CHAPTER 16

Responses to Stress, Toxic Chemicals, and Other Pollutants in Aquatic Ecosystems

Contents

Freshwater Ecology
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Figure 16.1 Organic pollutants burn on the Cuyahoga River in 1952. *Courtesy Cleveland State University,* The Cleveland Press *collection.*

The modern aquatic environment has suffered greatly from physical disturbance as well as organic and inorganic toxic pollution. Although scientists recognized the negative effects of pollutants in the 1950s and before, it was not until Rachel Carson's book *Silent Spring* was published in 1962 that it became common public knowledge that organic and inorganic pollutants can have strongly negative, far-reaching, and unpredictable influences on human health and ecosystems (Biography 16.1). Furthermore, acid precipitation, thermal pollution, acid mine wastes, and increases in suspended solids all cause environmental damage. More recently, scientists have developed concerns over the plastics released into the environment, the release of chemicals with endocrine activity, and nanomaterials. The relative importance of various types and causes of lake and river pollution has been determined in the United States from state reports (Fig. 16.3). These data suggest that 36% of the river and stream miles and 37% of lakes were impaired in the last decade. The US Environmental Protection Agency (1997) defines impairment as having evidence of damage to aquatic life, unsuitability for drinking, production of fish that are not safe to eat, or being unsafe for swimming. Large improvements in water quality have not occurred in the United States over the last decades; developed countries around the world had the largest improvements in the 1960s and 1970s but are subject to slow continued degradation of many aspects of water quality since then.

Pristine aquatic habitats no longer exist, except perhaps the deepest, most isolated groundwaters. The atmosphere transports pollutants throughout the world in our atmosphere (Ramade, 1989). Climate change is ubiquitous. Most major watersheds are disturbed. The question is no longer if the pollutants are present, but rather in what quantities, and what are their effects?

BIOGRAPHY 16.1 Rachel Carson

The positive influence of Rachel Carson (Fig. 16.2) may exceed that of any academic aquatic ecologist. In 1962, she published a book titled *Silent Spring* that became a best-seller and had a tremendous impact on public awareness of the pollution caused by pesticides. Her ability to take a technical subject and make it accessible to the public led to some of the first laws enacted to control the release of pesticides into the natural environment. Lear (1997) chronicles her life in an informative biography.

Figure 16.2 Rachel Carson. *Image courtesy of the National Oceanic and Atmospheric Administration.*

Carson's undergraduate studies in biology at the Pennsylvania College for Women (now Chatham College) prepared her to pursue a master's degree at Johns Hopkins University. Her research on the developmental biology of catfish eventually led to a job writing for the Bureau of Fisheries. She wrote her first book in 1941 (*Under the Sea-Wind*), followed by two critically acclaimed books and numerous popular articles that translated scientific concepts into lay terms. She then published *Silent Spring*, in which she chronicled the wanton use of pesticides and some of their effects on the environment, including biomagnification, death of wildlife (including the loss of bird life that leads to a silent spring), and potential influence on human health (toxicity and carcinogenic properties of toxic pollutants).

The completion of *Silent Spring* was a tremendous professional and personal accomplishment. While writing the book, Carson tended to her dying mother, and after her sister died, she became a single mother to her orphaned nephew. She also began the battle with breast cancer that claimed her life a few years later. Her careful attention to scientific detail was crucial because her book became the focal point of the debate over pesticide use, and she was called to testify to inform of the Senate on the issue. The exceptional popular response to her book led to strong backlash from many chemical companies, entomologists, and government officials; the detractors generally had a financial or professional stake in maintaining indiscriminant pesticide use. Carson documented her facts so well that her critics turned to personal attacks in their attempts to discredit *Silent Spring*.

The life and work of Rachel Carson prove that aquatic ecologists can make a difference in the world. She demonstrated that traditional academic and management careers are not the only ways to have a positive impact, and that combining two disparate strengths (in her case, excellent popular writing and science) can yield impressive results.

We do not know about much chemical pollution given all the chemicals released into the environment. For example, of the more than 72,000 chemicals in commercial use in the 1990s, toxicologists have only screened about 10% for toxicity and screened only 2% of the total for carcinogenicity. In the United States, federal and state governments only regulate about 0.5% of these chemicals (Miller, 1998). The drug database, drug bank, lists over 40,000 known drugs, and many of these end up in the waste stream that enters freshwaters. The Chemical Abstract Service lists over 133 million unique organic and inorganic compounds. In addition, humans create and release novel materials such as microplastics and nanomaterials into the environment with little knowledge of their effects. There are many impacts of humans on freshwaters, many of which are not well studied. For example, light pollution has substantial effects on stream-associated invertebrates (Meyer and Sullivan, 2013) as well as frogs (Hall, 2016), but this will not be covered in detail as little is known about it at this time. Here we discuss some general concepts of toxicology, causes and effects of pollution by inorganic and organic contaminants, and thermal pollution. We also cover mitigating solutions. Nutrient pollution has had a strong influence on aquatic systems; however, we will discuss this in Chapter 18.

BASIC TOXICOLOGY

Exposure to toxic substances can either come in large pulses over a short period of time (*acute*) or in low doses over a long time (*chronic*). Responses can be *lethal* or *sublethal* (not causing death) and can result from *instantaneous* or *cumulative* (a response to numerous events) reactions to exposure. Studies of toxicity require accounting for variability in responses of organisms. Thus, the *lethal dose*, the amount ingested that causes death, is labeled with a subscript that indicates the percentage of animals killed (e.g., LD_{50} is the lethal dose for 50% of the animals tested). Organisms can also be exposed to toxic substances through the water, including absorption across cell membranes, gills, and skin. Therefore, toxicologists also report lethal concentrations (e.g., LC_{50}). *Effective concentration* is the concentration that causes some effect other than death (e.g., on reproduction, growth, behavior); a subscript also denotes the percentage showing the effect (Mason, 1996).

Some toxicants have negative effects on reproduction while having little influence on the general health of the adult organism. These compounds can cause complete extinction of a population, but the effects may be difficult to demonstrate with standard laboratory tests (i.e., the LD_{50} is much higher than environmental concentrations). An example of deleterious effects on reproduction is the response of certain waterbirds to 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE), which is a

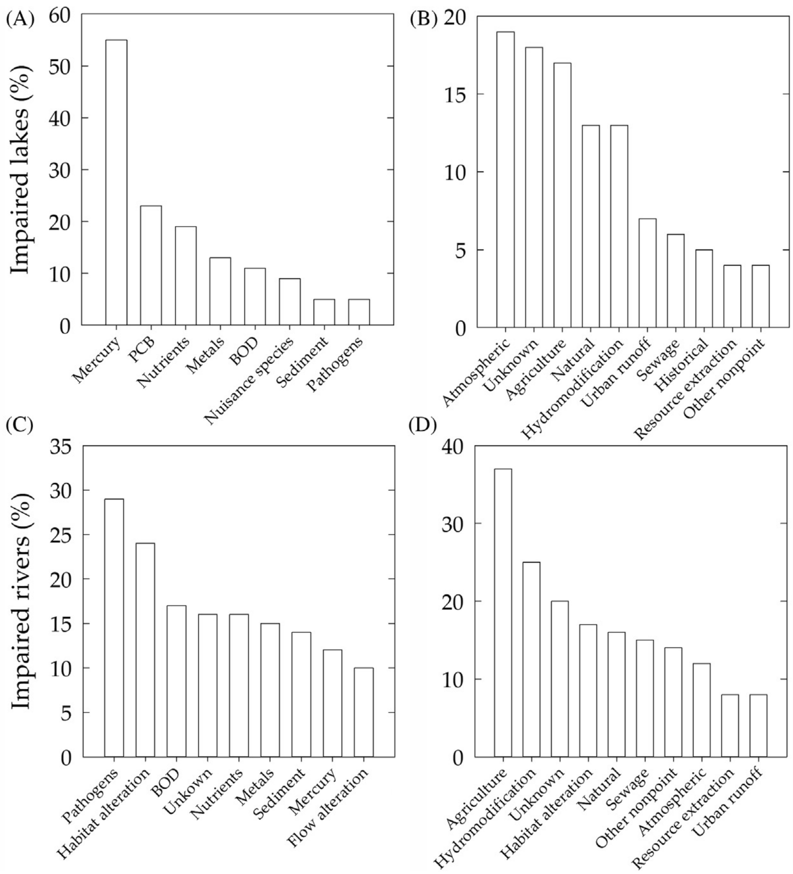

Figure 16.3 Percentages of impaired lakes (A), causes of impaired lakes (B), percentage of streams impaired (C), and causes of stream impairment (D) in the United States by type. *Data from the US Environmental Protection Agency for 2004 National Water Quality Inventory.*

metabolite of dichlorodiphenyltrichloroethane (DDT). DDE causes the birds to lay eggs with thin shells, leading to reproductive failure (Laws, 1993) and extirpation of local populations. This effect almost led to the extinction of the bald eagle; it still threatens many migratory birds, particularly in parts of the world where DDT is still used.

Some chronic effects do not occur immediately. Such delays are particularly the case with mutagenic substances in which prolonged exposure increases the chance of deleterious mutations. If these mutations lead to formation of cancerous cells, a substance is termed carcinogenic.

Several additional issues are important with regard to estimating the influence of pollutants on aquatic organisms and humans. Extrapolating effects to low concentrations of pollutants can be a problem. A threshold below which contaminants are not harmful may occur. A minimum threshold of toxicity is expected to be the case if an organism can repair a limited amount of damage caused by a toxicant, if it can be excreted up to some limited rate, or if the compound does not interact with biological molecules below some concentration. Scientists can have difficulty detecting such a threshold for toxic chemicals because the effects might be subtle, require long periods of exposure, or are sensitive to other environmental parameters. Identifying thresholds is particularly important in regulating human carcinogens in the environment. If no threshold exists, then scientists can extrapolate to very low concentrations of materials to predict the number of deaths or illnesses with exposure of a human population over many years. If there is a threshold, then exposure to levels below the threshold should not cause problems. Understanding human effects is more difficult as controlled exposure experiments are not ethically acceptable, so researchers need to use proxy organisms to study toxicity.

Low concentrations of toxicants may actually stimulate biological activity (Calabrese and Baldwin, 1999). This stimulation could be a negative stressor. The fact that stimulation or depression of biological activities can occur, and that the consequences are context dependent, further complicates regulation of a toxic substance and estimation of long-term effects. Such effects mean extensive testing of each suspected toxic substance with large sample sizes and extended exposure, while considering the life history of target organisms, is necessary before release into the environment. Nontoxic factors such as benign chemicals and temperature can alter toxicity, adding another level of complexity. Obviously, it is difficult to predict toxicity of a compound when it is a function of several other variable environmental factors. For example, zinc toxicity is greater for fishes in high temperatures and in low conductivity water (Fig. 16.4). Extrapolating laboratory results such as those from Fig. 16.4 to real world effects may yield inaccurate results; hence, a combination of field and laboratory approaches may be best for assessments of toxic substances (Blus and Henny, 1997).

It is difficult to know what the influence of two toxicants will be on one another. In some cases they may alleviate the influence of each chemical alone (*antagonism*), but in others the effects may be strictly *additive*. In the worst-case scenario, the sum of the effects is greater than simply adding the individual toxic effects (*synergistic*). Direct testing is generally necessary to establish an interactive effect. Additionally, toxic materials can alter sensitivity to other factors. For example, metal toxicity can increase susceptibility to ultraviolet radiation (Kashian et al., 2007).

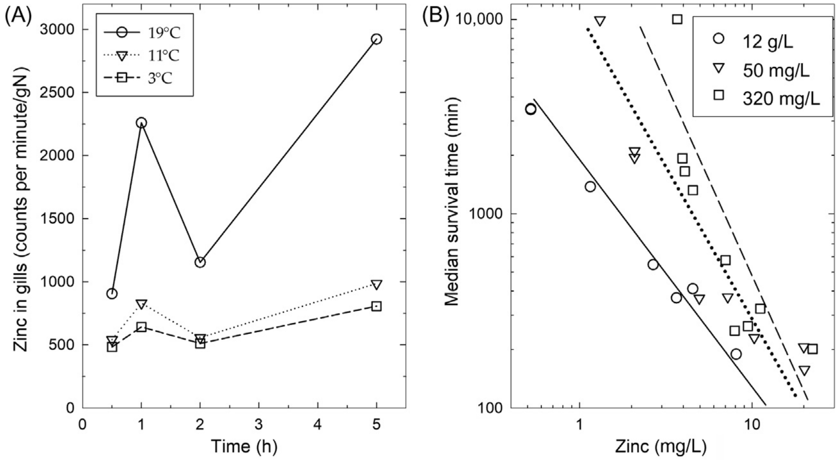

Figure 16.4 Effects of temperature on uptake of zinc into salmon gills (A) and influence of calcium carbonate (mg/L) on mortality of trout exposed to various concentrations of zinc (B). *Redrawn from Hodson (1975) and Lloyd (1960).*

Assessing and predicting the effects of any single substance in freshwater habitats is increasingly complex because pollutants rarely occur singly and may interact in antagonistic, additive, or synergistic ways with myriad other contaminants or natural environmental gradients. Aquatic species often suffer from *multiple stressors*. For example, fish and invertebrate communities inhabiting streams draining agricultural fields experience altered hydrology, degraded physical habitat structure, pesticide runoff, excess nutrients, and numerous other stressors, which may interact in an overwhelming array of ways. One study tested the interactions of increased sediments, nutrient addition, and temperature in stream mesocosms. The results were complex and not always predictable; effects of toxin interactions tended to be synergistic for populations and antagonistic for communities (Piggott et al., 2015). Toxicologists generally avoid this problem by performing laboratory studies on one or a few pollutants at a time. While this reductionist approach is necessary and critical for understanding potential toxic effects of substances, the environmental relevance of these approaches is decreasing as freshwater habitats receive increasing numbers of pollutants and other stressors. A review of 88 papers suggests that additive, synergistic, and antagonistic responses all occur in freshwater environments (Jackson et al., 2016). Somewhat comfortingly, they found that the most common response was antagonistic, indicating that there is a tendency for some stressors to cancel each other out.

Biota can concentrate toxicants. The first step in this process is *bioconcentration*, or the ability of a compound to move into an organism from the water. *Bioaccumulation* refers to the bioconcentration plus the accumulation of the compound from food. This process can lead to toxicological effects even if environmental concentrations are low. *Biomagnification* refers to the entire increase in concentration from the bottom to the top of the food web. Biomagnification is a particular concern with lipid-soluble organic contaminants and some metals. Less water-soluble organic compounds are more concentrated by organisms in laboratory studies (Fig. 16.5). However, the compounds that concentrate the most are only moderately hydrophobic and animals metabolize them slowly, as determined by inspection of 1,500 records of biomagnification (Walters et al., 2016).

Bioconcentration and bioaccumulation factors can be difficult to determine for animals and plants in their natural environment. Factors influencing uptake and retention of a contaminant (such as metabolic rate, rate of assimilation of contaminated food, heterogeneous distribution of the pollutant, and rate of excretion of the contaminant) can all depend on a variable environment. Some compounds that do not bioconcentrate in fully aquatic organisms can bioconcentrate efficiently in air-breathing organisms living in or near the aquatic environment because such compounds have volatile phases than can be transmitted in the air but are nonpolar so they dissolve poorly in water (Kelly et al., 2007). Despite the uncertainties, biomagnification is a well-documented problem and pollutants can be concentrated many millions of times, even if the range of concentrations and bioaccumulation factors is wide (Table 16.1).

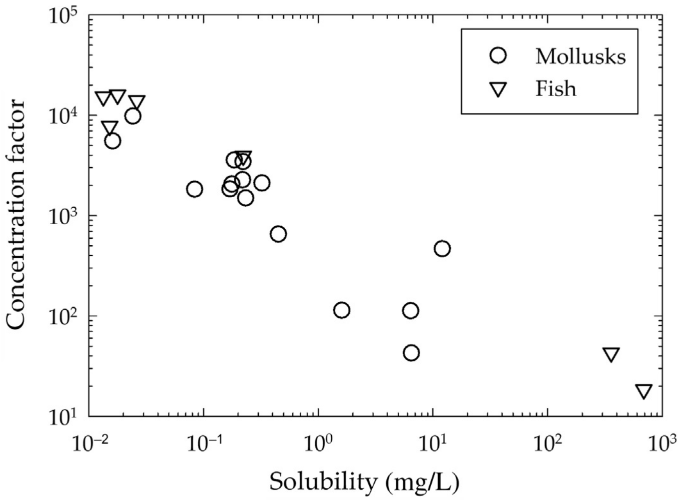

Figure 16.5 Relationships between water solubility and bioconcentration factors of various organic compounds in fishes and mollusks. *Adapted from Ernst (1980).*

Table 16.1 Range of concentrations (parts/trillion) and approximate biomagnification factors calculated for DDT and PCBs in Lake Ontario

Chemical	DDT	PCBs	DDT bioconcentration	PCB bioconcentration
Water	0.3–57	5–60	1	1
Benthic sediments	25,000–18,000	110,000–1,600,000	4,200	26,000
Suspended sediments	40,000	600,000–6,000,000	1,400	100,000
Plankton	63,000–72,000	110,000–6,100,000	2,300	94,000
Fish	620,000–7,700,000	1,378,000–7,000,000	143,000	278,000
Herring gull eggs	7,700,000–34,000,000	41,000,000–204,000,000	719,000	3,710,000

Source: Ranges from Allan (1989).

BIOASSESSMENT

Aquatic organisms, particularly invertebrates and fishes, are very useful for assessing the acute and chronic effects of pollutants because the diversity of organisms present and their characteristics correlate with the degree of pollution and environmental gradients (Loeb and Spacie, 1994). For instance, data on many stream invertebrate species (Fig. 16.6) can be used to demonstrate two possible responses to environmental extremes. This evaluation based on diversity of organisms is *bioassessment*. In the case of O_2 and pH, diversity is maximal at intermediate values (pH about neutral, O_2 about 8 mg/L). This is an example of Shelford's "Law of Tolerance" we discussed in the last chapter. In contrast, chloride and turbidity are always harmful as diversity is greatest at the smallest concentrations. These data illustrate that biodiversity can serve as an indicator of environmental conditions.

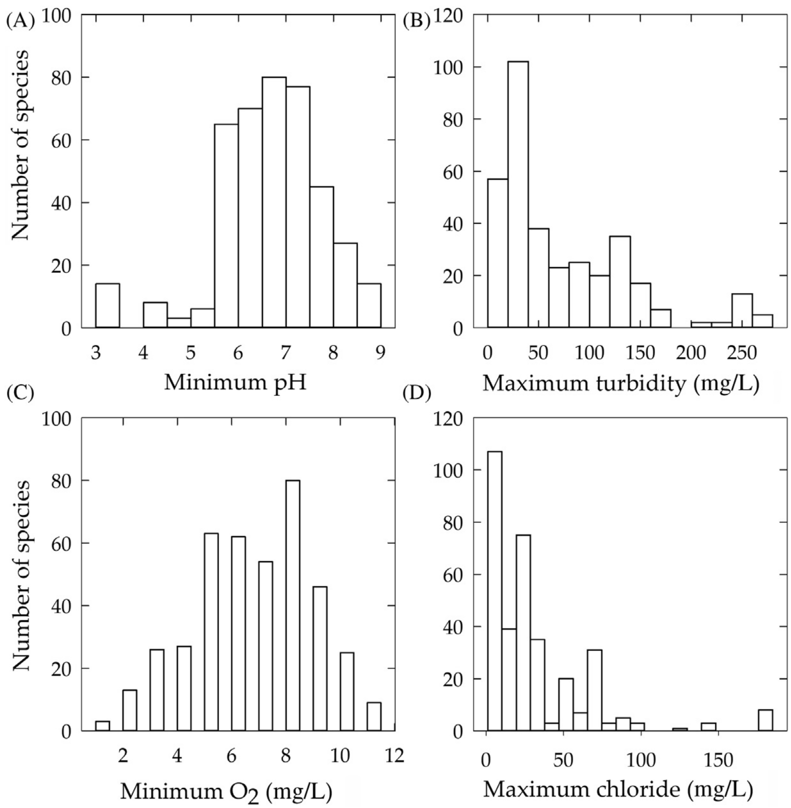

Figure 16.6 Number of invertebrate species as a function of pH (A), turbidity (B), minimum O_2 (C), and chloride (D). *Data from Roback (1974).*

Specific indices based upon more refined taxonomic characteristics are most reliable. Some species or groups are commonly found in eutrophic situations (e.g., cyanobacteria dominate eutrophic lakes, and *Tubifex* worms inhabit sewage outfalls) and others are sensitive to specific environmental factors (e.g., amphibians are susceptible to many types of pollution, and salmonid fishes are limited by water temperature and O_2 concentrations). Bioassessment methods are a common tool for resource managers monitoring water quality and overall ecosystem health. Researchers and managers have developed standard methods that use algae, plants, invertebrates, fish, and even riparian birds for use in streams, lakes, and wetlands (e.g., Karr, 1981; Danielson, 1998; Gerritsen et al., 1998; Barbour et al., 1999; Hilsenhoff, 2017).

A basic community-level indicator of stream health and water quality is the total number of insect taxa in the groups Ephemeroptera, Plecoptera, and Trichoptera (EPT). More species of EPT taxa usually inhabit cleaner waters because these groups are generally intolerant of pollution and low dissolved oxygen. The Index of Biotic Integrity provides a detailed rating for freshwaters using fishes as indicator species. It is a measure of stream quality composed of 12 indicators, including total number of fish species, pollution-tolerant species, food web structure, and fish condition (Karr, 1991). Such indices are useful for determining the suitability of habitats for supporting aquatic life and discerning chronic effects of pollutants, and become more useful when calibrated for specific regions.

Many indices include some measure of tolerance, whereby individual taxa are assigned tolerance values based on their distributions across pollution gradients (Hilsenhoff, 2017). For example, a species only found in pristine waters would be assigned a score of 0−1 (low tolerance for pollution) and a species found in highly polluted waters would be assigned a tolerance value in the range of 8−10. These values are applied to abundance and diversity data from field samples of fishes, invertebrates, or other groups to calculate an average tolerance value for the community in a habitat.

A more comprehensive approach combines several indices into multimetric indices for bioassessment. Here, individual metrics that assess diversity, community structure, and tolerance are tallied and combined into an overall rank or score of biotic integrity that is compared to other regional water bodies, historical data, or modeled predictions of biotic integrity for a given region. Habitat quality data aid in interpretation; if the physical habitat of a stream is degraded (e.g., a channelized stream with a concrete bottom and little natural habitat), poor biotic index scores might not be related to water quality *per se*.

Ecological function can also indicate the ecological health of freshwater systems, particularly litter decomposition (Gessner and Chauvet, 2002) and ecosystem metabolism (Fellows et al., 2006; Young et al., 2008). Decomposition and metabolism are functions governed by many physical and biological features and processes in a system and could relate more closely to specific ecosystem services. Most methods of biological assessment focus on elements of ecosystem structure that we refer to as biotic integrity (e.g., community composition and habitat quality). Wallace et al. (1996) studied invertebrate community and ecosystem responses to an experimental chemical removal of most invertebrates from a headwater stream. They found that both the EPT metric and North Carolina Biotic Index (based on taxa tolerance values similar to the Hilsenhoff index) tracked leaf litter decomposition and seston generation closely. As standard, efficient, and cost-effective methods are developed, future assessments of freshwater habitat health may include more functional measures along with standard structural metrics.

ORGANIC POLLUTANTS

There are millions of known organic compounds; more than 100,000 have been created and used by humans, and billions of years of evolution have led to many more. Humans synthesize at least several hundred new chemicals each year. The large number of compounds makes regulation difficult. Modern society has a consistent record of releasing toxic organic compounds into the environment, only to determine afterwards that they have negative effects on ecosystem and human health. We know almost nothing about how complex mixtures of these compounds at low concentrations will influence human health (Schwarzenbach et al., 2006). The effects of unregulated release of pollutants into a large ecosystem are exemplified by the experiences in the Great Lakes of North America. Problems associated with pollution of these lakes peaked in the 1960s, and the slogan "Lake Erie is dying" served as a rallying point for concerned citizens (Highlight 16.1). Fortunately, our society has mitigated the problems to some degree, though organic contaminants linger in the system and eutrophication and species introductions remain as problems.

The use of organic compounds in agriculture is widespread (Nowell et al., 1999). Worldwide, about 2.3 million metric tons of pesticides are used yearly, and in the United States about 630 different active compounds are employed. Corn, cotton, wheat, and soybean crop management accounts for about 70% of the insecticide use and 80% of the herbicide use in the United States. About 25% of the pesticide use occurs in urban settings, such as on lawns and golf courses (Miller, 1998). Use of pesticides by individuals in suburban areas is generally unregulated beyond recommendations on product packages, which can lead to overuse. The amounts of pesticides found in the waters of the United States have not decreased since the 1990s, and the

Highlight 16.1 "Lake Erie Is Dying"

Until the 1960s, most municipalities and industries surrounding the lake dumped sewage and other wastes into Lake Erie or rivers feeding it without treatment. The lake seemed so large as to be unaffected by such releases. As the population grew, the problems associated with the releases, such as organic chemical contamination, pathogenic bacteria, and eutrophication, worsened. Such problems led to public pressure to clean up the lake (hence the slogan "Lake Erie is dying") and confrontation between citizens, state and federal government officials, and entities causing the pollution (Kehoe, 1997).

Total loads of phosphorus increased fivefold from 1900 to 1970, leading to eutrophication problems. In this sense, the lake was not dying but actually becoming more productive as the phosphorus and nitrogen inputs stimulated algae. This stimulation of algae led to undesirable accumulations of the benthic filamentous green alga *Cladophora* that fouled beaches (Burns, 1985). Some areas of the lake became anoxic and taste and odor problems developed because of algal blooms.

Loading of mercury, lead, cadmium, copper, and zinc increased greatly, with sediment contents 12.4, 4.4, 3.6, 2.5, and 3 times greater, respectively, than in presettlement times (Burns, 1985). Mercury contents of fishes became so high that they were not healthy for human consumption. Inputs of toxic metals from industry have decreased in the past few decades, but contaminated sediments continue to cause problems.

The Great Lakes Water Quality Agreement of 1978 listed 22 hazardous or potentially hazardous organic compounds that were polluting the lake. Of these, polychlorinated biphenyls (PCBs), DDT, and dieldrin caused the greatest concern. DDT use was restricted in 1970, and the concentrations in the smelt taken from the lake decreased from 1.59 to 0.04 μg/g between 1967 and the late 1970s. Low levels of DDT contamination continue because DDT is sequestered in the sediments and slowly reenters the food webs. Manufacture and use of PCBs has been illegal in the United States since 1976; in 1978, PCBs were entering Lake Erie at about 0.9 metric tons/year, with the majority coming from atmospheric deposition. A decade later, fishes in Lake Erie had enough PCB content that consumption of more than 5 kg of fish per year was unsafe (Burns, 1985). The invasive zebra mussels now bioconcentrate PCBs and pass them on to the waterfowl that consume them (Mazak et al., 1997).

Human activities did not kill Lake Erie, but severe damage was done and it still has problems. Runoff from agriculture continues to cause eutrophication problems leading to large toxic blooms. In 2014, a toxic bloom forced people in Toledo Ohio to use bottled water out of concerns about toxic substances in their drinking water. Such blooms continue to plague the lake. The system is a good example of how multiple human impacts on a lake can decrease the value for recreation, fisheries, and drinking water. With careful stewardship, the water quality in the lake will improve, but slowly.

amounts found in urban streams have increased substantially since that time (Stone et al., 2014). A survey of 38 streams across the United States in 2014 found pesticides were the most common contaminant (Bradley et al., 2017). Annual costs estimated over 20 years ago associated with the use of pesticides include \$1.8 billion for cleaning groundwater, \$24 million in fishery losses, and \$2.1 billion in losses of terrestrial and aquatic birds (Pimentel et al., 1992). There is no reason to think these costs have decreased since this time, though we are aware of no more recent estimates.

Pesticides have clear negative effects on stream animals. Effects may extend to microbial communities (DeLorenzo et al., 2001). Stream invertebrate larvae can bioconcentrate pesticides, and adults move the contaminants to riparian areas after they emerge. The riparian predators, such as spiders, ingest the toxic substances (Walters et al., 2008; Laws et al., 2016), and insectivores eat the contaminated animals. A broad survey of pesticide effects on stream invertebrates across Australia and Europe indicated widespread impacts on diversity. The authors detected significant decreases of diversity even when pesticide concentrations were within the regulatory allowed limit (Beketov et al., 2013).

There is an increasing array of chemical types used as pesticides. In particular, widespread use of organophosphates, carbamates, pyrethrins, and organochlorines, which are all neurotoxins used to control a variety of pest species. These contaminate many freshwater habitats and species, even in relatively undisturbed regions. Agricultural insecticides are found in freshwaters globally, are rarely monitored, and when they are monitored, concentrations exceeding regulatory limits are common (Stehle and Schulz, 2015). Amphibian population declines in the Sierra Nevada Mountains correlate to the pesticides used in the agricultural Central Valley of California. Wind and precipitation transport pesticides used in the valley into freshwater habitats in the mountains (Sparling and Fellers, 2009).

Eliminating use of pesticides in the near future is unrealistic, and so careful regulation of their use and disposal is critical. Despite their negative consequences for freshwaters, pesticides and herbicides have had tremendous positive effects on humanity. Increased agricultural production to feed the world's human population is possible, in part, because of these compounds. Pesticides also aid in control of a variety of insect vectors of important diseases. Control of *Anopheles* mosquitoes has led to eradication of malaria in many parts of the world. Pesticides used on aquatic snails have been effective at controlling river blindness, with only moderate effects on non-target aquatic species (Resh et al., 2004).

Although biomagnification of toxic organic compounds is a serious problem, compounds that do not biomagnify as readily can still be of concern. Atrazine is a commonly used chemical for control of weeds in croplands in the United States and elsewhere. It is fairly water soluble (Nowell et al., 1999), persists 6−9 months, and bioconcentrates much less than many other pesticides do, although bivalves used in a laboratory study did bioaccumulate atrazine (Jacomini et al., 2006). The chemical properties of atrazine lead to efficient transfer through the environment (Pang and Close, 1999). Atrazine has seen widespread use in the Midwestern United States, with 32 million kg applied annually, with less use in the European Union where it was banned in 2004. Unfortunately, it is carcinogenic and harms aquatic life (particularly photosynthetic organisms) at levels of 2 μg/L (Carder and Hoagland, 1998). If agricultural producers discontinue the use of atrazine, they may use worse compounds (Vighi and Zanin, 1994). Given its persistence and water solubility, better management practices are necessary to keep atrazine from entering the surface waters in many agricultural regions.

The glyphosate herbicide (N-(phosphonomethyl)glycine), Roundup, has seen significant use, and has been the number one selling herbicide in the world since 1980. The use of this herbicide has increased because biotechnologists genetically modified crops to be resistant to the chemical (Roundup-ready). Commercially produced Roundup also contains a surfactant that is toxic to wildlife in addition to the glyphosate. Roundup is toxic to many aquatic wildlife species, and is particularly toxic to amphibians (Relyea, 2005).

Genetically-modified crops have also been engineered to produce toxins to deter herbivores. A particularly widespread crop with a genetic modification is Bt modified maize (corn). Bt corn is a variant of maize that has been genetically altered to express proteins from the bacterium *Bacillus thuringiensis*. These proteins are toxic to pests such as the European corn borer, which can cause serious damage to crops. The potential negative effects of these modified crops on aquatic organisms that come in contact with the pollen and residues are well established and have generated a substantial amount of controversy (Highlight 16.2).

Some of the toxic organic compounds found in aquatic systems readily move through the atmosphere. Volatile persistent organochlorine compounds occur worldwide (Simonich and Hites, 1995). The compounds condense from the atmosphere depending on temperature, with the most volatile organics condensing in the polar regions (Wania and Mackay, 1993) or at higher elevations. Atmospheric transport, in combination with biomagnification over a long food chain, can account for the unusually high concentrations of the toxic organic compound toxaphene in fish collected from a remote subarctic lake (Kidd et al., 1995). One would assume this lake is a pristine habitat because it is far from civilization. The fact that a toxic organic compound contaminates fishes in the lake illustrates the pervasive impacts of humans on aquatic environments.

Highlight 16.2 Transgenic crops and freshwater habitats

Considerable controversy has occurred regarding transgenic crops and potential adverse effects on the environment and human health. Although humans have been genetically modifying plants and animals for agriculture and other purposes through selective breeding for centuries, we now have the technology to make changes that are more radical over shorter periods, including transfer of genes across broad taxonomic lines.

Corn has been genetically modified to express crystalline protein toxins initially derived from the genes in the bacterium *Bacillus thuringiensis* (*Bt*). The proteins expressed by transgenic *Bt* corn plants are endotoxins, which are toxic to many common agricultural pests because they bind to receptors in the gut and cause lethal septicemia. These genetically engineered crops have been at the center of controversy for decades.

The bacterium *Bacillus thuringiensis* and its associated endotoxins have been used since the 1930s in the form of dried spores and crystal toxins to control agricultural pests. Its use increased in the 1980s as resistance to synthetic insecticides increased among agricultural pests. Ironically, *Bt* was developed primarily through organic farming because it is naturally occurring and different forms of the toxin affect specific insects, mostly those related to the Lepidoptera. It was not until *Bt* endotoxin genes were integrated into plant genomes to create genetically modified *Bt* corn and other crops that controversy began. Genetically modified *Bt* crops generally express the endotoxins in all plant tissues and can be used to control pests ranging from the European corn borer to corn rootworm, depending on variety.

In the late 1990s, a study by a group of scientists at Cornell University sparked heated debate over the potential adverse environmental effects of *Bt* crops. Losey et al. (1999) found that monarch butterfly larvae that consumed milkweed leaves with *Bt* corn pollen on them had much higher rates of mortality and lower growth than those fed milkweed leaves with non- *Bt* corn pollen. This study was highly publicized and subsequently heavily criticized for being somewhat preliminary and unrealistic in terms of the amounts of pollen to which the caterpillars were exposed. Debate over potential environmental impacts has continued since, with some subsequent studies showing adverse effects, and others showing no effects.

In 2007, a group of researchers at Midwestern universities began looking at whether *Bt* crops could influence food webs and ecosystem processes in streams draining Midwestern agricultural fields with ever increasing proportions of *Bt* crops. *Bt* corn represented over 75% of the corn planted in the US in 2017. Rosi-Marshall et al. (2007) examined detritus and pollen from *Bt* corn with toxins that target the European corn borer (Lepidoptera). The endotoxin protein is detectable in crop detritus from crop fields for at least 240 days (Zwahlen et al., 2003), and some of this material makes its way into streams via wind and water movements (Griffiths et al., 2017). Rosi-Marshall et al. (2007) and Chambers et al. (2010) found that significant amounts of crop residues, including corn leaf detritus and pollen, entered streams bordering agricultural fields. They also found that these materials still had active *Bt* endotoxins in them, the toxins could be transported significant distances downstream, and that caddisfly larvae, which are closely related to the target lepidopteran pest, were adversely affected in laboratory feeding studies using pollen and leaf material. Some of these studies were criticized for being preliminary and the authors were criticized for overstating the results. However, much of this criticism came from individuals whose research was funded by the industry producing and marketing *Bt* crops.

A recent study found that *Bt* toxins were widely detected in agricultural streams in the Midwestern US, but that the toxins degraded rapidly. However, despite its rapid degradation, the toxin was commonly found in stream water because of chronic inputs from crop fields. As such, Griffiths et al. (2017) considered *Bt* toxins *pseudo-persistent* in the environment, a term applied to chemicals with short have lives but chronic inputs.

Bioassays using *Daphia magna* showed toxic effects at far lower concentrations than expected (de Souza Machado et al., 2017). However, the possible effects of *Bt* toxins in aquatic ecosystems remain controversial and relatively poorly studied. *Bacillus thuringiensis* var. *israelensis* (B.t.i.) has been used to control black fly larvae in streams for years and studies indicate few effects on non-target aquatic insects (Jackson et al., 1994). The USEPA has asserted that not enough *Bt* toxin could enter the water to cause harmful effects on aquatic invertebrates (USEPA, 2005), but results of Rosi-Marshall et al. (2007) seem to contradict this. Further, the USEPA's stance that there should be no adverse affects in freshwater habitats is primarily based on 48-hour toxicity tests on *Daphnia* performed by scientists employed by the company developing *Bt* crops.

As research on possible negative impacts of *Bt* crops on freshwater habitats progresses, the costs and benefits need careful consideration. Recent field examinations of invertebrate communities from streams draining *Bt* and non-*Bt* corn fields showed no patterns; agricultural streams and the communities that inhabit them are subjected to myriad stressors including nutrients, sediments, hydrologic alterations, and channelization, and thus Bt toxins may be relatively inconsequential (Chambers et al., 2010). Further, a comprehensive assessment of the environmental impacts of transgenic *Bt* crops should consider the environmental and economic consequences of the alternatives, ranging from traditional pesticide applications to yield reductions that would occur with no pesticide use.

Petroleum products are another common source of aquatic contamination in many parts of the world. Urban runoff is a significant source of oil contamination, with about 1 g per person per day (Laws, 1993). Multiplying this by the U.S. urban population of 200 million yields 7.3×10^{10} g (about 14 million gallons) of oil entering aquatic habitats per year. Urban runoff is now treated in some developed countries, so this source of contamination is decreasing in these areas. In countries with increasing automobile use, the source is increasing. An unknown portion of the oil that enters freshwaters is consumed by microbes or flows to the ocean; the absolute damage to freshwater aquatic habitats is unclear. Another common source of contamination is leakage from underground gasoline storage tanks into groundwater. Cleaning spills from such leaks has cost billions of dollars. In addition, there are numerous pipelines used to transport oil across land and freshwater. These pipelines inevitably leak, particularly as they get older and can cause substantial environmental and economic damage, particularly if they enter freshwaters. These incidents are happening worldwide from the tropics to the Arctic (Jernelöv, 2010).

Hydraulic fracturing (Highlight 4.2) for oil recovery can cause release of organic compounds if the fluids used to pressurize the oil formations are released into the environment (He et al., 2017) or with leakage of the petroleum products that are being extracted (Vengosh et al., 2014). It is difficult to study release of the industrial fluids because many of the companies do not disclose what chemicals they use. One study demonstrated lethal and sub-lethal effects of the fluids on *Daphnia magna* (Blewett et al., 2017). Trout bioaccumulated organic compounds from fracturing fluids (He et al., 2017).

Oil and gas also leak into aquatic ecosystems from outboard engines used on watercraft. Visible slicks of oil and gas are common around busy marinas. Engine exhaust also pollutes water. Two-stroke engines release more pollution than four-stroke engines. The organic compounds in the exhaust of both engine types can kill zooplankton and bacteria. A 15-kW (20-hp), two-stroke engine that operates for 1 hour makes 11,000 m^3 of water undrinkable by causing bad taste and odor. Expensive treatment is required to reverse these effects (Jüttner et al., 1995).

Chlorinated hydrocarbons such as polychlorinated biphenyls (PCBs) are of concern in aquatic systems because of their persistence in the environment and their toxicity. Production of PCBs, which were used in a variety of industrial applications as coolants, lubricants, and liquid insulators, was banned for most purposes in the United States in 1979. However, PCB residues persist in sediments of freshwater habitats and organisms, particularly near urban areas. Analyses of biological samples in 2009 from across the United States indicated that PCBs were the most abundant, occurring in 93% of the samples (Batt et al., 2017). Before regulations banned their use, large-scale production and industrial use of PCBs resulted in severe pollution of some water bodies. The Hudson River in New York had significant PCB contamination, and citizens and local governments are now paying a high price because of closure of commercial and recreational fishing, and massive ongoing cleanup operations. Many regions of the world have shut down fishing and issued fish consumption warnings because of the presence of PCBs in fish tissues. Because they bioaccumulate readily, PCBs make their way into riparian predators such as birds, spiders, and amphibians, which feed on insects emerging from contaminated water bodies (Maul et al., 2006; Walters et al., 2008).

Additionally, many municipal sewage plants used to treat their final effluent with chlorine to kill pathogens. The chlorine reacts with dissolved organic materials and forms chlorinated hydrocarbons. These compounds are known carcinogens and toxins. Many municipalities are switching to ultraviolet radiation treatment schemes instead.

A common way to clean up spills of organic materials in the environment is *bioremediation* (Anderson and Lovley, 1997). Bioremediation uses organisms that can break down or inactivate pollutants. In some cases, people add organisms to do the job, and in other cases, native bacteria have the ability to degrade the organic pollutant. Some bacteria can metabolize novel organic compounds, an adaptation that arises because evolution favors microbes able to use unique carbon. Evolutionarily, this would have mostly been metabolites synthesized by other microorganisms. The number of individual bacteria is high, and their generation times are short. The probability that an individual microbe will have a mutation that allows use of a unique source of organic carbon is low. However, the probability that one of the millions of bacteria found in each mL of water will have a beneficial mutation that helps metabolize the compound is substantial. These features of bacteria lead to the rapid establishment of new genotypes capable of using pollutants.

Bioremediation is probably most important in cases of contaminated groundwater because spills of any size are extremely difficult to remove from underground, particularly if the compounds are not water-soluble and are associated with sediments. Several strategies for bioremediation exist, including pumping the water and treating it at the surface, using plants that bioconcentrate the compound taken into their roots, addition of engineered microbes to the aquifer to consume the pollutants, and use of *in situ* microbial activity to eradicate pollution. In most cases, workers release surfactants (compounds that decrease the ability of organic compounds to associate with solid surfaces) to dissociate the compounds from the sediments. They also commonly add nutrients and dissolved oxygen to groundwaters to stimulate microbial activity. An understanding of the ecology of groundwaters is useful in optimizing rates of bioremediation. For example, protozoan populations can decrease rates of bioremediation by consuming bacteria that would break down the pollutants (Kota et al., 1999).

The ability to metabolize or inactivate toxic substances is often coded upon plasmids (small circular pieces of DNA that are free in the cytoplasm), which can move within and among microbial species and allow transfer of genetic information. This lateral transfer is of concern in relation to genetically engineered microbes but also may be helpful in bioremediation efforts. In many cases, bacteria capable of metabolizing an organic compound disappear quickly upon release into a contaminated site, but the indigenous bacteria acquire the plasmid that codes for proteins that can degrade the pollutant. Movement of plasmids among natural populations of bacteria is well established.

We use so many organic chemicals that it is difficult to predict what their effects will be and where they will occur. For example, flame-retardants are commonly used on clothing and household materials. When researchers studied the Columbia River, they found 21 different flame retardant chemicals in the water (Schreder et al., 2014). How these compounds will affect the biota of the river is unknown, particularly given how many of them we release. A study of pesticide and personal care contaminants in Spain indicated complex interactive effects on structure of the periphyton community (Ponsatí et al., 2016).

Pharmaceuticals, personal care products, and endocrine disruptors

Humans produce and use numerous chemicals in their daily lives that have biological activity, and many of these eventually end up in freshwater habitats. Humans use at least 80,000 organic chemicals (Pimentel, 1996) and there is increasing concern over the widespread occurrence and potential environmental effects of these emerging contaminants in freshwater habitats (Ternes, 1998; Kolpin et al., 2002). These substances wash directly into the environment during storms when wastewater systems are overwhelmed, pass through sewage treatment plants, and run off from farms where livestock are treated with antibiotics and other drugs. A global analysis of the literature suggests that antibiotics, painkillers, antidepressants, blood lipid regulators, and other cardiovascular drugs are the most commonly found pharmaceuticals (Hughes et al., 2012). Significant amounts of antibiotics, hormones, disinfectants, fragrances, caffeine, and other substances are excreted or dumped by humans, and then enter wastewater treatment facilities that are not designed to remove them (Daughton and Ternes, 1999).

Researchers also routinely detect illicit drugs in wastewater (Petrie et al., 2015). For example, Lee et al. (2016) found amphetamines at stream sites near Baltimore, MD. They also documented that amphetamines in streams alter bacterial and diatom communities and negatively influence invertebrates.

The average residence time for a given compound in a wastewater treatment facility ranges from less than 1 hour to a few days, which is shorter than the degradation half-lives of many of them (Halling-Sørenson et al., 1998; Xia et al., 2005). Even natural estrogens, which are easy for organisms to degrade, can pass through sewage treatment plants (Liu et al., 2016). In addition to the known compounds, pharmaceuticals break down in the environment due to biological activity or abiotic factors such as UV light; there are few studies on the compounds formed as the pharmaceuticals decompose (Petrie et al., 2015). Aymerich et al. (2016) studied attenuation of 8 pharmaceuticals and 11 transformation products in wastewater plants and their receiving waters. They found only 5 of the 19 compounds were reduced to below 10% of their original concentrations.

A survey of US surface waters found numerous pharmaceuticals and personal care products, including hormones, caffeine, antacids, and painkillers at detectable levels (Barnes et al., 2002; Buxton and Kolpin, 2002; Kolpin et al., 2002). While some of the increased attention to these substances has likely resulted from improved analytical procedures for detecting their presence, there are likely ecological and human health consequences, particularly in urban streams where sewage effluent can dominate discharge.

Most measured concentrations of pharmaceuticals and related contaminants are relatively low (e.g., less than 1 part/billion). The products can bioconcentrate; Arnnok et al. (2017) found pharmaceutical concentrations up to 3,000 times greater than background in Great Lakes fishes. However, different products vary greatly in their observed bioaccumulation (Chen et al., 2017). They found antidepressants and their metabolic byproducts at the greatest concentrations in the brains of the fishes. Bioaccumulation of pharmaceuticals also occurred in fishes from a stream in Czechoslovakia (Grabicova et al., 2017).

Chronic exposure to low concentrations may result in sublethal effects including changes in behavior, growth, or reproductive capacity (De Lange et al., 2006). Richmond et al. (2016) exposed stream organisms to low concentrations of antidepressant drugs. They found that the drugs suppressed primary production by 29% and eplilithic respiration also decreased. Additionally, the chemical exposure altered development of dipteran midge larvae.

Some of these compounds could persist in the environment for many years; a Swedish study documented that the antianxiety/insomnia drug oxazepam persisted in lake sediments in active form for 40 years (Klaminder et al., 2015). Science knows little about the potential ecosystem-level effects of these compounds (Rosi-Marshall and Royer, 2012).

While many consequences of pharmaceuticals and other emerging contaminants in freshwaters are not well established, there is evidence that organism assimilate them and the compounds can have deleterious effects (Kinney et al., 2008; Vajda et al., 2008). Some emerging contaminants are *endocrine-disrupting compounds* in that they act as biological signals. The presence of endocrine disruptors in the environment is of great concern, as these substances can seriously influence the development and reproduction of organisms (Highlight 16.3).

The presence of antibiotics in freshwater is a concern because of their potential role in development of antibiotic resistant bacteria, particularly pathogenic forms, and possible negative impacts on microbially mediated ecological processes (Halling-Sorensen et al., 1998; Maul et al., 2006). Researchers have detected numerous antibiotics in streams receiving sewage effluent and those located below confined animal operations such as cattle feedlots. Intensive farming with manure additions leads to widespread occurrence of antibiotic resistant bacteria in New Zeland (Winkworth-Lawrence and Lange, 2016). Bacteria resistant to multiple antibiotics are now common in aquatic environments (Leff et al., 1993; McKeon et al., 1995). Bacteria resistant to human-synthesized antibiotics have been isolated from many rivers and billabongs in remote rural areas of Australia (Boon, 1992); both are regions with low human densities.

Highlight 16.3 Ecoestrogens: compounds that mimic natural hormone activities

Numerous organic compounds can mimic natural metabolic compounds, leading to endocrine disruption (Sonnenschein and Soto, 1997; Stahlschmidt-Allner et al., 1997). An example of this form of pollution is the release of compounds that mimic estrogen (variously called oestrogens, ecoestrogens, or environmental estrogens). These compounds include pesticides and even ingredients in sunscreens (Schlumpf et al., 2001; Klann et al., 2005).

Exposure to the pesticide DDT correlates positively to nonfunctional testes in male alligators, and other reports of feminized wildlife have begun to surface. In this case, DDT behaves like estrogen; this adds a new dimension to the documented effects of organic compounds intentionally released into the environment (McLachlan and Arnold, 1996). Endocrine-disrupting compounds influence reproduction of fishes, birds, mollusks, mammals (Colborn et al., 1993), and reptiles (Crain et al., 1998). Other possible cases of influence of environmental estrogens include male fishes in polluted waters that produce abnormal amounts of the egg yolk protein normally produced by female fishes and sex reversals of turtles when exposed to estrogenic chemicals. Ecoestrogens can bioaccumulate and be passed to offspring (Crews et al., 2000).

Water samples from 34 of the 35 steam sites sampled across the United States reacted with estrogen receptors in laboratory assays (Conley et al., 2017). An examination from 1995 to 2004 of fishes in 111 US water bodies by the US Geological Survey found that 33% of smallmouth bass and 18% of largemouth bass were intersex, in that they had both male and female reproductive structures (Hinck et al., 2009). While the exact cause for the intersex condition of so many fishes has yet to be determined, estrogens from human birth control pills and other sources are the most likely cause because rates were highest in densely populated regions and examinations of museum specimens collected decades ago show no intersex individuals. However, naturally occurring materials (oak leaves) and salt pollution can alter sex ratios of tadpoles (Lambert et al., 2016), so determining exact causes of these changes in the environment can be challenging. On the positive side, the number of intersex fishes decreased downstream of a sewage treatment plant that had been upgraded to improve efficiency (Hicks et al., 2017).

Some researchers attribute the highly controversial reports of reduced human sperm counts to environmental chemicals, and others report no effects. Meta-analysis is inconclusive on the effects of ecoestrogens on human sperm counts and more research is needed before conclusive results are available (Perry, 2008). Endocrine-disrupting compounds have also been linked to formation of human cancers (Gillesby and Zacharewski, 1998). Apparently, combinations of organic chemicals can also activate the estrogen receptor (Arnold et al., 1996). Such inadvertent biological signaling may have far-reaching and unpredictable effects in aquatic habitats. Fortunately, standard water purification techniques can remove ecoestrogens (Fawell et al., 2001). Regardless of the strength of an individual claim, the topic of ecoestrogens illustrates that wholesale release of organic contaminants into the environment can have unintended effects.

A study found significantly higher numbers of tetracycline-resistant bacterial gene types in water from wastewater treatment plants as compared to nearby lakes (Auerbach et al., 2007), indicating that human antibiotic use can stimulate the prevalence of antibiotic resistance. Antibiotic resistance genes were associated with both human sewage and animal feeding operations in a large study on the Platte River (Pruden et al., 2012). Antibiotics are used as a routine addition to livestock feed in the United States because they increase growth in healthy animals. In 2006, the European Union banned the feeding of all antibiotics and related drugs to livestock for growth promotion (but allowed them to treat sick animals). Increasing reliance on aquaculture for fish production around the world is further contributing to the problem; fish farms can use large quantities of antibiotics and other drugs, and aquaculturists apply them directly to water. The escalating prevalence of antibiotics or microbes exposed to antibiotics (e.g., animal feedlot runoff) that enter freshwater environments increases the probability that microbes that cause human disease will possess plasmids coding for resistance to antibiotics used to treat those diseases. This is because harmless bacteria in the environment can develop and transmit these plasmids into disease-causing bacteria. Furthermore, viruses that attack bacteria can transmit the genes for antibiotic resistance, moving resistance from benign bacteria into disease-causing bacteria (Calero-Cáceres and Muniesa, 2016).

Plastics

Plastics are very resistant to microbial degradation, and can occur in the environment as large pieces ($>$5 mm, macroplastics), as microparticles of plastics (1 μm−5 mm, *microplastics*), or as even smaller sub μm particles (*nanoplastics*). Smaller pieces form when larger pieces break down or as additives to commercial products (exfoliants in personal care products, cleaning products, and for industrial cleaning processes). Exposure to UV or high temperatures makes plastic more fragile and more likely to break down. An additional source of microplastics is microfibers, which are released from synthetic clothing when it is washed and dried, with most released during drying (Pirc et al., 2016). Most plastic is disposed of on land, but some moves out of the terrestrial system into freshwaters or is directly deposited there. Commonly used plastics, such as polystyrene or polyethylene are highly resistant to biodegradation and Horton et al. (2017) claimed that essentially all the plastic produced by humans is still in the environment in one form or another. There have been calls for bans on using microbeads in personal care products and elsewhere (Rochman et al., 2015). The United States banned them in 2017, and a few other countries worldwide have as well. Bans on plastic bags are also becoming more common.

Research on microplastics is most advanced in marine systems (e.g., Green et al., 2017), but microplastics are common in freshwater environments (Eerkes-Medrano et al., 2015; Horton et al., 2017). Microplastics in rivers are most common near urban environments. Levels are variable in the water column but concentrations in freshwater sediments are similar to those found in marine sediments. Microplastics pass through animal guts, but there is some evidence they can cross the gut out of the digestive tract into the animal. Studies on copepods revealed that nanoplastics were more lethal than microplastics. In freshwaters, aged nanostyrene plastics were more toxic to *Daphnia* than were unaged particles. Terrestrial earthworm studies have also revealed negative effects, suggesting that aquatic oligochaetes could have similar responses (Horton et al., 2017). There are pigments associated with microplastics, so they are optically active along with paint chips that enter freshwaters (Imhof et al., 2016). These pigments could alter the optical properties of lakes, leading them to appear less clear and potentially intercepting light that would fuel primary production.

Microplastics also serve as habitat for microbial organisms. McCormick et al. (2014) studied a highly urbanized river in Chicago and found very high concentrations of microplastics originating in sewage treatment plants. High-throughput sequencing indicated microbial communities associated with the microplastics were less diverse and distinct from other habitats within the river. They also found evidence for plastic-degrading microbes and pathogens. Hoellein et al. (2017) studied microplastics downstream from a sewage input. They found the bacterial communities associated with microplastics became more similar to those associated with natural particles in the river when sampled further from the sewage input. Microplastics can also alter the growth rate and community composition of microbial primary producers (Yokota et al., 2017).

Microplastics can be sources or transporters of pollutants. Many of the chemicals used to create plastics (plasticizers) are toxic. These chemicals leak into the environment from the plastics as they break down or are exposed to environmental factors. Microplastics bind hydrophobic compounds, and can concentrate pollutants such as PCBs, dioxin, and heavy metals. If animals, including people, ingest these plastics there is risk of exposure to toxic compounds (Horton et al., 2017). However, one review suggests that biomagnification from eating other organisms is still more important than exposure from ingested plastic particles with bound harmful organic compounds (Koelmans et al., 2016).

ACID PRECIPITATION

Contamination by acid precipitation has had enormous environmental and economic impacts on aquatic systems. Loss of fisheries and concomitant loss of many tourist dollars are common in affected areas. Here, we discuss sources of acid, distribution of the problem, biological effects, and potential solutions to problems associated with acid precipitation. There are additional sources of acid contamination that are not specifically covered, such as mine drainage (Gray, 1998) and natural acidic systems, but the generalities of the following discussion apply to pH effects regardless of source.

A recent study demonstrated some surprising, long-term impacts of chronic acidification on streams. Somewhat contradictory to what one might predict, long-term effects of acidification are actually increasing stream water alkalinity. Kaushal et al. (2013) examined long-term water chemistry patterns in 97 rivers in the eastern United States and found that 62 of them showed significant increases in alkalinity. These increases in alkalinity are a result of the long term accelerated weathering of bedrock in watersheds from acidic rain water, and the trend has been referred to as "rivers on Rolaids" by the researchers who documented the pattern. The ultimate ecological impacts of these changes in stream water chemistry are not completely understood, but the increased alkalinity stimulates growth of some algae and bacteria, and this increased production can lead to decreased dissolved oxygen levels. When ammonia is present in the water, such as near confined animal operations and sewage outflows, the increased alkalinity also drives conversion of ammonia to ammonium, which is less toxic to animals. Although acid rain has decreased since the Clean Air Act, precipitation in many regions still remains acid enough to continue the weathering and increasing alkalinity.

Sources and geography of acid precipitation

Acid precipitation has far-reaching effects on aquatic ecosystems. It is primarily associated with industrial activity and vehicle use that combust hydrocarbons. Acid rain has acidified lakes and streams in all industrialized regions of the world. The US Environmental Protection Agency surveyed more than 1,000 lakes and 211,000 km of streams during the 1980s. About 75% of the lakes and 50% of the streams surveyed suffered the effects of acid precipitation. The areas most impacted were the Adirondacks, the mid-Appalachian highlands, the upper Midwest, and the high-elevation West. In the worst case, 90% of the streams in the New Jersey Pine Barrens were acidic. In mid-Appalachia, there were 1,350 acidic streams. Furthermore, the Canadian government estimates that 14,000 lakes in eastern Canada are acidic. The Norwegian government sampled 1,000 lakes and found that 52% of the lakes were endangered. In the southern part of Norway, 60%–70% of the lakes had lost their fishes (Henriksen et al., 1990). Although scientists identified the problem in the 1970s and 1980s, and regulators established emission control regulations, biological and chemical recovery has been slow and incomplete (e.g., Arseneau et al., 2011; Hesthagen et al., 2011).

The proximate cause of acid precipitation is sulfuric and nitric acids in rain, snow, and fog. Combustion of coal and petroleum products forms these acids in the atmosphere, which dissolve in the water droplets of clouds, ultimately reaching the ground. Acid precipitation is concentrated downwind from industrial and urban areas because they have more concentrated emissions from factories and automobile exhaust. Acid deposition in the United States has historically been greater in the heavily populated and industrialized northeast. Acid deposition correlates most closely with sulfate deposition, but also with nitrate deposition. The control of acid precipitation is an environmental victory in the United States (Fig. 16.7). The Clean Air Act controlled acid precipitation and recovery has accelerated in the last decade (Strock et al., 2014). While acid deposition has decreased, nitrogen deposition in the form of ammonium (instead of nitrate) has increased (Li et al., 2016), which could have other effects.

When acid precipitation reaches the ground, it can react with the terrestrial ecosystem. If sufficient base is present, it will neutralize the acid. The ability of a soil or water body to absorb acidity without a change in pH is called *buffering capacity*. The most common material that confers the ability to resist changes in pH is the

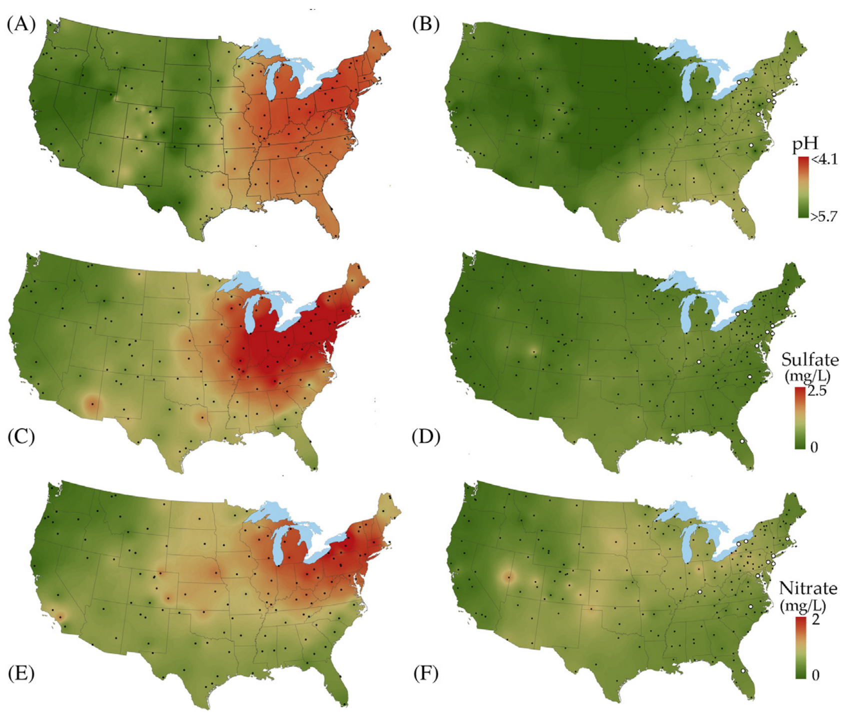

Figure 16.7 Concentrations of acid, sulfate, and nitrate in US precipitation from 1985 (A, C, and E, respectively) and 2015 (B, D, and F, respectively). *Images courtesy of the National Atmospheric Deposition Program (NRSP-3). 2017. NADP Program Office, Illinois State Water Survey, University of Illinois, Champaign, IL.*

bicarbonate in limestone. The bicarbonate equilibrium (discussed in Chapter 13) leads to neutralization of the acid and release of CO_2. Watersheds and aquatic systems that have a significant amount of limestone have a high buffering capacity and are able to resist the effects of acid precipitation. Responses have been variable since regulatory control; anion concentrations such as chloride have decreased in some areas, cation concentrations remain high, and organic acids have replaced inorganic acids to lower pH (Futter et al., 2014). As such, regional recovery across Europe and North America is variable following regulations (Stoddard et al., 1999).

Biological effects of acidification

Acid rain has major effects on biological systems ranging from altered microbial activity to the impaired ability of fishes to survive and reproduce (Table 16.2). Naturally acidic habitats include acid peat bogs (*Sphagnum* bogs) and blackwater swamps (Benner et al., 1989). Lakes and streams in watersheds dominated by such bogs or swamps can be relatively acidic (~pH 3–4). Some geothermal springs are very acidic and have very distinct microbial communities associated with them. Much of our understanding of the effects of long-term acidification on aquatic ecosystems derives from the study of naturally acidic habitats. Amazingly, an iron-oxidizing archaeal isolate from acid mine drainage can grow at pH 0 (Edwards et al., 2000).

One of the basic ecosystem influences of acidification is the lowered rate of decomposition mediated by microbes. Microbes from the naturally acidic Okefenokee Swamp are less efficient at metabolizing low-molecular-weight carbon compounds relative to those in nearby neutral wetlands (Benner et al., 1989). The microbes in acidic habitats are less able to metabolize recalcitrant cellulose and lignin, although some

Table 16.2 Influences of decreasing pH on several groups of aquatic organisms

Organism or process	Approximate pH value
Bacterial decomposition slows/fungal decomposition takes over.	5
Phytoplankton species decline/green filamentous periphyton dominate.	6
Most mollusks disappear.	5.5–6
Most mayflies disappear.	6.5
Beetles, bugs, dragonflies, damselflies disappear.	4.5
Caddis flies, stoneflies, Megaloptera disappear.	4.5–5
Salmonid reproduction fails, aluminum toxicity increases.	5
Most adult fishes harmed.	4.5
Most amphibians disappear.	5
Waterfowl breeding declines.	5.5

Source: After Jeffries and Mills (1990).

degree of adaptation to the acids does occur (Fig. 16.8). Inhibition of microbial activity by low pH leads to greater rates of deposition of organic material and may partially explain the stable existence of acidic depositional wetlands (i.e., once a wetland sediment becomes acidic, microbial activity maintains acidity and carbon continues to accumulate). Rates of microbial decomposition of leaves are also lower in acidified streams (Clivot et al., 2013, Fig. 16.9), which may increase carbon accumulation and alter the associated food webs.

Acidification alters algal populations. Filamentous green algae characteristically bloom in the littoral zones of acidified lakes. When these blooms collapse, the resulting O_2 depletion can have negative impacts on animals (Turner et al., 1995). Diversity of planktonic and benthic algae decreases with lower pH (Dickman and Rao, 1989). Similar decreases in algal diversity and replacement with filamentous green algae occur in acidified streams (Meegan and Perry, 1996).

Shifts in algal communities in lake sediment cores resulting from pH changes verify historical trends in acidification (Mallory et al., 1998). Such verification is required before politicians are willing to enact stringent and potentially costly emission controls. In this technique, existing lakes serve as a baseline to create an index that correlates current water column algal communities with pH. This index

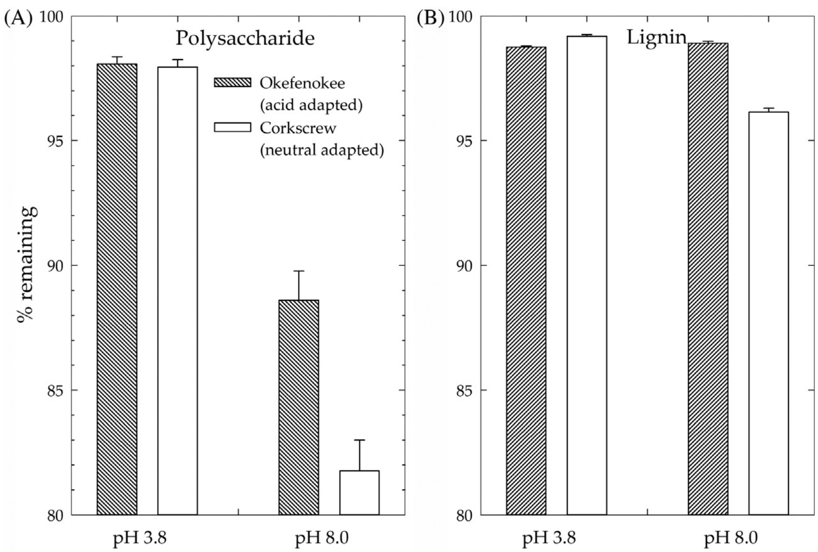

Figure 16.8 Percentage of remaining polysaccharide (A) and lignin (B) compounds after degradation by microbes from a naturally acidic swamp (Okefenokee Swamp in Georgia, pH 3.4–4.2) and a neutral swamp (Corkscrew Swamp in Florida, pH 6–8) after incubation at different pH levels. *Modified from Benner et al. (1989).*

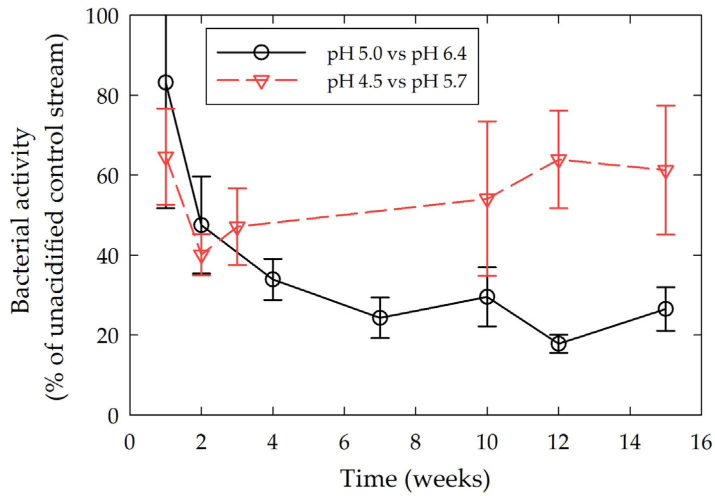

Figure 16.9 Microbial activity on leaves placed in acid and neutral streams as measured by the rate of thymidine incorporation into nucleic acids in two acidified streams compared to two nearby neutral streams. *Modified from Palumbo et al. (1989).*

indicates pH using species with parts that remain preserved in the sediment, such as diatom frustules or chrysophyte scales. Analysis of sediment cores can establish changes in the community over time. The deeper in the sediments, the longer ago the algae were deposited. This index, coupled with isotope analyses to date specific depths of sediments, yields a record of pH in a lake over time (Fig. 16.10). In the case of Big Moose Lake, New York, some chrysophyte species are dominant in low pH, whereas others occurred only at the higher pH values associated with preindustrial conditions.

Diversity of plants and animals also decreases as aquatic systems become more acidic. Macrophyte diversity decreases in low pH lakes and streams (Thiébaut and Muller, 1999). Fungal diversity is reduced in acidic streams (Fig. 16.11). Invertebrates exhibit a wide range of acid sensitivities. Perhaps the most sensitive invertebrates are those that require calcium bicarbonate for shells (e.g., Mollusca). These shells dissolve or are unable to form when pH decreases. However, a few species from these groups are adapted to survive in waters with pH <5 (Freyer, 1993). As aquatic systems become acidified, biomass and diversity of crustaceans (Fig. 16.12) and other invertebrates decreases. Among aquatic insects, mayflies are particularly sensitive to low pH (Herrmann et al., 1993). In lakes, not only does the diversity of zooplankton decrease with increased acidification, but also the efficiency of energy transfer up the food web is lowered (Havens, 1992a,b).

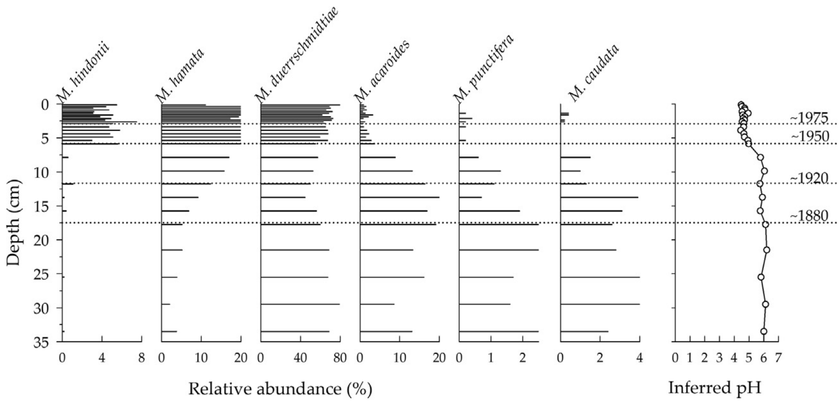

Figure 16.10 Distribution of *Mallomonas* spp. scales (a chrysophyte) with depth and reconstructed pH from Big Moose Lake (New York). Sediments were dated by ^{210}Pb content. *From Majewski and Cumming (1999) with kind permission from Kluwer Academic Publishers.*

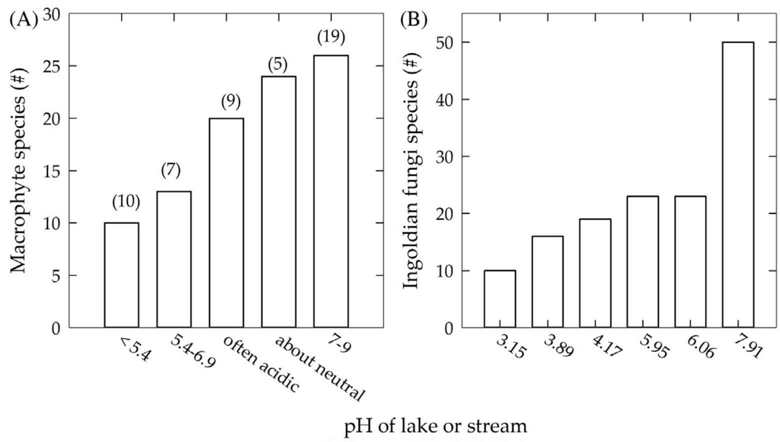

Figure 16.11 Number of macrophyte species as a function of lake water pH (A) and number of species of Ingoldian fungi as a function of stream water pH (B). The numbers of lakes sampled are shown in parentheses. *Data from Hutchinson (1975). (A) and Dubey et al. (1994).*

Fishes are susceptible to acidification. Many examples of pH damages to fishes come from salmonids because they are of the greatest economic importance in the areas most polluted by acid precipitation. One study suggests that economic benefits of fisheries drop from \$38 per angler day in lakes with quality trout fisheries to <\$4.50 day^{-1} in lakes with pH < 4.5 (Caputo et al., 2017). Acidification increases the concentration of aluminum (Fig. 16.13), which causes damage to fish gills. The low pH increases the toxicity of the aluminum (Gensemer and Playle, 1999). Subsequently,

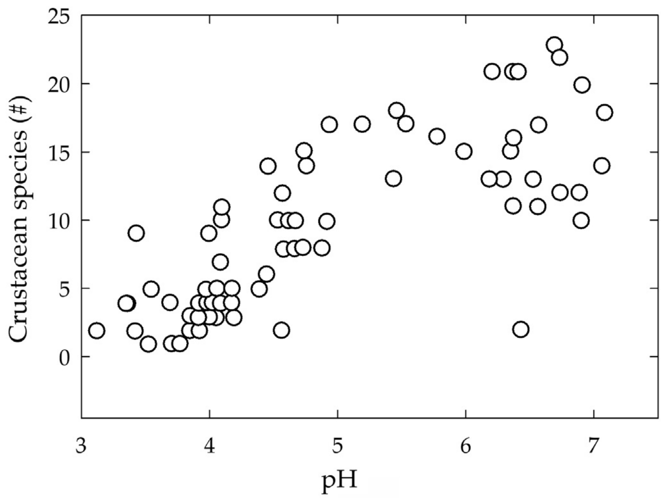

Figure 16.12 Crustacean species diversity as a function of pH. *Reproduced with permission from Freyer (1980).*

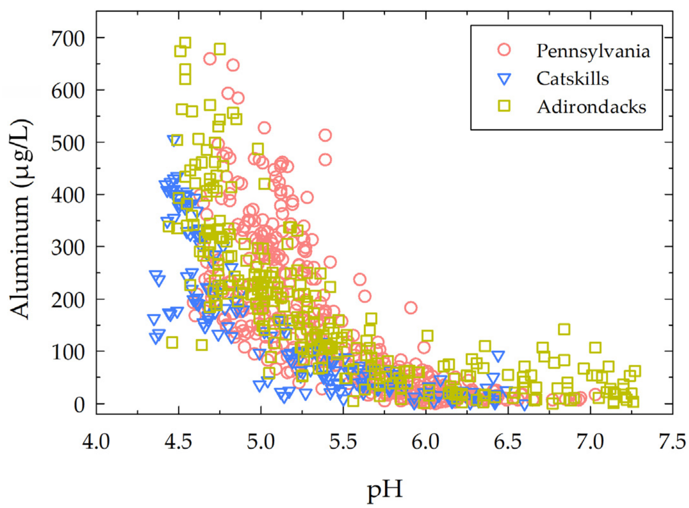

Figure 16.13 Relationship of aluminum concentrations to pH. *Reproduced with permission from Wigington et al. (1996).*

the number of sensitive fishes decreases in acidified waters (Fig. 16.14), and the most acidified waters have no fishes.

Treatments to reverse acid precipitation effects

Several treatments are available to counter the effects of acid precipitation. The most obvious is stopping the source by burning low-sulfur fuels for industry and power

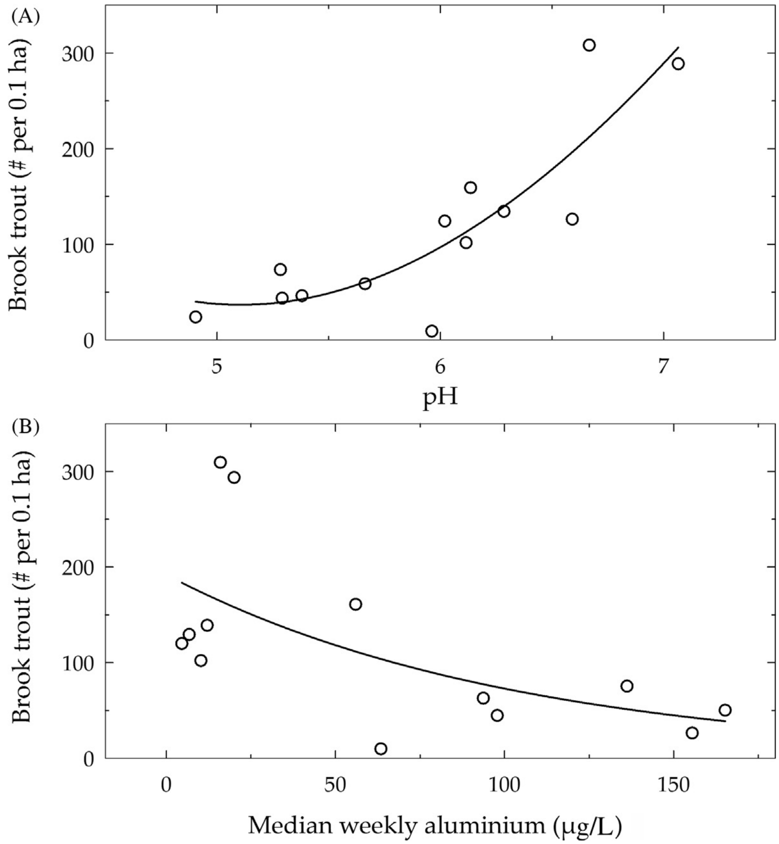

Figure 16.14 Biomass of trout in Adirondack streams as a function of pH (A) and aluminum (B). *Reproduced with permission from Baker et al. (1996).*

production, and decreasing the emission of nitrogen compounds in automobile exhaust. The most common local treatment is to add lime (calcium carbonate) to lakes and watersheds to neutralize the effects of the acid (Fairchild and Sherman, 1990). Directly adding calcium carbonate to the lake causes short-term (years or less) increases of pH and recovery of some biota (Hörnström, 1999). Adding calcium carbonate to the entire watershed may have longer lasting effects but is costlier (National Research Council, 1992). Unfortunately, even if acidification is reversed, losses of calcium and magnesium from soils and internal sulfate cycling may lead to long-term changes in water chemistry (Likens et al., 1996; Miles et al., 2012). Research by Gene Likens has illustrated that knowledge of biogeochemical cycling is important in understanding causes and effects of acid precipitation (Biography 16.2). Another possible solution is to fertilize the lake and allow the biota to reverse the problem

(Davison et al., 1995), but as discussed in Chapter 18, eutrophication has its own problems.

Emission controls have led to decreases in acid deposition in North America and Europe and associated reversals in surface water acidification (Stoddard et al., 1999). The biological community has recovered in some areas (e.g., Arseneau et al., 2011). However, some areas have not recovered in North America; those watersheds received so much acid deposition that they were not able to respond to decreased sulfate loading.

Another cause of acidification of surface waters is mine drainage. Acid mine drainage and metal contamination are related in many instances. Metal pyrites weather when exposed to oxygenated surface waters and metals dissociate with concurrent formation of sulfuric acid. This acid mine drainage results from coal mining and metal mining operations. Treatment options include neutralization with limestone (Hedin et al., 1994), oxidation in wetlands, and various combinations of these treatments (Robb and Robinson, 1995).

METALS AND RADIOACTIVE POLLUTANTS

A wide variety of metals and some other inorganic materials act as toxic pollutants in aquatic ecosystems (Table 16.3). Arsenic, chromium, lead, zinc, mercury, cadmium, and other metals are naturally occurring, but human activities create situations where concentrations are higher than they would be naturally and are toxic to aquatic life. Metals can bioaccumulate in many organisms starting at the base of the food web (Kassaye et al., 2016) and can be bioconcentrated in food chains. Bioconcentration has led to problems such as excessive lead contamination of freshwater fishes throughout all areas with cities. Complex pelagic food webs with many lateral links transfer less metals up the food chain (Stemberger and Chen, 1998), an additional argument for maintenance of biodiversity. Atmospheric deposition and industrial waste releases, particularly mining (Table 16.4), are common sources of metal contamination. Such mining activities have had extensive negative impacts in some aquatic habitats (Highlight 16.4).

Chemical conditions can alter the bioconcentration and toxicity of metals. For example, cadmium, silver, nickel, and zinc uptake by invertebrates is highly influenced by reactive sulfides in sediments (Lee et al., 2000). High-sulfide sediments bind the metals and render them less toxic. Also, the redox state of metals can influence toxicity; hexavalent chromium (oxidized) is much more toxic than trivalent chromium.

Lead toxicity in waterfowl has been a particular concern in freshwater systems because of the historical use of lead shot pellets for hunting. Waterfowl such as ducks, geese, and coots ingest the pellets as grit for their crops. Less than 10 lead pellets will

BIOGRAPHY 16.2 Gene E. Likens

Figure 16.15 Gene Likens. *Courtesy Gene Likens.*

The study of biogeochemistry is arguably the most related area of freshwater science to water quality, the links between aquatic and terrestrial habitats, and the influence of aquatic pollutants. Dr Likens (Fig. 16.15) is one of the foremost contemporary scientists specializing in the biogeochemistry of ecosystems. He has received numerous honorary degrees and awards, including the Tyler prize (a World Prize for Environmental Achievement), election to the US National Academy of Sciences, and top awards from the American Society of Limnology and Oceanography, the Ecological Society of America, and many other international societies. He has more than 330 publications, including 12 books.

Likens grew up on a farm in northern Indiana, where he fished, collected aquatic organisms, and generally enjoyed exploring aquatic habitats. Likens maintains that a love of natural history is the single best predictor of success for an aquatic ecologist. He attended a small liberal arts college (Manchester) and obtained a PhD from the University of Wisconsin. Following a lecture on the conservation of aquatic resources, he told the professor he was interested in the subject and wondered if he could get paid for that type of work. Obviously, the answer was yes.

Fortunately for the aquatic sciences, Likens did not follow his other career goal; he also wanted to be a professional baseball player and played for 2 years in the rookie league in Kansas, a league that also gave rise to baseball great Mickey Mantle. Likens was a most valuable player, but he decided that the life of an academician was preferable to that of a professional athlete.

Likens says he feels lucky to have been able to travel to and study some of the most beautiful places in the world, including Hubbard Brook, where he conducted important research on the influence of logging on nutrient transport by streams (Likens et al., 1978). Hubbard Brook is also the site of much of his research on acid precipitation effects; it has been the site of experimental watershed acidification and produced crucial insights into the long-term impacts of acid leaching of soils (Likens et al., 1996). Likens predicts that a major future challenge in aquatic ecology will be to understand the implications of complexity. He suggests we currently do a good job at assessing the influence of one or two factors, but that to truly understand ecosystems we need to account for the simultaneous influence of multiple biotic and abiotic factors.

Table 16.3 Maximum allowable concentrations of some toxic metals in natural waters used by humans for the United States, and potential human health problems associated with each (after Budavari et al., 1989; Laws, 1993)

Metal	Chemical symbol	Maximum conc. (μg/L)	Some responses to acute poisoning	Some chronic effects
Mercury	Hg	0.144	Death within 10 days, severe nausea, abdominal pain, blood diarrhea, kidney damage	Loss of teeth, kidney damage, muscle tremors, spasms, depression, irritability, birth defects
Lead	Pb	5	Anorexia, vomiting, malaise, convulsions, brain damage	Weight loss, weakness, anemia
Cadmium	Cd	10		Cancer, throat dryness, headache, vomiting
Selenium	Se	10		Nervousness, depression, liver injury (this is an essential element in small amounts, but toxic at higher concentrations)
Thallium	Tl	13	Nausea, vomiting, diarrhea, tingling pain in extremities, weakness, coma, convulsions, death	Weakness and pain in extremities
Nickel	Ni	13.4		Cancer, dermatitis, nausea, vomiting, diarrhea
Silver	Ag	50		Bluish color of skin, skin and mucous membrane irritation
Manganese	Mn	50		Languor, sleepiness, weakness, emotional disturbances, paralysis
Chromium	Cr	50		Cancer, skin and respiratory irritation, renal damage (chromium III is not toxic; chromium II is)
Iron	Fe	300		
Barium	Ba	1,000	Excessive vomiting, violent diarrhea, tremors, death	

kill a bird, but marshes frequented by hunters may have 6 or 7 pellets/m^2 in the sediments. For this reason, the US Fish and Wildlife Service has phased out use of lead shot in favor of steel shot (Laws, 1993). In upland areas of the United States, it is still legal to use lead shot and this shot can move into aquatic habitats or water birds, such as geese, that use upland areas part time and can ingest these poisonous pellets. Lead fishing weights are still in use and can cause wildlife deaths. In addition, atmospheric lead deposition increases lead concentration in lakes throughout the

Table 16.4 Some effects on aquatic environments related to various mining activities

Type of mining	Potential impacts
Sulfide ores (copper, nickel, lead and zinc)	Acidification by sulfuric acid, possible arsenic contamination, sediments
Gold and silver	Same as sulfur ores, possible mercury, cyanide or arsenic contamination
Uranium	Acid tailing drainage; runoff of radioactive materials, toxic metals, sediments, and organic compounds
Iron	Heavy water demand; runoff of sediments, toxic metals
Coal	High water demand, high sediment load in runoff, acid runoff from high sulfur deposits
Salt	Salinization of waste water

Source: After Ripley et al. (1996).

world. Analysis of peat bog sediments in Switzerland indicated that anthropogenic inputs increased lead contamination starting 3,000 years ago, and in 1979 deposition rates were 1,570 times the natural background values found prior to 1000 BC (Shotyk et al., 1998). A similar sediment analysis in Michigan indicates lead contamination from copper mining by indigenous people 7,000–8,000 years before the present day (Pompeani et al., 2013).

Mercury is a neurotoxin and microbes transform it to its most toxic state, methylmercury, in anoxic conditions. It is a worldwide contaminant influencing all environments (Driscoll et al., 2013; Ozersky et al., 2017). This is an old problem; mercury accumulation in a Spanish peat bog increased about 2,500 years ago, at a time when mercury mining began in the region (Martínez-Cortizas et al., 1999). In some countries, people use mercury indiscriminately to extract gold in mining operations and can heavily contaminate freshwater systems (Cursino et al., 1999).

Mercury contamination of fish is a problem that has beset many areas. About half the streams with large piscivorous fishes in the Western United States have fishes with mercury concentrations exceeding safe limits (Peterson et al., 2007). Organisms assimilate and concentrate methylmercury in aquatic food webs. Mercury most commonly enters aquatic systems from atmospheric fallout from coal burning, trash incineration, and industrial emissions; once methylated under anaerobic conditions in water-saturated sediments, it readily moves into the food web. Periphyton mats can be an important site of mercury methylation and its entry into the food web (Cleckner et al., 1999). Biomagnification then can cause levels of mercury in fish high enough to warrant consumption advisories. Such restriction on consumption may be problematic for people that use fishes as a large component of their diet (Egeland and Middaugh, 1997).

Highlight 16.4 Massive contamination of the Doce River (Brazil) and the Clark Fork River (United States) by mining waste

In 2015 a dam containing mining wastes burst, releasing a wave of toxic mud that spread down the Doce River in Brazil and killing 20 people (Garcia et al., 2017). This toxic waste decimated the biological communities of the river leading to a loss of $521 million/year of ecosystem services. The pollution moved down the river and eventually contaminated Atlantic coastal waters. The fines assessed to the mining company did not cover the estimated costs of all losses. Furthermore, experience from the United States indicates these costs will accrue for many decades to come. In January 2019 another mine dam collapsed in Brazil in the state of Minas Gerias, leading to deaths of hundreds of people and massive environmental damage.

Over 100 years of mining (primarily copper) in the region of Butte, Montana, has resulted in numerous contamination problems in the Clark Fork River. Mines discharged waste from the mines directly into the river or allowed it to wash into tributaries. The operations discharged an estimated 99.8 billion kg of waste into the system prior to 1959, and 2 or 3 million m^3 of contaminated sediments is present in the floodplain. Contamination has affected the upper 200 km of the river.

Mine operations installed treatment ponds to trap wastes over the years, and initiated liming to precipitate metals in the waste in 1959. However, cadmium, copper, lead, and zinc in the water column continue to exceed criteria for protection of aquatic life. Metal waste that drains into the groundwater influences microbial communities (Feris et al., 2004). This extensive contamination has led to designation of the upper Clark Fork River as a Superfund site. Cleanup of the site started in the late 1980s and continues, costing US$123 million as of 2016.

Historic fish surveys in 1950 showed no fishes in regions of the upper Clark Fork River. With improved water quality, fisheries managers have reintroduced trout into the upper river. However, thunderstorms cause episodic contamination events during high discharge, and significant fish kills happened in 1983−1985 and 1988−1991. Physiological abnormalities of fish and concentration of the contaminants in the food chain still occur. The data suggest that metal contamination problems are likely to defy attempts at remediation for significant periods after contamination (Phillips and Lipton, 1995). The Milltown dam, upstream of Missoula, Montana, is filled with contaminated mine waste that accumulated in 1908, shortly after it was built. The dam is currently being removed and sediment is being removed from the river. These two examples illustrate the potential impacts of mining on water quality.

Eutrophic systems can have less severe problems with production and concentration of methylmercury in the food web (Gilmour et al., 1998), but generalizations may be difficult since the relationships between organic C and methylmercury concentrations are complex (Hurley et al., 1998). A global synthesis of mercury magnification in food webs suggested that biomagnification was greatest in cold, low productivity high-latitude systems; additionally, it was greater when dissolved organic C concentrations were higher (Lavoie et al., 2013).

Mercury is one of the major problems influencing the Everglades, where public health officials have issued fish consumption advisories because methylmercury concentrations in fish tissues exceed 30 ng/g (Cleckner et al., 1998). A landscape-level study found that concentrations of mercury in tissues of most species of stream invertebrates increased significantly with stream size, and this pattern was attributed to in-stream production of methylmercury along the stream network. This production was greatest in *Cladophora* mats (Tsui et al., 2009).

Selenium has caused severe problems in some wetlands. Irrigation mobilizes selenium naturally found in soils and concentrates the selenium as the water evaporates. In Kesterson Reservoir, a National Wildlife Refuge in central California, selenium contamination caused congenital deformities and mass mortality of waterfowl. Although selenium is a required nutrient in trace levels, it bioaccumulates and becomes toxic at higher concentrations. The US Geological Survey has identified about 500,000 km^2 in the western United States that are susceptible to similar problems. The worst cases occur where irrigation runoff is reused for irrigation, and water ends up in terminal wetlands or lakes. Such lakes and wetlands have no outlets and concentrate selenium by evaporation.

Arsenic can cause problems because it can be present in high concentrations naturally or as runoff from industrial uses. Historically, arsenic was a common pesticide and subsequently contaminated aquatic systems. There are widespread problems with arsenic in drinking water in China; an estimated 19.6 million people are at risk for contaminated drinking water (Rodríguez-Lado et al., 2013). In a particularly horrible case, thousands of drinking water wells in West Bengal, India, contain naturally occurring arsenic (Bagla and Kaiser, 1996). An estimated 200,000 people in this area have arsenic-induced skin lesions and hardened patches of skin that may become cancerous. More than 1 million Indians may be drinking this contaminated water. Successful management includes providing safe drinking water and uncontaminated food (groundwater-irrigated crops concentrate the arsenic). However, in a study where clean water and food were provided for 5 years, moderate cases of skin lesions were reversed, but severe cases of lesions and chronic lung disease were not (Bhowmick et al., 2018).

The West Bengal problem could be related to recent large-scale withdrawal of groundwater for agriculture, leading to rapid fluctuations in groundwater level and input of O_2, which allows for release of the arsenic from sulfides in the pyrite-rich rocks of the area. Phosphorus from fertilizers also increases arsenic release rates. Microbes can oxidize arsenic (Oremland and Stolz, 2003) and could control arsenic release, which starts after iron is oxidized from the system (Islam et al., 2004). The microbial effect provides a potential partial explanation for the phosphorus effect since phosphate tends to bind with iron. More research by groundwater geochemists and hydrologists is needed to study this problem and find solutions.

We mine rare earth elements for various technical uses. We know little about how they concentrate in the environment and their biological effects. Amyot et al. (2017) studied food webs in 14 lakes in Quebec that were not subject to mining in their watersheds. They summed the rare earth elements analyzed in the biota, including Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. They found clear trends of biomagnification and bioconcentration with concentrations in fishes several orders of magnitude greater than in the water, but concentrations in lake sediments greater than in biota.

Radioactive compounds can be contaminants of water. These usually occur naturally. The primary contaminants are isotopes of radium, radon, and uranium. Radium contaminates approximately 1% of drinking water supplies with radium above acceptable levels, and radium and uranium occur in significant concentrations in many surface and groundwaters. Numerous human deaths are attributed anually to exposure to radium (6−120), uranium (2−20), and radon (80−800) in the United States (Milvy and Cothern, 1990).

The effects of natural radioactive materials on aquatic habitats are difficult to gauge. Laws (1993) states a made up example to illustrate why we do not know much about biological effects of many pollutants. "While the deaths of 250,000 Americans out of a population of 250 million (i.e., 0.1%) might seem an alarming statistic to many persons, the loss of 0.1% of a population of crabs or tunicates would not be likely to cause much public alarm." Consequently, we do not know the effects of many contaminants on aquatic organisms, given the limited information on the effects of most chemicals on humans. Most of the research on the influence of radioactive compounds on aquatic habitats has occurred downstream from nuclear power-generation plants. Perhaps the greatest concern is with biomagnification; body tissues retain many radioactive isotopes, and concentrations increase with each increase in trophic level.

NANOMATERIALS

Nanomaterials are very small molecules or clusters of molecules (on the nanometer scale), often of materials that usually occur in large aggregations. Nanomaterials can be organic or inorganic. While these compounds can occur naturally, people are now engineering these particles and the can ultimately enter freshwaters. The products have many benefits due to their unique properties, but environmental research on their influences is in its infancy (Wilson, 2018). Small clusters of molecules behave differently from larger aggregates because of quantum mechanical properties. For example, silver particles are more toxic at nanosize because the silver is more likely to release into solution, and titanium oxide nanoparticles (but not larger titanium oxide particles) react with UV light to form hydroxyl radicals that are harmful to cells. We discussed nanoplastics earlier in this chapter. While the unique properties of these materials make them useful in many applications, and humans are using them, their effects on the freshwater environment are unclear. There is some concern about the effects of these products on human health and how they will enter our drinking water supplies (Troester et al., 2016). Understanding their influences in freshwaters is difficult because there are so many types, they have different modes of action, they can interact with other pollutants, they can be difficult to work with in environmentally realistic ways, and they interact with the environment (e.g., light), which alters their toxicity (Bundschuh et al., 2016).

Some commonly used nanomaterials include titanium dioxide (TiO_2), silver particles, zinc oxide (ZnO), carbon nanotubes, fullerenes, and cerium dioxide (CeO_2). These particles generally occur in freshwaters in <1 μg/L except for TiO_2, which is commonly found in the 10s of μg/L (Bundschuh et al., 2016).

Titanium dioxide is used as a whitener in products such as paints, sunscreens, foods (e.g., powdered sugar doughnuts), and many other applications. The use of standardly ground TiO_2 powders is being rapidly replaced by nanosized particles. Bacteria exposed to nanosized TiO_2 take up the particles and have lower metabolic capacity (Combarros et al., 2016). A pulse of TiO_2 to an experimental stream system caused an immediate decrease of bacterial abundance with recovery over three weeks. Analysis of 16S rRNA genes suggested no influence on the composition of the bacterial community, indicating that the effects were very broad spectrum and did not target specific groups of bacteria (Ozaki et al., 2016). Additionally, TiO_2 exposure can increase accumulation of toxic arsenate in *Daphnia magna* (Li et al., 2016).

Silver is one of the most toxic metals in freshwaters, and the use of nanosilver particles as an antimicrobial agent has increased dramatically. Nanosilver is synthesized in particles less than 100 nm diameter, and the tiny particles are more toxic than larger particles. Hundreds of products, such as child toys and textiles, contain silver nanoparticles and much of the silver will eventually enter aquatic environments. While silver nanoparticles are undoubtedly reaching freshwater environments, and they are strongly toxic to microbes, researchers know little about how large their effects are (Zhang et al., 2016). These particles can come in several forms, all of which accumulate in duckweed (Stegemeier et al., 2017). Silver particles at environmentally relevant concentrations can alter behavior of the snail, *Physa acuta* (Bernot and Brandenburg, 2013). Particles in short term laboratory experiments can have deleterious effects on bacteria, but one lake mesocosm study found only modest effects of nanosilver (Blakelock et al., 2016).

Carbon materials (e.g., bucky balls, carbon nanotubes, graphene compounds) are becoming more and more prevalent. While these compounds are relatively unreactive, the consequences of their release into the environment are a mystery. Carbon nanotubes can bioconcentrate in *Daphnia* (Petersen et al., 2009). Graphene nanomaterials are probably more toxic than carbon nanotubes to green algae (Zhao et al., 2017). Influence of nanomaterials in freshwaters is certainly a ripe area for future research, as people tend to release compounds into the environment first and worry about the effects later.

SALT POLLUTION

Salinization of freshwaters by human activities is widespread and has strong negative consequences for biota (Cañedo-Argüelles et al., 2016). A variety of human activities can increase the salinity of freshwater habitats. Applications of salt to roadways and sidewalks can directly influence nearby freshwater habitats when snow and ice melt (Kaushal et al., 2005), and has salinized many lakes in North America (Dugan et al., 2017). A study in Ontario, Canada indicated that ~50% of the total salt applied to a major highway eventually washed away with overland flow and the remainder entered shallow groundwater habitats, resulting in degradation of groundwater resources (Meriano et al., 2009). Studies in the northeastern United States indicate that the salinity of many urban and suburban streams has been increasing for decades and already exceeds lethal limits for many freshwater organisms (Fig. 16.16) (Kaushal et al., 2005). Retention ponds, often used to control floods in urban areas, exacerbate the salt effects by prolonging a slow release of runoff from snowmelt from salted roads (Snodgrass et al., 2017). If these trends continue, many surface waters in the northeastern United States will be unfit for human consumption within the next century.

Direct applications of salt are not the only cause of increasing salinity of freshwaters. Agricultural and urban runoff, as well as point sources such as sewage effluent, can increase salinity of receiving waterways by increasing concentrations of chloride and other ions. Dewatering of rivers, groundwaters, and coastal wetlands facilitates salt intrusion into formerly freshwater habitats in coastal regions (Fig. 4.7). Industrial activities, such as production of soda ash, generate large quantities of waste products that

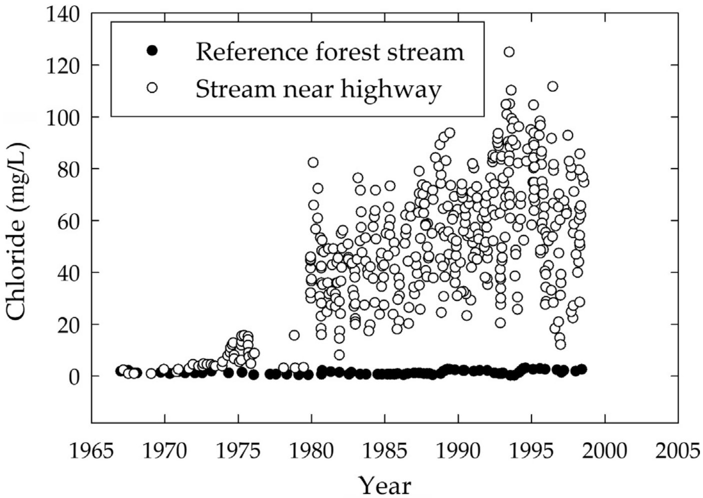

Figure 16.16 Long-term data showing a significant increase in baseline chloride concentration in a stream following highway construction and a nearby control stream with no roads and no change in chloride concentrations over the same time period. *Adapted from Kaushal et al. (2005).*

can greatly increase salinity in regional freshwater habitats if not carefully contained. Groundwater extraction activities, including coalbed methane extraction, pump deep groundwaters to the surface that are often naturally saline, which can contaminate surface and shallow groundwater habitats.

Agricultural irrigation can increase salinity of downstream waters. Continued application of water will cause concentration of salts as evaporation leaves salt behind. A slight excess of irrigation water is added to wash away concentrated salts. Runoff from such practices leads to higher concentrations of dissolved salts. Such problems affect many drier irrigated areas; most of the irrigated lands in California's Imperial and San Joaquin Valleys have salinity problems, and salts and agricultural chemicals contaminate runoff.

Climate change may also increase salinity of freshwater habitats in some regions as increased frequency and magnitude of droughts and warmer temperatures enhance evaporation of surface waters, concentrating solutes. In some regions, such as the Murray-Darling River Basin of Australia, which has been experiencing increasing salinity for decades, identification of specific causes has proven difficult because of complex interactions, mostly among weather, geology, and human activities. However, natural weathering processes are contributors to some degree (Morton and Cunningham, 1985; White et al., 2009).

Regardless of the ultimate cause, increased salinity has detrimental effects on aquatic life for reasons discussed above; osmotic stress can result in slower growth, reduced reproduction, and ultimately death, depending on the degree of pollution and tolerance of individual species. Unlike most marine habitats, salinity of freshwater habitats can be quite variable in time and space, and thus tolerances of individual species vary greatly. Above certain levels (e.g., above 2.0 g NaCl/L), few species can persist in salt-polluted habitats. Chronically salt-polluted habitats have reduced biological diversity and ecosystem functions such as primary production and decomposition rates. Even modest chronic additions lower stream microbial leaf decomposition rates (Tyree et al., 2016).

SUSPENDED SOLIDS

Turbidity and suspended solids or sediments are natural parts of all freshwater environments. Some habitats are naturally highly turbid, but human activities have increased levels of suspended solids in many habitats (Fig. 16.3). Agricultural and urban runoff, watershed disturbance (e.g., logging, construction, and roads; Forman and Alexander, 1998), removal of riparian vegetation, alteration of hydrodynamic regimes, and introduction of species such as common carp that stir up sediments all can lead to anthropogenic increases in total suspended solids. In addition, alterations in flow can increase sediment loads, and understanding the sources and causes of excess sedimentation is complex (Belmont et al., 2011). Arctic warming and melting of permafrost will also increase sediment pollution (Chin et al., 2016), and clearing channels of macrophytes to increase water flow or navigability can lead to high sediment concentrations (Greer et al., 2017).

Sediments can have different biological and physical effects depending on the type of suspended solids (Table 16.5). High concentrations of suspended solids can lower primary productivity of systems by shading algae and macrophytes, at times leading to almost complete removal. Suspended solids can also have negative effects on aquatic animals by interfering with reproduction, respiratory O_2 transport, filter feeding, and habitat availability. The negative impact of excessive sediments on stream biota is clear (Hynes, 1970; Waters, 1995). Such sediments lower incoming light and primary production, increase scour, harm sensitive invertebrate species, reduce biodiversity, and lower the aesthetic values of streams and lakes. Excess sediments can also decouple the food web in streams. For example, Louhi et al. (2016) found that sediment additions to artificial stream channels reduced the effects of predators on grazing invertebrates, altering a top−down trophic cascade. Probably the strongest negative effect of sediments is filling and embedding gravel and cobble habitat through deposition, leading to reduced water and oxygen flow through substrata and increased anoxia. Sediment

Table 16.5 Classification of suspended solids and their possible impacts on freshwater systems

Type of solid	Physical and chemical influences	Biotic influences
Fine inorganic particles	Decrease light, impede flow, increase scour, metals, and other ions can associate	Clog respiratory organs, reduce metabolite flux, light limitation, alteration of habitat
Fine particulate organic matter (natural)	Clogging sediments, decreasing oxygen flux. Lower redox	Food source for heterotrophs, stimulation of respiration
Fine particulate organic matter (sewage)	High nutrient, carbon, and potential metal content. Lower redox	Food source for heterotrophs, stimulation of respiration
Fine particulate organic matter (microplastics)	Potential light absorption, disruption of flow	Carry toxicants, filter feeders may be deceived
Toxicants on particles	Movement of hydrophobic compounds, survival of viruses	Toxicity and disease

Source: After Wilber (1983).

clogging can harm interstitial invertebrates and eggs of many spawning fishes. Lowering flow through gravels can cause O_2 levels to decrease below levels necessary for eggs to develop successfully. Salmonids are sensitive to sediments (Wilber, 1983), but some other species are tolerant (e.g., many catfishes and carps).

Light attenuation in lakes may comprise a large part of the influence of suspended solids on the biota. A highly turbid lake or reservoir may have limited rates of primary production. However, if there is sufficient organic material in the suspended particles, a productive food web based on microbial use of the suspended particulates can occur.

THERMAL POLLUTION

Human alterations to natural temperature regimes of freshwater habitats cause thermal pollution. Thermal pollution is any deviation from the natural temperature in a habitat and can range from elevated temperatures associated with industrial cooling activities to discharges of cold water into streams below large impoundments. Given that the metabolic rates of ectotherms are controlled by temperature, and that the vast majority of freshwater organisms are ectothermic, thermal pollution can strongly affect freshwater communities. Alterations to normal water temperature regimes have myriad biological effects, including interfering with temperature cues for spawning fishes, facilitating establishment of exotic species, and altering growth and development of aquatic organisms (Langford, 1990). Further, aquatic organisms evolved in relatively thermally buffered environments, and thus they are generally more sensitive to temperature fluctuations than are their terrestrial counterparts.

Temperature tolerances among species of freshwater organisms are highly variable, but all have an optimal range and low and high limits within which they can survive. Increases in temperature cause an increase in growth rate up to a point. Above some threshold, damage occurs. Because temperature governs rates at multiple levels of biological organization (e.g., from enzymatic reactions to metabolism of whole organisms), changes in temperature associated with thermal pollution ultimately influence rates of ecosystem processes and functions such as nutrient cycling and decomposition.

Most forms of thermal pollution involve temperature increases, and while the effects of extreme temperature increases are obvious, relatively small changes can also be biologically significant. We discussed molecular adaptations to temperature in Chapter 15. Temperature increases as little as 1°C–2°C can alter communities because they are lethal to some species and can affect growth and reproduction of others. Raising water temperatures just 2°C–3°C above the optimal for some aquatic insects can greatly reduce the number of eggs produced by females because more energy is used to support higher metabolic rates and less is available for egg production (Vannote and Sweeney, 1980; Firth and Fisher, 1992).

Thermal pollution associated with sewage effluent is linked to differences in leaf litter decomposition rates in Lake Titicaca in South America (Costantini et al., 2004). Trees can die when thermal pollution alters wetlands. As temperatures increase, cyanobacteria dominate over green algae and diatoms. One of the key issues in thermal pollution is the replacement of cold-water fishes with warm-water fishes.

Power plants and industrial factories are major point source contributors to thermal pollution. In this case, plant operators withdraw cool water from streams, use it to cool generators and other machinery, and then return it to the stream at elevated temperatures. Rapid changes in temperature associated with power plant operations can kill fishes by thermal shock (Ottinger et al., 1990). Mitigating the thermal effects of power plant effluent obviously has a significant financial cost. Temperature regimes of small lakes or near-shore portions of lakes are also altered by human activities including effluent from municipal facilities and industry.

Along with industrial sources, urban and suburban runoff can contribute to thermal pollution, particularly during short, intense thunderstorms in watersheds with high amounts of impervious surfaces such as asphalt (Herb et al., 2008). Depending on local groundwater inputs, discharge, and other factors that influence thermal regimes, even small municipal discharges can alter stream temperatures for considerable distances downstream.

Reductions in stream flows or lake volumes alter temperature regimes by reducing the thermal buffering capacity of the water body. Water withdrawals for irrigation, hydroelectric, and other human uses reduce stream flows and lead to significantly increased water temperatures during warm periods. This warming can ultimately result in increased fish kills associated with high temperatures (Caissie, 2006).

Impoundments that release water from the surface can result in higher stream temperatures during warm periods because water velocity is decreased and solar penetration enhanced in the impounded water. Along with the direct effects of warmer temperatures on aquatic life, the solubility of O_2 in water decreases with increasing temperature, so O_2 stress increases as temperatures rise. During cold periods when stream water temperatures are normally near freezing, hypolimnetic releases can artificially warm streams.

Deforestation is also a major contributor to thermal pollution in streams, small ponds, and wetlands, as removal of riparian vegetation greatly increases solar penetration and temperature (Beschta et al., 1987). Small streams and ponds in forested regions are particularly vulnerable because they are normally shaded during warm months and have less thermal buffering capacity. Studies in forested headwater streams show increases in summer maximum temperatures of 5°C−8°C after logging, and recovery periods to normal thermal regimes can take 5−15 years (Caissie, 2006).

Anthropogenic cooling of freshwaters can also have strong effects on aquatic life. Releases of cold water from the hypolimnia of large reservoirs alter stream thermal regimes for long distances. Hypolimnetic releases can greatly alter seasonal temperature patterns, lower maximum temperatures by more than 10°C, and dampen normal diurnal temperature fluctuations (Baxter, 1977; Ward and Stanford, 1979; Ward, 1985). The overall effect is a dampening of normal diel and seasonal temperature fluctuations. Water temperatures below large impoundments (like the Glen Canyon Dam on the Colorado River in the southwestern United States) are now much cooler in the summer than they were historically. Fisheries managers often stock non-native cold-water fishes such as salmonids in temperate zone streams below large impoundments. This occurs in regions where natural summer stream temperatures exceed the upper limits for most cold-water species. Although important for recreation, these tailwater fisheries (fisheries downstream from dams) differ substantially from natural river systems and are often detrimental to native species.

While many forms of thermal pollution originate at point sources, climate change (discussed throughout this book) represents a nonpoint source of thermal pollution that is already influencing a wide range of freshwater habitats. The long-term impacts of climate change on freshwater habitats remain to be seen, but predictions indicate significant shifts in structure and function of streams, lakes, and wetlands, particularly in higher latitudes. Responses will vary; in a specific example, wetland plant cover will expand on the Mississippi delta with increased temperatures associated with global climate change (White and Visser, 2016).

ANTHROPOGENIC INCREASES IN UV RADIATION

Freshwater organisms living in high light environments have adapted defenses against damaging radiation. However, human activities are increasing UV-B radiation in freshwater habitats through a variety of mechanisms, including reducing atmospheric ozone, which absorbs incoming UV radiation; reducing water depths and thus attenuation of UV radiation; and altering amounts of suspended particles and dissolved organic matter in water columns, which absorb UV radiation. Freshwater habitats in polar regions and at high latitudes are most susceptible, as they have higher exposure.

Ultraviolet radiation harms primary producers (see Highlight 12.1). Increased UV-B radiation adversely affects oceanic bacterioplankton activity (Herndl et al., 1993), lake phytoplankton productivity (Harrison and Smith, 2009), and lake zooplankton communities (Williamson et al., 1994). Increased UV-B exposure also causes to abnormalities and death of amphibian larvae (Bancroft et al., 2008). Exclusion of UV radiation from stream mesocosms in New Zealand increased the abundance of aquatic insects by 54% (Clements et al., 2008). Ultraviolet radiation can interact with other toxic substances such as metals and pesticides, and nutrient levels can determine the level of damage from UV radiation (Carrillo et al., 2008). These interactions can be *synergistic*, in that effects are more than simply additive.

URBANIZATION

We have covered some of the areas where urbanization can influence aquatic habitats, but not in a cohesive fashion. Recently, the concept of *urban stream syndrome* has emerged in the literature as a pressing area of research given the fact that over half of the world's population lives in urban areas. Urban areas also have detrimental influences on lakes and wetlands. Urban stream syndrome includes flashier hydrographs, simplification of stream channels, concrete-lined channels, urban pesticide contamination, runoff of petrochemicals and salt from roadways, increased frequency/intensity of algal blooms, and reduced species richness (Walsh et al., 2005; Wenger et al., 2009; Cunha et al., 2017). Most of the research so far occurred in developed countries, but developing countries have their own set of problems (Booth et al., 2015; Capp et al., 2015; Loiselle et al., 2016). For example, cities do not treat their sewage in many developing countries, so streams become open sewers with the potential for disease transmission.

Urbanization can cause unnatural changes in streams, and understanding them requires comparison to local native conditions of streams. For example, in the desert Southwestern United States, watering lawns leads to runoff and formation of permanent streams where none existed before (Kaye et al., 2006). Stream channels can have open riparian canopy where they would naturally have closed canopy, and vice versa.

With respect to wetlands, the most common result of urbanization is draining and filling for development. However, some cities construct small retention ponds or wetlands to mitigate the flashy runoff caused by impermeable surfaces. Many of these wetlands are not hydrologically or biogeochemically similar to their natural counterparts (Stander and Ehrenfeld, 2009).

Urban lakes are often shallow, hypereutrophic, and have unnatural hydrology and morphology (Birch and McCaskie, 1999; Schueler and Simpson, 2001). Most people never experience a natural lake. These lakes are often used for runoff control and are exposed to many contaminates associated with cities. It is common for people to dam small streams to provide artificial lakes, which people find enticing and can increase residential property values. People want lakes that are crystal-clear and produce many big fish. This is very rare considering the anthropogenic pressures on such lakes and their drainage basins.

SUMMARY

1. Humans influence all surface waters on Earth.
2. Toxicologists are concerned with the acute and chronic effects of pollutants. Natural variations in uptake, sensitivities, concentration, additive effects of different pollutants, and effects of other environmental factors all complicate predictions of how a particular toxicant will influence a specific organism.
3. Biomagnification of pollutants can cause high concentrations of toxic compounds in the tissues of organisms at the top of food webs. The most lipid-soluble compounds usually magnify to the greatest degree. Metals, organochlorine pesticides, and PCBs are examples of highly persistent pollutants that readily bioaccumulate.
4. Bioassessment protocols are tools to assess the impacts of pollutants and other habitat alterations on aquatic communities. Indices for bioassessment are generally constructed using data on invertebrates or fishes that are present and the state of their habitat, but methods have been developed for all types of aquatic organisms and habitats.
5. Acid precipitation is mainly caused by humans burning fossil fuels, leading to increased sulfuric and nitric acid in the atmosphere. Acid mine drainage is also of concern in many regions of the world.
6. Acidification of aquatic ecosystems impacts all aquatic organisms.
7. Under acidic conditions, microbes degrade complex organic compounds more slowly, cyanobacteria and diatoms are selected against, filamentous green algae are selected for, invertebrates that use calcium carbonate become rare, aluminum has

a greater impact on fish gills, and reproduction of many animals is impacted negatively.

8. Metals can have a broad array of negative impacts on aquatic ecosystems. Mining wastes often cause contamination, but runoff from industrial applications and naturally occurring sources can cause problems as well. Mercury contamination of freshwater habitats has resulted in fish consumption warnings in many regions of the world.
9. Tens of thousands of organic compounds are discharged by humans into aquatic habitats, including pesticides, oil, and materials in urban runoff. Only a small percentage of these compounds have been tested for toxicity. In some cases, microbes can break down these compounds (bioremediation) given enough time.
10. Endocrine disruptors act as biological triggers and are linked to reproductive deformities in a variety of freshwater species.
11. Increasing prevalence of antibiotics from human and livestock waste in freshwater habitats leads to development of antibiotic resistant bacteria.
12. Freshwater organisms experience multiple stressors, which may interact in antagonistic, additive, or synergistic ways. This makes identification of the effects of one particular type of pollutant difficult.
13. Nanomaterials are becoming common contaminants with little understanding of their influences in fresh waters.
14. Suspended solids can cause harm to aquatic organisms. Generally, sediments interfere with photosynthesis from increased light attenuation and with respiration by clogging water flow. In streams, fine solids fill up and destroy gravel and cobble habitats, can increase scour associated with high flow, and reduce movement of water into subsurface habitats.
15. Thermal pollution can cause shifts in community structure. These shifts may allow for establishment of exotic species and local extinction of native species.
16. Urban areas have heavily altered freshwater habitats. Lakes, streams, and wetlands in urban areas receive substantial amounts of pollutants and are hydrologically altered; they generally do not represent natural habitats nearby.

QUESTIONS FOR THOUGHT

1. Why is biomagnification worse with lipid-soluble compounds that are resistant to abiotic and biotic deactivation?
2. Are there any habitats on Earth that have not been influenced by human activities?
3. What political conditions have led to a world in which toxicants are released routinely into the aquatic environment before even cursory testing of their effects on organisms, including humans, has been conducted?

4. Why can controls on emissions of greenhouse gasses ultimately decrease acid precipitation?
5. Why can acid precipitation lead to lower iron availability and greater phosphorus in some lakes and wetlands with anoxic sediments?
6. Why is bioremediation of metal contamination more difficult than that of contamination by organic compounds?
7. Why are microbes able to more rapidly evolve ways to inactivate toxicants and develop resistance than are fishes?
8. Under what conditions may suspended solids have positive influences on aquatic ecosystems?
9. Should aquatic scientists assume a role of advocacy with regard to issues of aquatic pollution, or should their role be primarily to provide data for informed decisions to be made by managers and policymakers?