concentrated? Reconcentration is a phenomenon often associated with sediments and persistent organic chemicals such as PCBs. Dilution of waste streams containing high concentrations of suspended solids may prevent significant pollution near the discharge site, but such sediments may eventually settle out of the water column and concentrate in depressions in the streambed, where they can cause a variety of problems. Even in the ocean, waste disposal can lead to accumulation of sediments in the seabed. With persistent organic chemicals, whose solubility in water is low and whose affinity for sorption to animal tissues is high, adverse bioaccumulation can occur even from highly diluted mixtures. Thus, dilution may or may not solve a potential concentration-related problem.

### 18.12.1 Dilution in Streams and Rivers

Aside from concentration–toxicity considerations, social and economic considerations enter into the decision to use dilution. In addition, its use is also dependent on the avail-

ability of a sufficient quantity of dilution water. In the arid southwestern United States, for example, many streams are ephemeral; that is, they contain water only after major rainfall events. In other streams in arid climates, the effluent from municipal treatment plants is the predominant flow for more than 50% of the year; that is, they are effluent-dominated streams. In such situations, dilution is somewhere between small and nil, except during storm runoff. For example, if the stream flow is 10 million liters per day and the effluent flow is 30 million liters per day, the contaminants dissolved in the effluent will be reduced in concentration by just 25%, assuming the concentration of each contaminant upstream is zero (generally, the effective dilution will be even less than that because there is almost always some measurable concentration of contaminants upstream).

The general equation used in determining the concentration after dilution is

$$c_f = \frac{c_e v_e + c_a v_a}{v_e + v_a} \quad (\text{Eq. 18.7})$$

where:

$c_f$  = cross-sectional average final concentration in the stream

$c_e$  = concentration in the effluent

$v_e$  = volume flux of the effluent

$c_a$  = concentration in the ambient dilution water upstream

$v_a$  = volume flux of the ambient dilution water

In large rivers, the amount of dilution achieved depends on the method used to discharge the effluent into the river. To maximize the dilution, it is necessary to employ a diffuser, which consists of a pipeline with many exit orifices across the width of the river. Thus, if the river flow is 120 MLD, an effluent discharge of 30 MLD yields an 80% reduction in concentration of contaminants if the ambient concentration is zero. That is, the final concentration would be one-fifth the effluent concentration. Of course, the ambient concentration is almost always greater than zero, so Equation 18.7 must be used to estimate the final concentration accurately.

In many streams, construction of diffusers may be either inappropriate or prohibited. Consequently, the amount of dilution depends on natural mixing processes that occur during stream flow. But in large streams, the effluent plume may hug the bank for many miles, so it is not actively diluted with the main flow. In cases like this, it is not possible to estimate a range of values for the dilution rate. It is reasonable to assume that without a physical structure, like a diffuser, to mix the effluent into the river, we may consider only the natural die-off process in assessing the impact of bacterial contamination on downstream water uses. Similarly, if there is no dilution of the BOD, we can count only on the decomposition of organics and reaeration to restore or maintain the DO resource of the river.