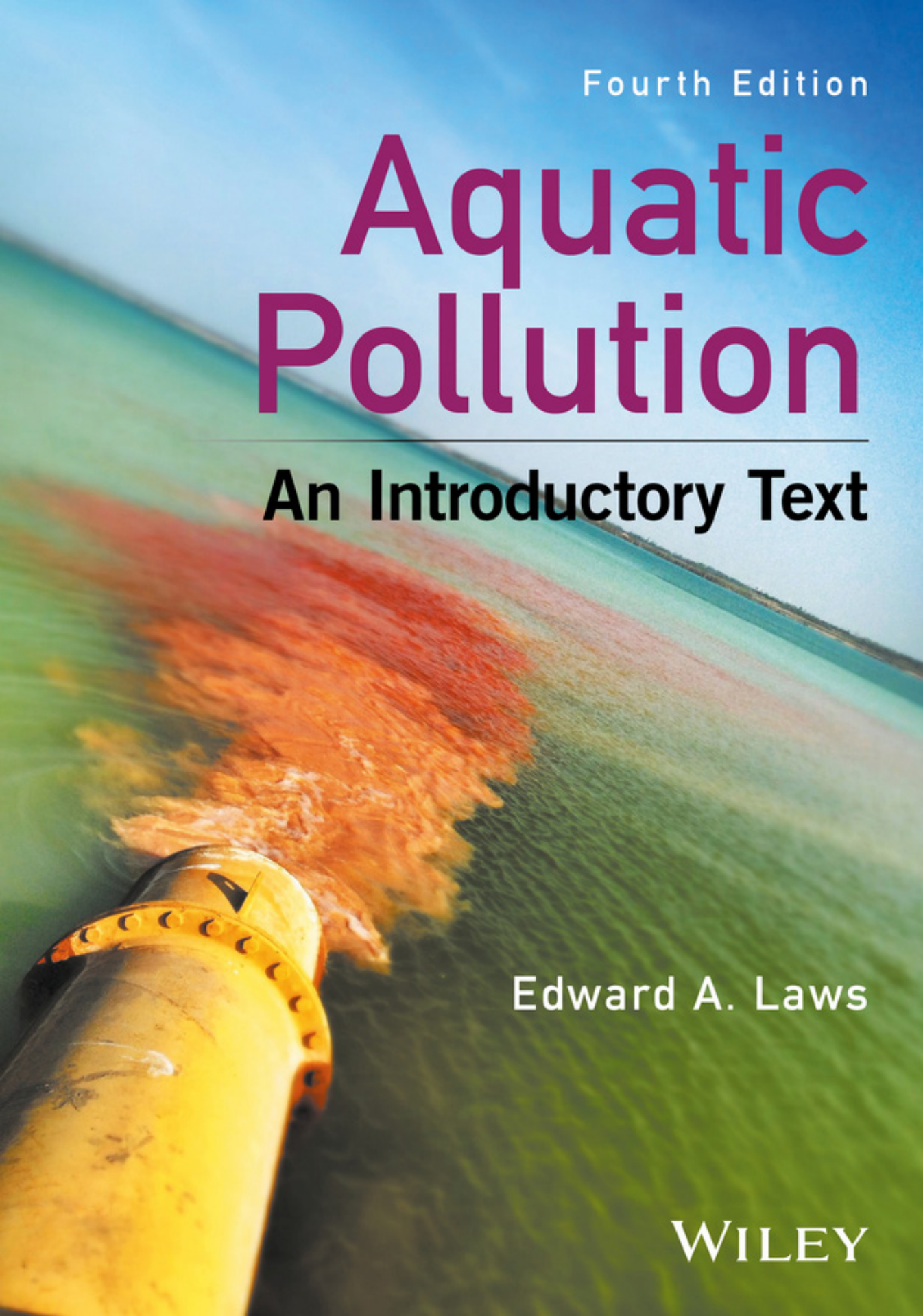




Fourth Edition

# Aquatic Pollution

**An Introductory Text**

Edward A. Laws

**WILEY**



## **Aquatic Pollution: An Introductory Text**



# **Aquatic Pollution: An Introductory Text**

*Edward A. Laws*

*Los Angeles, US*

Fourth Edition

**WILEY**

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## Preface

Since the first edition of *Aquatic Pollution* was published in 1980, the book has served as an introduction to the subject of water pollution for many undergraduate students. The fourth edition is organized in a similar way to the first three editions. The first three chapters serve as an introduction to physical, chemical, and biological concepts that are essential to understanding the impact of pollutants and stresses on aquatic systems. Chapter 8 is likewise an introduction to toxicological concepts relevant to the remaining chapters in the book. Each of the other chapters focuses on a particular kind of pollution, and in each of these chapters, the subject is illustrated with one or more case studies. The case studies include numerous examples from events and developments that had happened since the third edition of *Aquatic Pollution* was published in 2000.

Some of the news since 2000 has certainly been good. Phase I of the City of Chicago's tunnels and reservoir project (TARP) was completed in 2006; TARP is now capable of handling about 85% of the pollution caused by combined sewer overflows from an area of 842 km<sup>2</sup>. The concentration of phosphorus in Onondaga Lake, New York, sometimes characterized as the most polluted lake in the United States, dropped from 730 µg L<sup>-1</sup> in 1970 to less than 20 µg L<sup>-1</sup> in 2010 as a result of restrictions on the use of phosphorus in laundry detergents and tertiary treatment for phosphorus removal from wastewater. Brown pelicans, whose populations had been seriously impacted by the use of dichlorodiphenyltrichloroethane (DDT) and similar pesticides, were taken off the endangered species list in the United States in 2009. Likewise, bald eagles, whose population in the contiguous 48 states had been reduced to 417 pairs in 1963, have now increased to more than 11,000 pairs. The use of insecticides on corn declined by a factor of 10 between 1995 and 2010 as a result of the planting of genetically modified corn resistant to insect pests. In 2001, the EPA issued regulations that required closed cycle cooling systems on all new electric power plants to eliminate the killing of organisms drawn into once-cycle cooling systems, and in 2014, it promulgated additional regulations that required existing power plants that draw more than 2 million gallons per day of cooling water to take steps to minimize internal plant kills. In 2016, most use of mercury in the United States had been phased out, with the exception of its use in dental amalgams, and in 2008, the European Union issued a directive that restricted most uses of cadmium. The directive was amended in 2013 to specifically prohibit the use of cadmium in most nickel–cadmium batteries, which account for over 80% of cadmium use globally. Modifications to the International Convention for the Prevention of Pollution from Ships required a transition to double-hull oil tankers for all oil tankers greater than 20,000 deadweight tons by 2007, and analogous stipulations of the US Oil Pollution Act required a phaseout of single-hull tankers that operate in US waters by January 1, 2015, in order to reduce the frequency of oil spills from tanker accidents. Emissions of sulfur oxides from electric power plants in the United States declined by 84% between 1970 and 2014,

primarily as a result of the installation of scrubbers to eliminate emissions of sulfur oxides in stack gases. In 2015, the US Department of Agriculture announced the Ogallala Aquifer Initiative, which addresses the problem of overdrafting the Ogallala Aquifer, the largest aquifer in the United States. And in 2006, the US Congress passed the Marine Debris Research, Prevention, and Reduction Act, with the goal of reducing the amount of marine debris and its adverse effects on marine organisms. Under the auspices of the US Environment Program, the Stockholm Convention on Persistent Organic Pollutants was adopted in 2001 by 179 nations with the goal of protecting human health and the environment from persistent organic pollutants. The convention initially identified 12 persistent organic pollutants, the so-called dirty dozen, the use of which was to be banned or greatly restricted. The original list of 12 has now been extended to 22.

Unfortunately, not all the news has been good. Despite considerable efforts aimed at improving the water quality of the Chesapeake Bay, the area of benthic grasses in the bay has not increased since 2000 and is far below the target of 750 km<sup>2</sup> that was established in 2003. The catch of eastern oysters in the Chesapeake Bay declined from more than 10,000 tonnes in 1980 to 40 tonnes in 2004, and although there has been some improvement since then, the productivity of the eastern oysters is very much constrained by poor water quality and infection by parasites. Although water quality standards have been established, they are met only 30–40% of the time and seasonal hypoxia is a problem throughout the Chesapeake Bay.

Literally billions of dollars have been spent to improve the water quality of Lake Erie, but problems persist. The biggest problems have been the benthification of the lake by zebra mussels and quagga mussels; the ongoing nonpoint source runoff of nutrients, particularly from the Maumee River; and the domination of the phytoplankton community by cyanobacteria of the genus *Microcystis*, which produce a very potent liver toxin called microcystin. On August 2, 2014, the 500,000 residents of Toledo, Ohio, were advised not to drink their tap water when microcystin was detected at unacceptable concentrations in the water supply.

Monitoring of recreational waters to ensure that they are safe for water contact remains a very unsatisfactory state of affairs. Counts of indicator bacteria vary widely over time and space. The fecal indicator bacteria being used (*Escherichia coli* and enterococcus) are not uniquely associated with human feces<sup>1</sup>; some human pathogens (e.g., leptospira) are not even associated with feces. The length of time required to assay for fecal indicator bacteria, combined with the temporal variability of their abundance, confounds interpretation of monitoring results. Although the use of molecular methods may greatly improve the specificity of the assays and reduce the time required to obtain a result, the use of such methods will first require careful epidemiological studies that relate assay results to human health outcomes.

The number of malaria cases in countries such as Sri Lanka, Mexico, and Namibia has declined dramatically since 2000; the use of bed nets and other forms of integrated pest management has been an important component of successful strategies to reduce the incidence of the disease. However, there were still 214 million cases and 438,000 deaths from malaria in 2015, primarily in sub-Saharan Africa.

Although flesh-eating screwworm flies were eradicated in the United States in 1983, they reappeared in 2016 in the Florida Keys, where they were responsible for the deaths of 10% of the population of Key deer, an endangered species. Eradication of the screwworm flies via release of sterile males is expected to take six months.

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1 They are also found in soils and sand in tropical, subtropical, and temperate latitudes.

In 2014, the public water supply of the City of Flint, Michigan, became contaminated with lead, and the state of Michigan subsequently identified 43 people suffering from elevated levels of lead. The problem was caused by leaching of lead from pipes in the water distribution system, the result of an unfortunate decision to switch the water supply from Lake Huron to the Flint River. Water from the latter turned out to be highly corrosive to the pipes in the distribution system.

The largest accidental oil spill ever occurred in 2010 as a result of the blowout of the Deepwater Horizon oil platform in the Gulf of Mexico approximately 80 km from the coast of Louisiana. About 700,000 tonnes of oil and the oil equivalent of an additional 280,000 tonnes in the form of gaseous hydrocarbons were released. About 0.77 million gallons of a dispersant, Corexit 9500, was applied to the oil emerging from the wellhead in an attempt to break it up into small droplets that would remain submerged, and an additional 1.4 million gallons of a combination of two dispersants, Corexit 9500 and Corexit 9527, was applied to the oil that reached the surface. The full extent of the damage caused by the oil and dispersant may not be known for several years, but more than 400 km<sup>2</sup> of coastal land was lost as a result of the killing of wetland vegetation along the shoreline.

The following year, an undersea earthquake, the fourth most powerful earthquake to occur in the world since modern record keeping began in 1900, generated a tsunami that breached the 10-m seawall protecting the Fukushima Daiichi nuclear power plant in Japan. Loss of electrical power resulted in failure of the pumps that provided cooling water to three of the plant's nuclear reactors, which subsequently overheated as a result of the radiation emitted by fission products in their fuel elements. A series of chemical reactions then resulted in a number of hydrogen–air explosions during the next several days that blew the roof off one of the reactors and destroyed the upper part of the building housing another. The accident resulted in a release of radioactivity equal to 6–15% of the radioactivity released 25 years earlier by the Chernobyl power plant accident in Ukraine. Roughly 80% of the radioactivity entered the Pacific Ocean. Approximately 300,000 people were evacuated from the area surrounding the reactor. As a result of the accident, Japan shut down all but two of its nuclear reactors and Germany announced that it would close all of its nuclear power plants by 2022.

In addition to these recent developments, the book also includes many examples from the past, primarily because of their didactic value. Those examples include the accounts of Minamata disease and itai-itai disease in Japan, the recoveries of Lake Washington in Seattle and Kaneohe Bay in Hawaii after diversion of sewage, the history of use of DDT both in the United States and globally, the impact of the Exxon Valdez oil spill in Alaska, the consequences of the Chernobyl nuclear power plant accident in Ukraine, and the contamination of groundwater by improper disposal of toxic wastes at the Rocky Mountain Arsenal in Colorado.

The text of the fourth edition has been supplemented by a glossary of words and terms that may not be familiar to a student being introduced to the subject of water pollution. These words and terms are set in boldface where they first appear in the text, and the chapters where they first appear are noted in the glossary.

I am indebted to several people who provided me with suggestions and feedback concerning the fourth edition. Those persons include Dr Fred Dobbs at Old Dominion University, Dr Nicolas Cassar at Duke University, Dr. Alexandria Boehm at Stanford University, and Dr Eric DeCarlo at the University of Hawaii, all of whom have used the third edition in courses that they teach. I would also like to acknowledge the outstanding help of Brooks Bays, Jr., at the University of Hawaii for his help with the graphics. I am also indebted to Louisiana State University for granting me a sabbatical leave that provided me with the time I needed to complete much of the writing. I would also like to acknowledge the support of Dr Siyuan Ye at the

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## 1

## Fundamental Concepts

The introduction of pollutants into aquatic systems is a perturbation that can set off a complicated series of biological and chemical reactions. Some knowledge and appreciation of basic ecological concepts is necessary to understand and anticipate the nature of those reactions. Let us consider a simple example. Assume that an industry is discharging wastewater into an estuary. The wastewater contains mercury, which is a toxic metal. The mercury in the water reduces the photosynthetic rates of algae in the vicinity of the discharge.

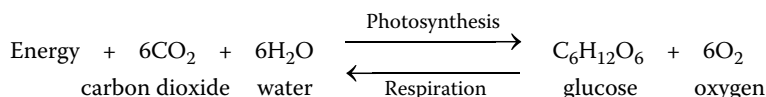
Would the stress on the algae be the extent of the impact? Unfortunately, the answer is no. The reduction of photosynthetic rates would be only the first step. To the extent that photosynthetic rates were lowered, the food supply of herbivores would be reduced, and their biomass and production rates would also be lowered. Furthermore, the herbivores would assimilate some of the mercury absorbed by the algae and become stressed by the presence of the mercury in their tissues. Thus the herbivores would be affected adversely both by a reduction in their food supply and by the presence of mercury in their bodies. Using the same logic, it is easy to imagine how animals that preyed on the herbivores could be affected through similar mechanisms and how predator/prey interactions could ultimately spread the mercury to every organism in the water. Obviously some understanding of the feeding relationships in a natural aquatic system is necessary to appreciate and anticipate the effects of such pollutants.

Now suppose that the mercury discharges ceased. Would the system recover and return to its original condition? Perhaps, but not necessarily. The stability of natural systems to perturbations such as pollutant discharges is a fundamental area of study in systems analysis and a critical consideration in the understanding of pollutant effects. The fact that a natural system is in equilibrium by no means guarantees that the system will return to the original state following a perturbation. To cite a popular example, had a very small meteor struck Earth 65 million years ago, it is possible that a few dinosaurs might have been killed or injured. However, the condition of the dinosaur population would have very likely returned to normal within a short time through natural processes. It is now generally agreed, however, that the extinction of all the dinosaurs was probably caused by a very large meteor that struck Earth about 65 million years ago. Conditions on Earth for a period of time following that event are believed to have been incompatible with the survival of dinosaurs, the result being that the system did not return to its pre-event status.

## Simple Food Chain Theory

With this introduction, let us consider some basic ecological principles that relate to the movement and transformation of pollutants within aquatic systems. All animals require food. Food may be burned (respired) to provide energy or incorporated into the animal's body in the form

of proteins, fats, carbohydrates, and other compounds to provide essential structural or metabolic components. Plants are by far the most important producers of food in most aquatic systems, although certain **bacteria** may be significant producers in some parts of the deep sea (Jannasch and Wirsen 1977). Plants utilize sunlight as an energy source to manufacture **organic compounds** from carbon dioxide, water, and various inorganic nutrients in a process called **photosynthesis**. For example, a simplified equation describing the manufacture of glucose may be written.

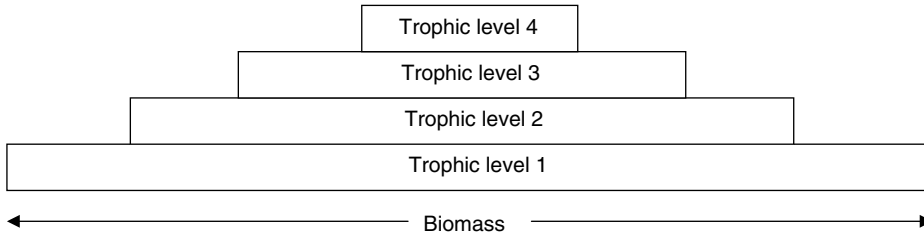


In this case glucose is the organic compound; the term organic means that the compound is found in organisms. If the reaction proceeds from left to right, the energy source is sunlight. Part of this energy is stored chemically in the glucose molecule. If the glucose is then oxidized by burning it with oxygen, the reaction proceeds from right to left, and the energy stored in the glucose is released. Some of that energy is made available to the organism mediating the respiratory process and is used to perform various metabolic functions. It is common practice to use either organic carbon or its associated chemical energy content as a metric for food supply, 1 g of organic carbon being associated with an energy content of 8–11 kilocalories (kcal). All animals have the ability to transform organic compounds from one form to another and hence to convert their food into the compounds they require. However, only plants and certain bacteria have the ability to manufacture organic high-energy compounds from inorganic low-energy constituents, and it is this transformation that is referred to as **primary production**. If the energy needed to drive the transformation comes from light, the process is called photosynthesis. If the energy is obtained from chemical reactions involving inorganic compounds, the process is called **chemosynthesis**. Only certain types of bacteria and **fungi** are capable of mediating the latter process. All living organisms depend either directly or indirectly on primary producers as a source of food. Organisms that can produce most or all of the substances they need from inorganic compounds are called **photoautotrophs** or **chemoautotrophs**, depending on whether the energy needed to effect the conversion comes from light or the reactions of inorganic chemicals, respectively. Organisms that lack autotrophic capabilities are called **heterotrophs**. The production of biomass by heterotrophs involves the conversion of some form of organic matter (food) into living biomass and is called **secondary production**.<sup>1</sup> Plants are **autotrophs**, and animals are heterotrophs. Most bacteria are heterotrophs, although some bacteria do have well-developed photoautotrophic or chemoautotrophic capabilities.

A plant-eating heterotroph, or **herbivore**, may consume food initially produced by a plant. The herbivore may in turn be eaten by another heterotroph, or **primary carnivore**, which converts part of the herbivore biomass into primary carnivore biomass. The primary carnivore may in turn be eaten by another heterotroph, or **secondary carnivore**, which in turn may be eaten by a **tertiary carnivore**, and so forth. Ecologists refer to such a system of successive food transfers as a **food chain**. Each component of the food chain is called a **trophic level**. In the example given, plants would make up the first trophic level, herbivores the second trophic

<sup>1</sup> The term secondary production has sometimes been taken to mean the production of organisms that consume primary producers (Levinton 1982) or the production of biomass by animals (Lalli and Parsons 1997). The definition given here implies that secondary production includes the production of both animal and bacterial biomass by heterotrophic processes and is consistent with Strayer (1988) and Scavia (1988).





**Figure 1.2** Trophic level biomass through trophic level four in a hypothetical food chain.

The decrease in biomass on successive trophic levels is, however, less than the factor of 5 that one might expect based on an ecological efficiency of 20%. The reason follows from the fact that the ratio of the fluxes of organic matter between trophic levels 3 and 4,  $F_{34}$ , and between trophic levels 2 and 3,  $F_{23}$ , for example, can be written as follows:

$$\frac{F_{34}}{F_{23}} = E = \frac{F_{34} \left( \frac{B_3}{B_3} \right)}{F_{23} \left( \frac{B_2}{B_2} \right)} = \frac{T_3 B_3}{T_2 B_2} \quad (1.1)$$

where  $E$  is the ecological efficiency,  $B_2$  and  $B_3$  are the biomasses on trophic levels 2 and 3, respectively, and  $T_2$  and  $T_3$  are the **turnover rates** of organic matter on trophic levels 2 and 3, respectively, and are equal to  $F_{23}/B_2$  and  $F_{34}/B_3$ , respectively. The turnover rates are just the rates at which organic matter on one trophic level is being consumed by the next trophic level divided by the biomass of organic matter on that trophic level. From Eq. (1.1), it follows that

$$\frac{B_3}{B_2} = E \frac{T_2}{T_3} \quad (1.2)$$

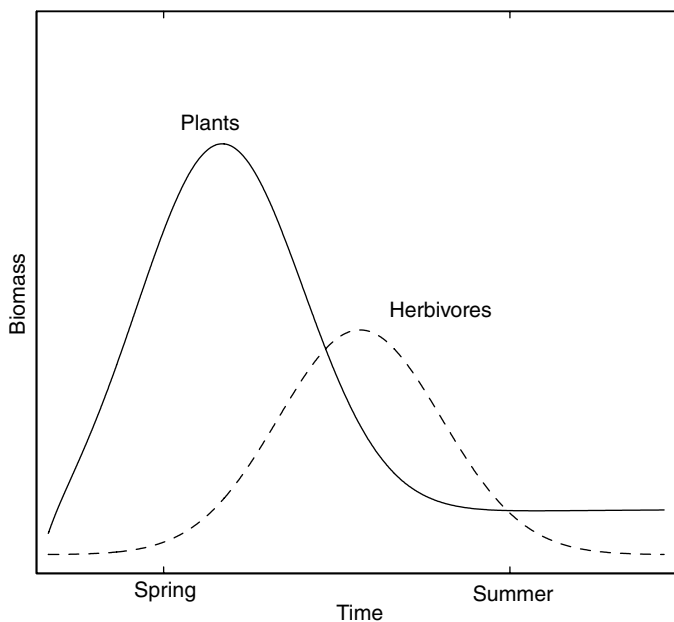
If the turnover rates on successive trophic levels were all the same, Eq. (1.2) implies that the ratio of biomasses on successive trophic levels would equal the ecological efficiency, but in fact the turnover rates of organic matter on successive trophic levels are typically not the same. In general, one expects predators to be larger than prey, and hence higher trophic level organisms tend to be larger than lower trophic level organisms. This expectation is generally fulfilled, although there are certainly exceptions to the rule (Longhurst 1991). For example, animals that hunt in groups or packs, such as wolves or killer whales, may kill organisms larger than themselves. However, predators are usually larger than their prey, and as a result the number of organisms on successively higher trophic levels decreases even more rapidly than the total biomass. Although it is generally true that large organisms consume more food than small organisms, it is also generally true that large organisms consume less food per unit biomass (i.e., have a lower turnover rate) than do small organisms. The relationship between organism size and metabolic rate is such that, if two organisms differ in weight by a factor of 10,000, the larger organism can be expected to consume only 10% as much food per unit body weight as the smaller organism. In other words, the larger organism would consume about 1000 times as much food as the smaller organism, or  $1000/10,000 = 1/10$  as much food per unit body weight.

Now consider a case in which the size of individual organisms on successive trophic levels differs by a factor of 10,000, and the ecological transfer efficiency between the trophic levels is 20%. In this case the ratio of turnover rates on trophic levels 2 and 3, for example, would be 10,



and a steady-state situation might exist in which the total biomass of trophic level 3 was twice that of trophic level 2. In other words, in Eq. (1.2),  $E = 20\%$ ,  $T_2/T_3 = 10$ , and the ratio of biomasses equals 20% of 10, or 2. Although the third trophic level received only 20% as much food as the second trophic level, the third trophic level would need only 10% as much food to support a given amount of biomass as the second trophic level. Thus the logical arguments that lead us to expect an ecological pyramid of biomass need not apply to food chains in which the size of organisms on successive trophic levels differs greatly, because these arguments implicitly assume the food requirements per unit biomass of all trophic levels to be identical. The fact that normal ecological pyramids of biomass are found in most natural aquatic food chains (e.g., Odum 1971, p. 80; Sheldon et al. 1972) indicates that differences in organism size on successive trophic levels are not sufficiently great to invert the pyramids. Nevertheless, the difference in successive trophic level biomasses is often less than the factor of 5 that would be expected to result from transfer efficiencies of 20% if all organisms required the same amount of food per unit biomass (see Question 1.8). Thus organism size differences tend to reduce, but not eliminate, the effect of low ecological transfer efficiencies on trophic level biomass structure.

A caveat to the scenario depicted in Figure 1.2 is the fact that it is quite possible in non-steady-state systems for the distribution of biomass in two or more trophic levels to become temporarily inverted. In other words, trophic level biomass increases rather than decreases with increasing trophic level number. For example, in temperate oceans and lakes, a so-called bloom of plant biomass may occur in the spring as the water temperature and average daily solar insolation increase. This plant bloom generally does not occur at a time when the herbivore biomass is large, but the herbivore biomass begins to rapidly increase shortly thereafter in direct response to the increase in herbivore food. Typically herbivore grazing reduces the plant biomass to a low level. Herbivore biomass peaks and then declines. The fall in herbivore biomass is caused both by the decrease in herbivore food and by grazing pressure from primary carnivores. Figure 1.3 shows qualitatively how plant and herbivore biomass may vary with time during this period.



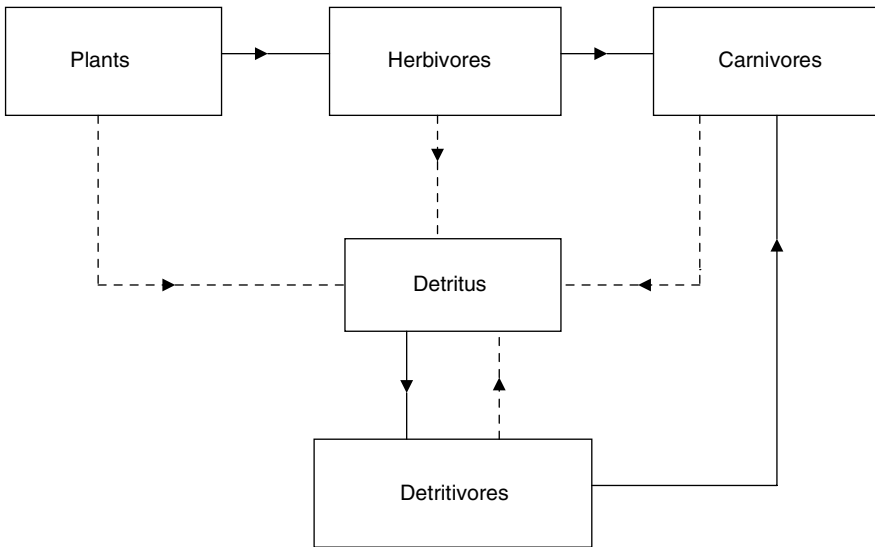
**Figure 1.3** Biomass of plants and herbivores during spring and early summer in a hypothetical temperate aquatic ecosystem.

A system in which the herbivore biomass is greater than the plant biomass for a short period following the plant bloom is apparent in Figure 1.3. Such a condition may exist for a short time in many aquatic systems that are subject to large-scale seasonal cycles. During this period the first two trophic level biomasses form a so-called inverted pyramid, because the second trophic level biomass is greater than that of the first. This situation lasts for only a short time, and the average distribution of biomass is similar to Figure 1.2. The logical arguments that lead us to expect a normal pyramid of biomass do not necessarily apply in a non-steady-state system, because over short time intervals predators may consume more food than prey are producing and hence reduce the prey biomass to a low level. Obviously this situation cannot persist for long; otherwise the predators would destroy their food supply. Hence on the average one does expect to see a normal pyramid of biomass.

### Recycling and the Microbial Loop

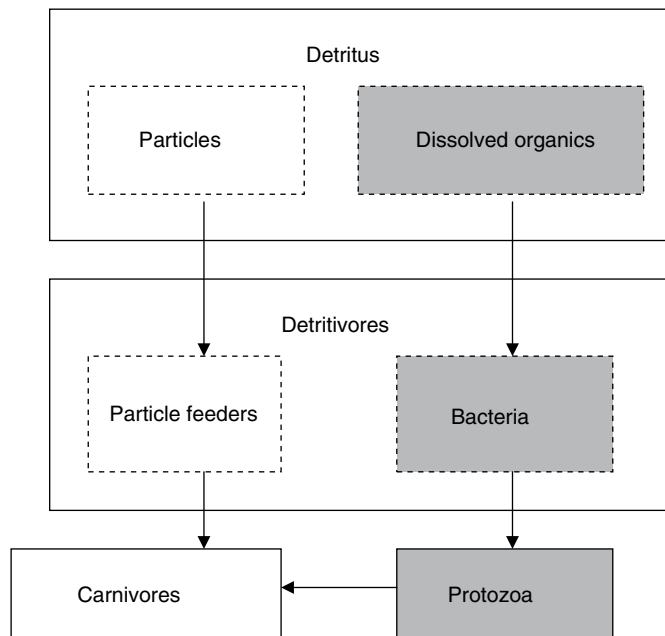
The food chain we have discussed up to this point is called the **grazing food chain**, because the second and higher trophic levels consist of predators that graze upon prey. Primary producers occupy the first trophic level of the grazing food chain. A very important companion of the grazing food chain in any healthy aquatic system is the **detritus food chain**. The first trophic level in the detritus food chain is the nonliving organic matter produced by living organisms. This nonliving organic matter may exist either as particles or as dissolved organic substances and is referred to as **detritus**. The detritus provides food for a category of organisms called **detritivores**, a designation that includes both bacteria and certain metazoans. Bacteria have no mouthparts and hence, strictly speaking, must feed entirely on dissolved organics. However, by exuding enzymes they are able to solubilize and hence make use of particulate material as well. Metazoan detritivores such as benthic worms feed primarily on particulate detritus. Because detritivores are living organisms, they respire and excrete organics, just as do the members of the grazing food chain. The organic compounds excreted by detritivores may very likely be used as food by other detritivores, and as a result only the most refractory organic compounds accumulate in the system. Most of the organic matter initially synthesized by the primary producers is ultimately respired, either by organisms in the grazing food chain or by detritivores. Animals or protozoans consume the detritivores, and in this way some of the organic carbon excreted by the grazing food chain is recycled back into the grazing food chain. The process is illustrated schematically in Figure 1.4. The portion of the detritus food chain involving dissolved organics, bacteria, and **protozoans** is often referred to as the **microbial loop** (Fig. 1.5) and is believed to account for much of the degradation of detritus in aquatic systems.

It is apparent from Figure 1.4 that the grazing food chain and the detritus food chain are interconnected and do not function independently of each other. The interaction between the two food chains is a mutualistic one, that is, favorable to both and obligatory. The grazing food chain benefits the detritus food chain by excreting much of the organic matter needed by the detritivores for food; the detritus food chain benefits the grazing food chain by removing potentially toxic waste products excreted by both food chains. An approximate balance between the **anabolism** and **catabolism** of organic matter is essential to the maintenance of a stable aquatic ecosystem. In a system in which primary production on the average exceeds respiration, organic matter in the form of either plant or animal biomass or detritus will accumulate in the system. Eventually the whole system may fill up with organic sediments. In fact, exactly this process does occur, although often at a very slow rate, in most freshwater habitats and in some marine basins. This gradual accumulation of organic debris results in part from the fact that some detritus is rather refractory and not efficiently broken down by detritivores. In contrast, if respiration exceeds primary production, then a net consumption of biomass is occurring



**Figure 1.4** Box model of the grazing and detritus food chains and the interactions between the two food chains. Solid lines represent feeding relationships. Dashed lines represent excretion.

**Figure 1.5** Box model of the detritus food chain leading to the carnivore trophic level of the grazing food chain. The gray shaded boxes constitute the microbial loop.



within the system. Such a system cannot persist unless subsidized by an external input of organic compounds, as, for example, from stream runoff.

It is important to realize that primary producers and detritivores use the waste products resulting from respiration and excretion, respectively, to create living biomass. For example, carbon dioxide, which is a direct product of respiration, is the source of carbon for primary production. Ammonia (as ammonium ions), which many aquatic organisms excrete, can be

directly assimilated by primary producers as a source of nitrogen for the production of proteins and nucleic acids. Waste products can be, and often are, toxic to the organisms that produce them. However, in a well-balanced ecosystem, waste products never reach high concentrations, because they are constantly being used as a source of food by other organisms in the system. Detritivores play a crucial recycling role in aquatic systems by consuming organic wastes and converting them to inorganic forms that are used by primary producers. The grazing food chain uses the organic matter synthesized by the primary producers and releases part of it in the form of detritus, which in turn provides the food for the detritus food chain.

Because of this internal recycling, there is a tendency for both organic and inorganic compounds to accumulate in aquatic systems. Inorganic carbon can of course escape to the atmosphere as carbon dioxide, and inorganic nitrogen may similarly escape as ammonia,  $N_2O$ , or  $N_2$ , all of which are gases. However, under normal circumstances, the latter escape routes are not very efficient for nitrogen, and removal of organic compounds and essential nutrients via washout rarely occurs with 100% efficiency. The accumulation of refractory organic debris in the sediments and buildup of organic matter and nutrient concentrations in the water column are natural processes in most aquatic systems. Associated with these phenomena are increases in the rates of primary production and respiration and a decrease in the depth of the system caused by sediment accumulation. The whole process is referred to as **eutrophication**. Eutrophication eventually causes most lakes to fill up with sediments after a time of perhaps hundreds, thousands, or even tens of thousands of years. Sediments do accumulate at the bottom of the ocean, but the sediments are removed by tectonic processes at subduction zones at rates that approximately balance their rate of formation. Obviously there is no danger that the oceans will fill up with sediments. However, some regions of the ocean are much more productive than others, and this fact directly reflects the relative efficiency with which essential nutrients are recycled by the grazing and detritus food chains in different parts of the ocean.

Eutrophication is sometimes considered to be an unnatural phenomenon, but the imbalance between photosynthesis (P) and respiration (R) associated with eutrophication is nothing new. It was a fact of life on Earth literally billions of years ago.<sup>2</sup> The atmosphere of Earth was initially devoid of oxygen, and the oxygen in the atmosphere and ocean today is the product of photosynthesis. The first primitive plants evolved in the ocean, where the water shielded them from ultraviolet radiation. The oxygen produced by those plants eventually accumulated in the ocean and atmosphere, and photochemical reactions in the atmosphere converted some of the oxygen to ozone. The oxygen and ozone in the atmosphere then became a shield against ultraviolet radiation. It was only after the establishment of this oxygen and ozone shield that organisms were able to leave the ocean and evolve on land. Thus the very habitability of the terrestrial environment today depends on the fact that there was an excess of photosynthesis over respiration on a grand scale during the early evolution of life on Earth. However, the imbalance between P and R has had other profound implications. Oxygen is one product of photosynthesis. The other product is organic matter. The imbalance between P and R during the geologic history of Earth has resulted in the accumulation of both oxygen and organic matter. The existence of oil and coal deposits is an obvious manifestation of the imbalance between P and R over geologic time.

Any unnatural acceleration of the eutrophication process due to the activities of humans is called **cultural eutrophication**. Cultural eutrophication could be caused, for example, by the discharging of sewage containing a high concentration of nutrients and organic matter. Instances of cultural eutrophication constitute one of the most common and widespread examples of water pollution problems. We will explore a few of these examples in detail in Chapter 4.

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2 Earth is approximately 4.5 billion years old. Primitive forms of life began to appear about 3.5–4.0 billion years ago.

### Food Chain Magnification

Respiration and excretion obviously play a critical role in controlling the flux of organic and inorganic materials between the grazing and detritus food chains. However, from the standpoint of water pollution, respiration and excretion are also important in determining the movement of pollutants both between and within these same food chains. If the pollutant is biodegradable, it may of course be catabolized and rendered harmless. However, if the pollutant is nonbiodegradable, it may be passed from prey to predator and in this way be spread throughout the grazing food chain. If some of the pollutant is excreted, then it may spread to the detritus food chain as well. One of the most important applications of food chain theory to water pollution problems has been the effort to explain how these transfers of a pollutant between food chains and trophic levels affect the concentration of the pollutant in organisms. In cases where it has been possible to examine in some detail the distribution of pollutant concentrations among the trophic levels in a simple food chain, results have sometimes indicated a steady increase in concentration with increasing trophic level number. Table 1.1 shows concentrations of the pesticide DDT (plus the closely related compounds DDD and DDE) in the water and in various organisms taken from a Long Island, New York, salt marsh. The residue concentrations increase steadily from the plankton to the small fish to the larger fish and finally to the fish-eating birds. The total concentration factor from plankton to fish-eating birds is roughly 600. Observations such as this one led some scientists to believe that a common mechanism or explanation might underlie similar observations of increasing pollutant concentrations at higher trophic levels in some food chains, a phenomenon that they termed **food chain magnification**.

A logical explanation for food chain magnification is forthcoming from food chain theory if one assumes that certain pollutants ingested with an organism's food are not as effectively respired or excreted as is the remainder of the food. A metabolite of DDT, DDE, would seem to be a likely candidate for such a pollutant, because it is resistant to biological breakdown and

**Table 1.1** DDT residues in organisms taken from a Long Island salt marsh.

| Organism                         | DDT residues (ppm) <sup>a</sup> |
|----------------------------------|---------------------------------|
| Water                            | 0.00005                         |
| Plankton                         | 0.04                            |
| Silverside minnow                | 0.23                            |
| Sheepshead minnow                | 0.94                            |
| Pickrel (predatory fish)         | 1.33                            |
| Needlefish (predatory fish)      | 2.07                            |
| Heron (feeds on small animals)   | 3.57                            |
| Tern (feeds on small animals)    | 3.91                            |
| Herring gull (scavenger)         | 6.00                            |
| Fish hawk (osprey) egg           | 13.8                            |
| Merganser (fish-eating duck)     | 22.8                            |
| Cormorant (feeds on larger fish) | 26.4                            |

Source: Woodwell et al. (1967).

a) Parts per million (ppm) of total residues, DDT + DDD + DDE (all of which are toxic), on a wet weight whole-organism basis.

tends to be stored in an organism's fatty tissues rather than being directly excreted with other waste materials that the organism is unable to use. Equation (1.2) tells us that the ratio of the biomass of organic matter on successive trophic levels in a food chain is equal to the product of the ecological efficiency and the ratio of **turnover times** of the organic matter on successive trophic levels. The logical reasoning that led to Eq. (1.2) also applies to a pollutant. Therefore

$$\frac{P_3}{P_2} = E_p \frac{T_{2P}}{T_{3P}} \quad (1.3)$$

where  $P_2$  and  $P_3$  are the amounts of the pollutant on trophic levels 2 and 3, respectively;  $E_p$  is the efficiency with which the pollutant is transferred from one trophic level to the next; and  $T_{2P}$  and  $T_{3P}$  are the turnover rates of the pollutant on trophic levels 2 and 3, respectively. The flux of the pollutant from trophic level 2 to trophic level 3 is equal to  $F_{23}(P_2/B_2)$ , and  $T_{2P}$  is equal to this flux divided by  $P_2$ . Therefore  $T_{2P} = F_{23}(P_2/B_2)/P_2 = F_{23}/B_2 = T_2$ . The turnover rates of the pollutant are therefore the same as the turnover rates of organic matter. The ratio of the concentrations of the pollutant on trophic levels 3 and 2 is therefore

$$\frac{(P_3 / B_3)}{(P_2 / B_2)} = \left( \frac{P_3}{P_2} \right) \left( \frac{B_2}{B_3} \right) = \frac{E_p \left( \frac{T_{2P}}{T_{3P}} \right)}{E \left( \frac{T_2}{T_p} \right)} = \frac{E_p}{E} \quad (1.4)$$

Therefore the ratio of the concentrations of the pollutant on successive trophic levels is equal to the ratio of the efficiency with which the pollutant is transferred between successive trophic levels to the ecological efficiency.

Consider, for example, a case in which the ecological transfer efficiency of food between trophic levels is 20%, but in which the transfer efficiency of DDE, caused by its resistance to respiration and excretion, is 60%. As a result, the steady-state concentration of DDE in a predator will be about three times the DDE concentration in its food, because the predator retains three times (60% vs 20%) as much of the DDE that it eats as it does of its food. If this process is repeated through four trophic level transfers, the concentration of DDE in the fifth trophic level will be  $3^4 = 81$  times the DDE concentration in the first trophic level.

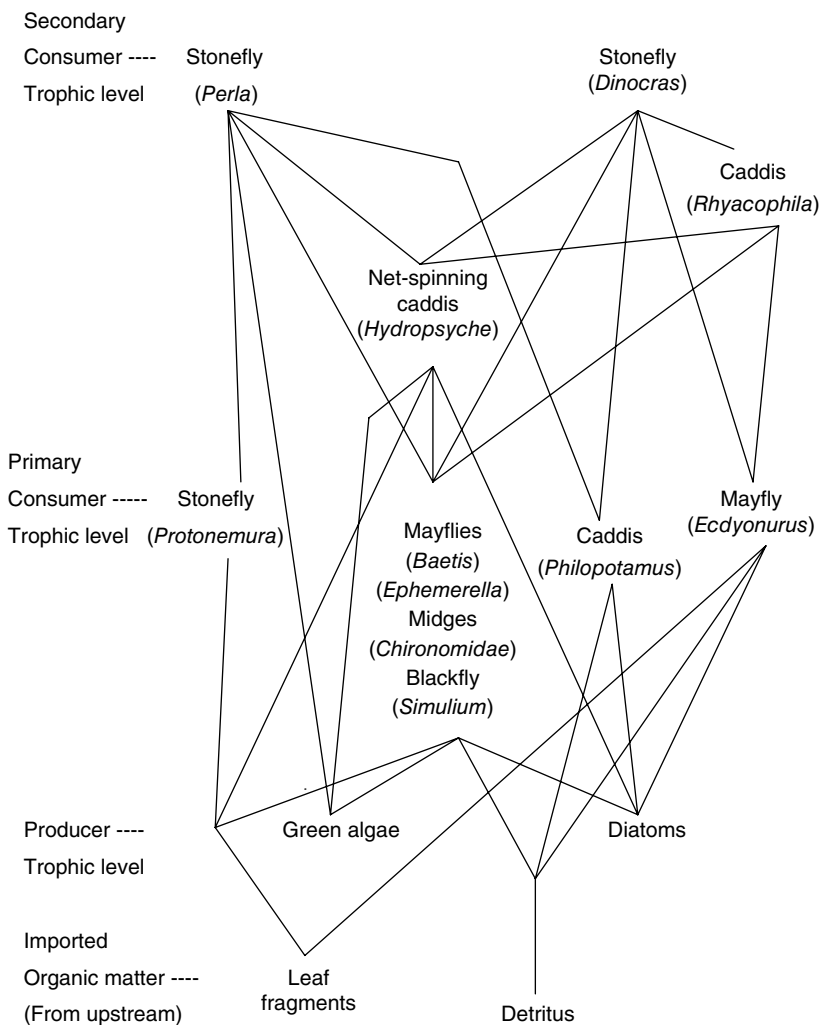
Although this reasoning is logical enough, the logicity of the reasoning by no means guarantees that food chain magnification of the sort described is responsible for observations such as those in Table 1.1. Pollutant concentration trends of exactly this sort may be produced by mechanisms very different from food chain magnification. Only carefully designed experiments can sort out the possible causes of such concentration trends. In Chapter 10 we will examine one such experiment in some detail. The point here is not to argue the pros and cons of the theory of food chain magnification, but rather to show how some knowledge of the characteristics of food chains can lead to a logical hypothesis regarding pollutant effects that is worth testing with further study. Logical thinking and hypothesis testing of this sort, based on sound ecological principles, represent the best means for studying and solving water pollution problems.

## Food Webs

Now that we have developed a simple food chain model as a conceptual basis for examining ecological problems, it is best to back up a step and remind ourselves that the world is not really so simple. The feeding behavior of many animals is such that they cannot be assigned to a

unique trophic level. Some animals, such as shrimp, will eat almost anything they can swallow, including plants, detritus, and other animals. Obviously they cannot be assigned to one or even a few trophic levels. Other organisms may feed on one trophic level as juveniles, a second trophic level at a later developmental stage, and a third trophic level as adults. In such a case one would have to treat each developmental stage of the species as a different organism in order to make unique trophic level assignments. Certainly the kind and quantity of available food influence the feeding habits of many organisms. Figure 1.6 indicates the complex feeding relationships found in a small stream community.

The pattern of lines indicating the feeding relationships in such a system forms a sort of web, and the feeding pattern has therefore come to be known as a food web. Certainly a food web depicts a more complex system than that represented by a food chain. One may therefore ask whether any of the implications deduced from food chain theory are relevant to a world that seems to be much more complex. The answer to this question is “yes” for the following reasons.



**Figure 1.6** Diagram of the feeding relationships in a small stream community in South Wales. Source: Jones (1949).

First, even though it is true that many organisms feed on more than one trophic level, it is also true that many organisms show a preference for one kind of food or another and can be reasonably defined as belonging to primarily one or two trophic levels. Although there are exceptions to this rule, the exceptions are not so numerous as to warrant discarding the concept of food chains.

Second, and perhaps more important, is the fact that some implications of food chain theory do not even require one to assign specific organisms to specific trophic levels. The idea that a large percentage of a prey will be either respired or excreted by the predator is valid regardless of the identity of the prey and predator. Thus food in an abstract sense is produced by plants and is passed through a series of feeding transfers from one trophic level to the next, with roughly 80% of the food's being respired or excreted at each transfer. Therefore, on average the biomass of food that has passed through  $m$  such transfers is likely to be much less than the biomass of food that has passed through  $m - 1$  transfers. If one thinks of trophic levels in terms of a series of food transfers, and not necessarily in terms of particular organisms eating particular organisms, the problem of assigning each organism to a unique trophic level disappears.

Despite this second point, it is in fact the case that the effect of pollutants on particular organisms is sometimes discussed with reference to an organism's position in the food chain. The relevance of food chain theory to such discussions is based on the first of the above two arguments, namely, that many organisms may be reasonably assigned to one or two trophic levels. For example, it is reasonable to assume that a pelican does not eat microscopic plants and animals, bacteria, protozoans, or even small fish, nor does a pelican eat whales, dolphins, or sea lions. Rather, a pelican eats fish of the size (approximately a few tens of centimeters) that can be conveniently scooped up in its mouth. Thus a pelican would be assigned to roughly the fourth trophic level in a grazing food chain. Such reasoning, while not flawless, is unlikely to be wildly in error. Nevertheless, whenever food chain arguments are invoked, one should keep in mind that the theory has its shortcomings and that the feeding relationships of some organisms can be very complex.

## Food Webs and Ecosystem Stability

The complexity of aquatic food webs is associated with another controversy that is particularly relevant to the problem of water pollution. The controversy concerns the stability of ecosystems. To what extent will a biological community resist change when stressed by pollution, and will the system return to its original state if the pollution stress is removed?

In the 1950s and 1960s, a number of publications appeared in the literature, suggesting that the complex interactions between organisms in a food web tended to stabilize the biological system. MacArthur (1955), for example, suggested that community stability might be roughly proportional to the logarithm of the number of links in the food web, a hypothesis that unfortunately has sometimes been accorded the status of a theorem. The hypothesis is based on conclusions derived from information theory, in which it is shown that such a logarithm provides a measure of the degree of organization or complexity. One then argues intuitively that the greater the number of links and pathways in the food web, the greater the ability of the system to damp down perturbations and hence the greater the chance that the system can absorb environmental shocks without falling apart. Examples of stable and very complex ecosystems include tropical rain forests and coral reefs.

A very elegant and understandable treatment of this issue has been provided by Robert May (1974). The somewhat counterintuitive result of May's analysis is that greater food web complexity *per se* does not impart greater stability to the ecosystem. In fact, the more complex the



linkages in the food web, the more unstable the system is likely to become. As noted by May (1974, p. 75), “The greater the size and connectance of a web, the larger the number of characteristic modes of oscillation it possesses: since in general each mode is as likely to be unstable as to be stable (unless the increased complexity is of a highly special kind), the addition of more and more modes simply increases the chance for the total web to be unstable.” The fact that tropical rain forests and coral reefs are highly complex systems may therefore be due more to the fact that these ecosystems exist in stable environments than to some inherent stabilizing characteristics conferred by the complex links in their food webs. May (1974) was careful not to rule out the latter possibility and noted that some very special and mathematically atypical sorts of complexity might enhance ecosystem stability but that it would be unwise to assume that as a general rule food web complexity implies stability. In fact, “If there is a generalization, it could be that stability [of the environment] permits complexity” (May 1974, p. 76).

An important point to bear in mind is that the foregoing discussion of stability and complexity pertains to complexity of food web linkages only. Other types of complexity may confer stability on ecosystems. For example, habitat complexity may provide refuges that allow some members of the biological community to survive adverse conditions. Similarly, complexity or diversity of the gene pool in a species may result in a subset of the population that is unusually resistant to a particular stress and hence better able to survive the impact of certain types of pollution. Similar considerations apply to the functionality of biological wastewater treatment systems. As we will see in Chapter 6, from a functional standpoint, a simple wastewater treatment system that relies almost entirely on bacteria to decompose the organic matter in sewage may be more easily perturbed by changes in the characteristics of the sewage than a system that relies on a more complex biological community. There are many types of complexity, and certainly not all of them are inherently destabilizing. However, it appears from May’s (1974) analysis that as a general rule increased complexity in food web linkages does not increase ecosystem stability.

## Questions

- 1.1 As is apparent from Table 1.1, concentrations of toxic substances in water and aquatic organisms may be very low. Concentrations are frequently reported in parts per million (ppm) or even parts per billion (ppb). One part per million of substance X in water is 1 g of X per million grams of water. Likewise one part per billion of substance X in water is 1 g of X per billion grams of water. A million grams is  $10^6$  g or 1 metric ton. A metric ton is often written **tonne** and equals about 2200 lb. A billion grams is  $10^9$  g or 1000 tonnes. To get some feeling for the meaning of 1 ppm and 1 ppb, calculate the amount of time in days equal to one million seconds and the amount of time in years equal to one billion seconds.
- 1.2 The ecological efficiency in a food chain is 20%. Pollutant X is transferred up the food chain from one trophic level to the next with an efficiency of 60%. The concentration of X on trophic level 4 is 36 ppm. If the concentration of X on other trophic levels in the food chain is determined entirely by food chain magnification, what would you expect the concentration of X to be on
  - (a) Trophic level 2?
  - (b) Trophic level 5?
- 1.3 Earth’s atmosphere presently contains about  $10^{21}$  g of  $O_2$ . Assuming that this oxygen was produced by photosynthesis, how many grams of organic carbon must have been produced to account for this much oxygen? The total inventory of organic carbon on Earth

is currently estimated to be about  $1.5 \times 10^{22}$  g (Berner 1994). Assuming that this organic carbon was produced by photosynthesis, how much oxygen would have been associated with its production? How would you account for the discrepancy between this figure and the amount of oxygen currently in the atmosphere?

- 1.4 The net production of organic carbon by aquatic and terrestrial plants is currently estimated to be about  $10^{17}$  g y<sup>-1</sup> on a global basis (Field et al. 1998). Heterotrophic respiration is estimated to convert about the same amount of organic carbon to CO<sub>2</sub> each year. The current imbalance between the production and consumption of organic matter is believed to be due to human activities – primarily the burning of fossil fuels. These activities are estimated to convert about  $6 \times 10^{15}$  g of organic carbon to CO<sub>2</sub> each year (Flavin and Lenssen 1990). About half of that carbon appears as additional CO<sub>2</sub> in the atmosphere each year. Assuming that the production of organic carbon amounts to  $10^{17}$  g y<sup>-1</sup> and that consumption exceeds production by  $6 \times 10^{15}$  g y<sup>-1</sup>, what is the current ratio of production to consumption of organic carbon?
- 1.5 Suppose that a giant meteor hit the Earth, creating a nuclear winter that blocked out enough sunlight to completely shut down photosynthesis. Assuming that the respiration of heterotrophs continued to oxidize organic carbon at a rate of  $10^{17}$  g y<sup>-1</sup>, how long would it take for heterotrophic respiration to consume all the oxygen in the atmosphere? Why is it unlikely that heterotrophic respiration would continue at its present rate for this length of time?
- 1.6 Current use of fossil fuels consumes about  $6 \times 10^{15}$  g of carbon per year. Total fossil fuel reserves (coal, oil, and natural gas) are estimated to be about  $4 \times 10^{18}$  g of carbon (Falkowski et al. 1998). If fossil fuel consumption continues at its present rate, how long will it take to consume all the fossil fuel deposits?
- 1.7 Current use of oil and natural gas amounts to about  $3.4 \times 10^{15}$  g of carbon per year (Flavin and Lenssen 1990). Total deposits of oil and natural gas are estimated to be about  $5 \times 10^{17}$  g of carbon (Falkowski et al. 1998). If the consumption of oil and natural gas continues at its present rate, how long will it take to consume all the oil and natural gas deposits?
- 1.8 Sheldon et al. (1972) have argued that the concentrations of particles ranging from microscopic algae to tuna and whales vary by no more than a factor of 2–3 in the ocean. In other words, there is an ecological pyramid of biomass, but the biomass of microscopic algae is only 2–3 times greater than the biomass of tuna and whales. How can we account for this observation if the ecological efficiency of the food chains leading from algae to tuna and whales is only 20%. More recently, Longhurst (1991) has presented data concerning the relative size of predators and prey in a wide variety of marine food chains and covering a range in organism size from protozoans to whales. The median ratio of predator length to prey length in Longhurst's dataset is about 10. Assuming that organism biomass scales as length cubed, the implication of Longhurst's analysis is that the biomass of a predator is roughly 1000 that of its prey. Assume that:
  - (a) The biomass of individual predators is 1000 times the biomass of their prey.
  - (b) Metabolic rate scales as individual biomass raised to the 0.75 power.
  - (c) Ecological efficiency is 20%.

Given these assumptions, in a grazing food chain, what would you predict the biomass on trophic level 6 to be relative to the biomass on trophic level 1? Is this result roughly consistent with the observations of Sheldon et al. (1972)?

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## 2

## Photosynthesis

As the organisms primarily responsible for the synthesis of organic matter from inorganic constituents, plants occupy a uniquely important position in aquatic food chains. Therefore, a study of the factors that control photosynthetic rates is a logical place to begin examining how changes in the environment may be expected to influence aquatic systems.

Aquatic plants are for the most part very different from the terrestrial plants with which most people are familiar. There are relatively few trees or grasses in aquatic systems. Along coastlines mangrove and cypress trees are, to be sure, aquatic organisms, and **benthic** algae such as kelp are somewhat analogous to terrestrial grasses or shrubs. In shallow lakes or along coastlines where the water is sufficiently shallow for light to effectively penetrate to the bottom, benthic algae may be the most important primary producers in an aquatic ecosystem. However, because plants need light to carry out photosynthesis and because water absorbs light, the depth range within which rooted aquatic plants can survive is obviously limited. In systems where there is a high concentration of particulate materials suspended in the water, water transparency is further reduced, because such particles scatter and absorb light. A similar effect is produced by certain dissolved organic substances such as tannic and humic acids, which also absorb light. In the clearest ocean water, only about 0.1% of surface light is transmitted to a depth of 150 m, and in clear coastal waters the 0.1% light level is typically reached at a depth of only 30 m. The net photosynthetic rate of most aquatic plants is close to zero at light intensities less than ~0.1% of surface light (Laws et al. 2014; Marra et al. 2014). The depth at which **net photosynthesis** equals zero is called the **compensation depth**. The lower limit of the **euphotic zone** (the region of the water column within which net photosynthesis is positive) equals the compensation depth. The euphotic zone is typically a few tens of meters in clear coastal waters and roughly 150 m in the clearest open-ocean water. These depth limits are reduced in waters containing significant concentrations of particulate or dissolved organic materials. Obviously benthic algae and/or rooted aquatic plants are not to be found in parts of aquatic systems where the bottom lies below the euphotic zone. Because the depth below about 93% of the surface area of the world's oceans is greater than 180 m (Ryther 1969), it is clear that benthic plants contribute nothing to primary production in most parts of the ocean. Furthermore many lakes are sufficiently deep and/or turbid as to prevent the development of benthic plants except in the immediate vicinity of the shoreline.

Based on the foregoing discussion, it is clear that aquatic plants found in the surface waters of the open ocean or of deep lakes must have the ability to float or drift about in the euphotic zone and must be able to derive all the essential nutrients for photosynthesis directly from the water. Seaweeds such as the *Sargassum* weed provide one example of such planktonic (drifting) plants. However, most such plants are microscopic or nearly so in size and are frequently unicellular. These tiny plants are called phytoplankton and may range in size from microscopic cells a micron or less in diameter to "giant" cells visible to the unaided eye with a diameter of

as much as 2 mm. Some species of phytoplankton form colonies or long chains of cells that are visible to the unaided eye, although the individual cells are not. It is perhaps surprising to realize that such tiny organisms are responsible for the vast majority of aquatic primary production and that top-level carnivores such as sharks and whales depend almost entirely, although indirectly, on such minute organisms as a source of food. However, despite their essential role as primary producers in virtually all aquatic food chains, phytoplankton may create serious problems, particularly when their concentrations in the water exceed certain limits. For example, **harmful algal blooms (HABs)**, which are an unwelcome but recurrent event in a number of coastal areas throughout the world, are caused by a population explosion of phytoplankton, typically certain species of **dinoflagellates** or **cyanobacteria**. At such times the concentration of phytoplankton becomes sufficiently great to visibly color the water over distances of as much as several kilometers. Blooms of dinoflagellates typically impart a reddish color to the water, and historically such HABs in marine waters were referred to as **red tides**, but the designation was confusing. The growth of the dinoflagellates had nothing to do with the tides, and certainly not all HABs cause the water to appear red.

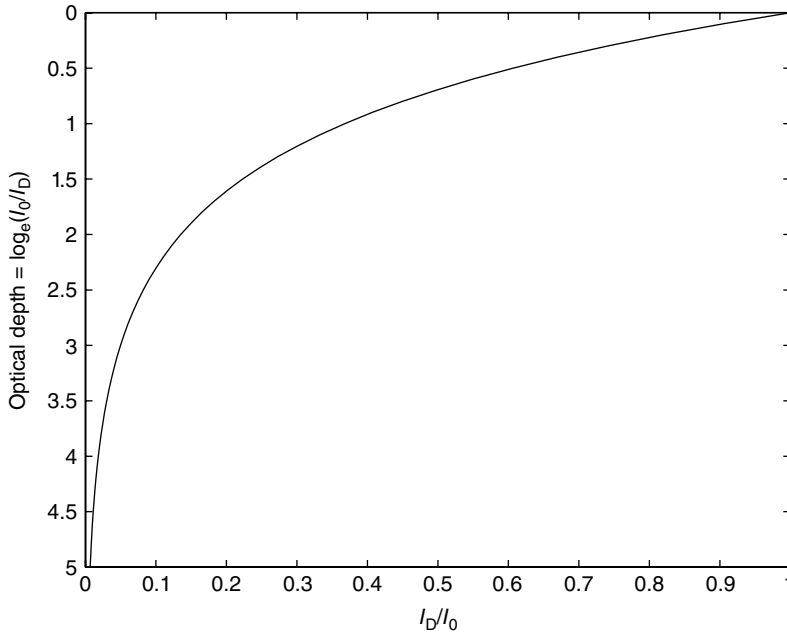
There are several kinds of problems caused by HABs. Some HAB species release neurotoxins into the water. During HABs these toxin concentrations may become high enough to kill great numbers of small fish, seabirds, turtles, and even marine mammals (Flewelling et al. 2005). Furthermore, the toxins may be concentrated by shellfish (which are seemingly unaffected) and subsequently poison humans who eat the shellfish. In severe cases this poisoning may result in paralysis or even death. The concentration of phytoplankton may become so great that the gills of fish and shellfish become clogged, and the animals suffocate. Finally, when the phytoplankton die, the decomposition of their cells may deplete the water of oxygen, the result being **hypoxia** or **anoxia** (Rabalais et al. 2002).

Although some phytoplankton population explosions are completely natural phenomena, there is no doubt that in many cases human activities have largely caused or greatly exacerbated conditions that lead to undesirably high phytoplankton concentrations. To avoid and/or correct conditions that stimulate excessive phytoplankton growth, it is obviously essential to first understand the factors that normally control phytoplankton growth rates, a problem to which we now turn our attention.

## Light Limitation of Photosynthesis

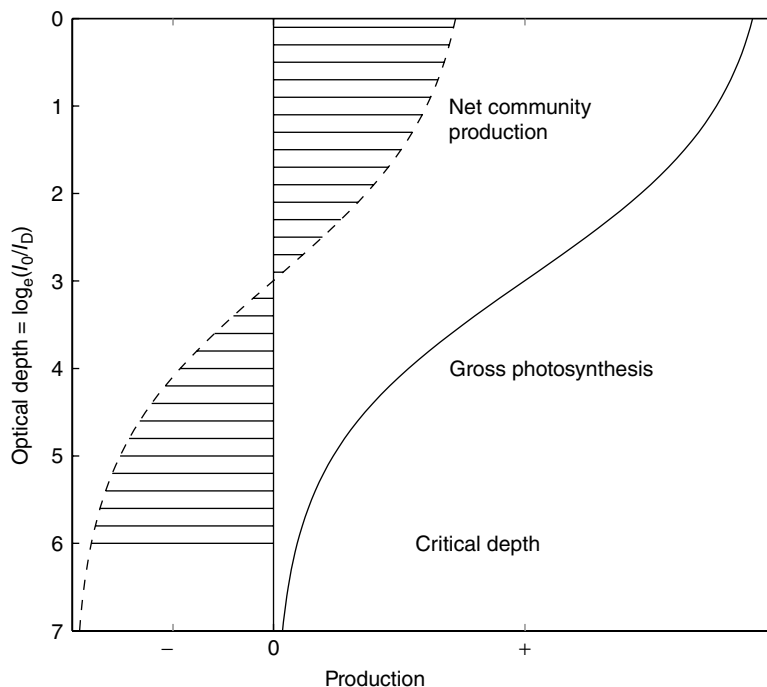
There is no doubt that light is the most important factor limiting photosynthetic rates in the world's oceans. Over 95% of the ocean's volume lies below the euphotic zone and is hence unable to support plant life. In addition, many lakes are sufficiently deep that the euphotic zone makes up only a small fraction of the lake's volume, and even shallow lakes may show pronounced seasonal patterns in plant production that are undoubtedly influenced in part by changes in insolation. Figure 2.1 shows the variation of light intensity with depth in a hypothetical body of water. The graph shows only visible light, because the plant pigments that absorb light are effective in absorbing only certain parts of the visible light spectrum. For example, **chlorophyll** absorbs predominantly blue and red light. In fact not all parts of the visible light spectrum are equally useful for photosynthesis, but the total quantity of visible light does provide a convenient, if approximate, measure of the amount of light available for photosynthesis.

As indicated in Figure 2.1, light intensity drops off with depth in the water column in approximately an exponential fashion, that is, at a rate proportional to the intensity of the light. Photosynthetic rates tend to become saturated at high light intensities and may be inhibited by the **ultraviolet (UV)** light in direct sunlight. However, UV light is rapidly attenuated by water,



**Figure 2.1** Variation of visible light intensity with depth in a hypothetical body of water.

and at a depth  $d$  where the irradiance ( $I_d$ ) is less than about 30% of surface values ( $I_0$ ), photosynthetic rates are almost directly proportional to light intensity. Thus a graph of **gross photosynthesis** versus depth in a body of water might appear qualitatively very similar to the solid curve in Figure 2.2. Therefore, to the extent that light limits photosynthesis, phytoplankton growth rates should be highest near the surface, where light intensities are close to optimal. However, most phytoplankton cannot position themselves in the water column, because they have very little locomotive ability, and for the most part are moved about by turbulence and currents, both in the horizontal and vertical directions. At the surface, winds blowing over the water generate waves and turbulence that keep the water column well mixed and the phytoplankton concentration correspondingly uniform. If the depth of this **mixed layer** is shallow enough, the production of organic matter by the phytoplankton in the mixed layer will exceed losses of organic matter to plant and animal respiration. This difference between the production and consumption of organic matter by the plant and animal community is called **net community production**. The dashed curve in Figure 2.2 qualitatively shows the relationship between net community production and depth in a hypothetical body of water. When net community production is positive in the mixed layer, biomass may accumulate in the mixed layer and/or be exported to deeper parts of the system. Sinking of detritus is a common mechanism that exports organic matter from the mixed layer to deeper water. If the depth of the mixed layer equals a certain depth known as the **critical depth**, net community production is zero when averaged over the depth of the mixed layer (Smetacek and Passow 1990). In Figure 2.2, net community production is positive above an **optical depth**  $[= \log_e(I_0/I_d)]$  of about 3 and is negative below that depth. The hatched area of positive net community production exactly balances the hatched area of negative net community production above an optical depth of 6. The critical depth in this example therefore occurs at an optical depth of 6. If the mixed layer is deeper than the critical depth, there will be a net consumption of organic matter within the mixed layer, that is, the average net community production within the mixed layer will be



**Figure 2.2** Relationship between gross photosynthesis, net community production, and depth in a well-mixed body of water. Average net community production is zero above the critical depth.

negative. Obviously this situation cannot persist indefinitely in the absence of **allochthonous** (external) inputs of organic matter, or there would be no organic matter left.

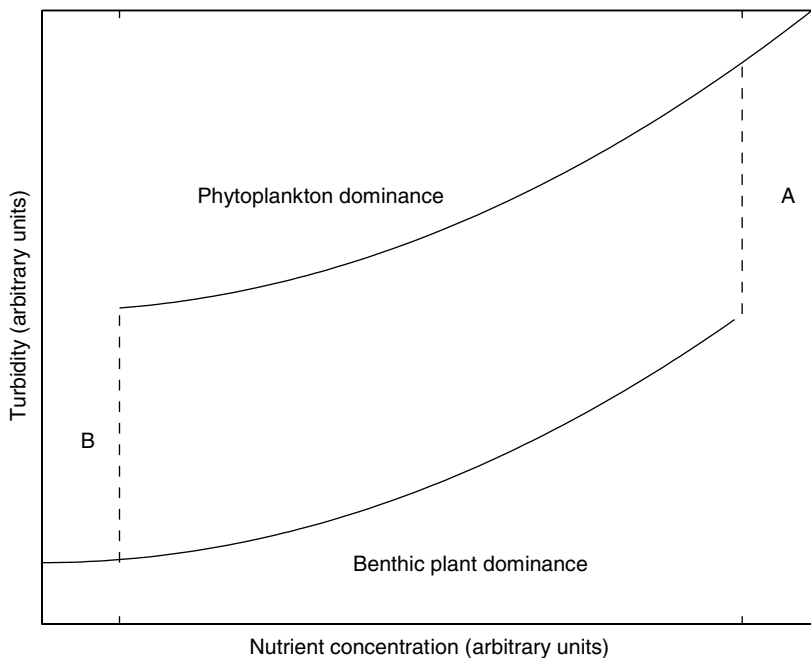
Certain kinds of pollution associated with human activities may reduce the depth of the euphotic zone by increasing the **turbidity** of the water. The result is a decrease in net community production and sometimes a dramatic change in the composition of the phytoplankton community. For example, sediment runoff from construction sites may greatly diminish water clarity and therefore decrease the amount of light available for phytoplankton. In such cases the phytoplankton population may become dominated by cyanobacteria (also referred to as blue-green algae), many species of which are able to maintain themselves near the surface of the water by means of special gas-filled vacuoles that give the plants a slight positive buoyancy. Cyanobacteria may form floating surface scums or mats that are aesthetically objectionable, particularly if they wash ashore and rot along the water's edge. Furthermore, the cyanobacteria may be unpalatable to the natural community of herbivorous zooplankton, and through this and other feeding relationships, the initial change in the composition of the phytoplankton community may impact the entire biological community.

Shallow bodies of water are susceptible to especially dramatic changes in the composition of their biological communities caused by changes in the availability of light because when the water is clear, benthic plants rather than phytoplankton typically dominate their plant communities. These systems tend to be stable as long as an adequate amount of light reaches the bottom. The resilience of these systems to perturbations is enhanced by the fact that the benthic plants stabilize the sediments, the resuspension of which by wind mixing would otherwise increase the turbidity of the water and reduce the amount of light reaching the bottom. Furthermore, benthic plants assimilate nutrients that would otherwise become available to the phytoplankton, they typically release allelopathic substances that inhibit the growth of



phytoplankton (Scheffer et al. 1993), and they provide a refuge from fish for herbivorous zooplankton whose grazing activities help to keep the phytoplankton population in check (Hosper 1989). Thus, through a combination of mechanisms, benthic plants help to create clear-water conditions by reducing the amount of suspended sediment and phytoplankton that would otherwise scatter and absorb light before it reached the bottom. However, the biomass of benthic plants is constrained by the area of the bottom, and if nutrient loading to the system becomes too great, the nutrients that cannot be exploited by the benthic plants become available to the phytoplankton. The result is an increase of phytoplankton biomass and turbidity. If the concentration of phytoplankton becomes too great, the amount of light reaching the bottom is inadequate to sustain the benthic plants, which die and decompose. Their decomposition releases nutrients, which then become available to the phytoplankton. Furthermore, the loss of benthic plants destabilizes the sediments, and sediment resuspension introduces even more nutrients into the water column. The net result is that the turbidity abruptly increases following the demise of the benthic plants, as indicated by the dashed line labeled “A” in Figure 2.3.

The plant community in the system is now completely dominated by phytoplankton, and the transition from this green-water condition to the original clear-water condition cannot be achieved by a small reduction of the nutrient concentrations. The reason is that there are no longer any benthic plants to compete with the phytoplankton for nutrients, release allelopathic substances into the water, provide a refuge for herbivorous zooplankton, or stabilize the sediments. If the nutrient concentrations in the system are reduced by a very large amount, the turbidity of the water may eventually be reduced to the point that the light reaching the bottom is sufficient to sustain benthic plants, and the system abruptly transitions from the green-water



**Figure 2.3** Relationship between benthic plant dominance and phytoplankton dominance as a function of nutrient concentrations and turbidity. Benthic plants dominate below the lower curve, and phytoplankton dominate above the upper curve. The transition from benthic plants to phytoplankton occurs along the dashed line labeled A, and the transition from phytoplankton to benthic plant dominance occurs along the dashed line labeled B. Transitions A and B are effectively one-way streets.

to the clear-water condition, as indicated by the dashed line labeled “B” in Figure 2.3. The behavior depicted in Figure 2.3 is one example of **hysteresis**, the dependence of the behavior of a system on both its current state and its history. In this case, whether phytoplankton or benthic plants dominate the plant community depends on the history of the body of water as long as the nutrient concentration is somewhere between the projections of the two dashed lines on the abscissa.

A more-or-less infamous example of the behavior depicted in Figure 2.3 is Lake Apopka in central Florida. **Lake Apopka** is a shallow lake with a mean depth at the present time of about 1.6 m. Prior to 1947 it was a clear-water lake with a “lush growth of submerged aquatic vegetation” (Schelske et al. 2010, p. 1201). However, it had transitioned to a green-water lake by 1950 and has remained in that condition ever since. What happened?

Beginning in the early 1940s, levees were constructed along the north shore of the lake so that the wetlands that bordered that part of the lake could be drained for agricultural development. One of the important ecosystem services performed by wetlands is nutrient removal (Reddy and DeLaune 2008), and the conversion of the wetlands to agricultural land transformed them from a sink to a source of nutrients. Furthermore, the water discharged to Lake Apopka from the draining activities contained high concentrations of dissolved organic substances that absorbed visible light and hence reduced the transparency of the water, and the amount of water released to the lake was sufficient to raise the lake level by 0.6 m. There is only anecdotal information about water quality in Lake Apopka just before or for several decades after 1947, but data reported by Schelske et al. (2010) indicate that in the mid-1980s the compensation depth in the lake was less than 1 m. The evidence strongly suggests that Lake Apopka transitioned from a clear-water to a green-water lake over a period of no more than 2–3 years beginning in 1947 when the amount of light reaching the bottom of the lake became insufficient to sustain benthic plants. Schelske et al. (2010) have characterized the transition as “The darkening of Lake Apopka.”

As suggested by Figure 2.3, merely reducing the nutrient loading to a shallow green-water lake can produce disappointing results if the desired outcome is a clear-water lake. One complementary action that may help is temporarily lowering the water level, so that more light reaches the bottom. Another potentially effective tactic is the introduction of fish to increase the grazing pressure on the phytoplankton. This strategy may be helpful if the fish feed directly on phytoplankton (e.g., silver carp in China) or if the fish are functionally secondary carnivores. In the latter case, grazing by the fish reduces the abundance of primary carnivores, which increases the abundance of herbivores, which reduces the abundance of phytoplankton. This sequence of predator/prey interactions is an example of what ecologists call a **trophic cascade**. We will examine the effects of one such trophic cascade in Chapter 4. Introduction of fish will not improve water clarity if the fish forage on the bottom and in the process resuspend sediments. In fact, removal of such fish (e.g., common carp or bream) can dramatically improve water transparency (Scheffer et al. 1993). Although manipulations of fish populations and water levels can be helpful, most efforts to address problems created by excessive algal growth have involved reductions of nutrient loads, and for that strategy to be effective and practical, it is important to know what nutrient or combination of nutrients to target, a subject to which we now turn our attention.

## Nutrient Limitation of Photosynthesis

Excessive stimulation of algal production by the addition of essential nutrients to the euphotic zone is more often the cause of algal pollution problems than changes in water clarity. In fact, even in cases where cyanobacteria come to dominate a phytoplankton community, the principal

cause of change is usually a shift in the relative input of certain nutrients to the euphotic zone rather than increased turbidity. The sensitivity of phytoplankton production and/or composition to changes in nutrient inputs arises because phytoplankton biomass in the euphotic zone is often controlled by the availability of certain nutrients that, in addition to light, are essential for growth. If the supply of these nutrients is increased to a nutrient-limited phytoplankton community, an increase in production and biomass roughly proportional to the increase in nutrient supply can be expected. Obviously no immediate increase in phytoplankton production will occur if such nutrient additions are made to the water column below the euphotic zone (the so-called **aphotic zone**), where light is inadequate to support photosynthesis even if nutrients are abundant. However, production in the surface waters will subsequently increase if aphotic zone water is later mixed into the euphotic zone, a process that occurs from time to time, albeit sometimes slowly, in all aquatic systems.

Usually only one or a few nutrients are limiting to the production of phytoplankton biomass in a given system at a given time, but the identification of these nutrients has proven to be a controversial problem. Table 2.1 lists chemical elements that are known to be essential for plants. **Macronutrient** elements are required in relatively large amounts compared with **micronutrients**, although for some elements the distinction is not clear-cut. Of the macronutrients, carbon, oxygen, and hydrogen are required in the largest amounts, because they are essential components of organic compounds such as **carbohydrates**, **lipids**, **proteins**, and **nucleic acids**. Nitrogen and phosphorus are required in somewhat smaller amounts, with the atomic ratio of nitrogen to phosphorus averaging about 16 (range: 3–30) in phytoplankton and 30 (range: 10–70) in macroalgae (Atkinson and Smith 1983; Ryther and Dunstan 1971). Nitrogen is an essential component of proteins, nucleic acids (**DNA** and **RNA**), **ribosomes** (protein–RNA complexes), and certain pigments (e.g., **chlorophyll**), and phosphorus is required to produce nucleic acids, ribosomes, phospholipids, and sugar phosphate bonds in molecules such as adenosine triphosphate (**ATP**). The high-energy phosphate bonds in ATP provide a convenient and essential storage unit for small amounts of energy derived primarily from the stepwise catabolism of organic molecules and may be used at any time by the organism as a source of energy for metabolic processes. The remaining macronutrient elements are required in even smaller amounts, and their concentrations in both marine and freshwaters are

**Table 2.1** Essential macro- and micronutrient elements for plants.

| Essential macronutrient elements | Symbol | Essential micronutrient or trace elements | Symbol |
|----------------------------------|--------|-------------------------------------------|--------|
| Oxygen                           | O      | Iron                                      | Fe     |
| Carbon                           | C      | Manganese                                 | Mn     |
| Nitrogen                         | N      | Copper                                    | Cu     |
| Hydrogen                         | H      | Zinc                                      | Zn     |
| Phosphorus                       | P      | Boron                                     | B      |
| Sulfur                           | S      | Silicon                                   | Si     |
| Potassium                        | K      | Molybdenum                                | Mo     |
| Magnesium                        | Mg     | Chlorine                                  | Cl     |
| Calcium                          | Ca     | Vanadium                                  | V      |
|                                  |        | Cobalt                                    | Co     |
|                                  |        | Sodium                                    | Na     |

Source: Odum (1971, p. 127).

more than adequate to supply the nutritional needs of aquatic plants. The micronutrients or **trace elements** are required in the smallest amounts, in many cases functioning as **catalysts** to speed up metabolic reactions. Such catalysts are not consumed or altered by the reactions they mediate, and therefore only small amounts are required by an organism.

Although there are some remarkable differences in the physiology of different species and taxa of algae, the elemental composition of most algae is remarkably constant with respect to carbon (C), hydrogen (H), and oxygen (O). The constancy of the CHO stoichiometry reflects the fact that many algae are very similar in terms of the macromolecular composition of their organic matter. Phytoplankton tend to allocate about 50% of their carbon to protein, 35% to carbohydrate, and 15% to lipids (Laws 1991). The corresponding percentages for macroalgae are 20%, 75%, and 5% (Atkinson and Smith 1983). Because the C, H, and O composition of protein, carbohydrate, and lipid tends to be very similar between species, there is a corresponding similarity in the C:H:O elemental ratios in phytoplankton and likewise in macroalgae.

Historically, the assumption of constant algal stoichiometry was extended to nitrogen (N) and phosphorus (P), based largely on the work of Redfield (1958), who noticed that the N:P ratio of plankton in the ocean was very similar to the molar ratio of nitrate to phosphate in the deep sea, 16:1. Redfield reasoned that the similarity of the ratios reflected the fact that the decomposition of organic matter originally synthesized by phytoplankton released N and P in the same ratio at which the two elements had been assimilated by the phytoplankton, and an atomic N:P ratio of 16:1 became known as the Redfield N:P ratio. The concept of constant phytoplankton stoichiometry was later extended to include carbon, and an atomic C:N:P stoichiometry of 106:16:1 then became known as **Redfield stoichiometry**. In macroalgae these atomic C:N:P ratios are higher, roughly 550:30:1 (Atkinson and Smith 1983), because compared with phytoplankton, macroalgae contain more carbohydrate, which consists of C, H, and O. The higher N:P ratio of macroalgae reflects the fact that they grow more slowly than phytoplankton and hence contain more protein relative to ribosomal RNA.

Redfield stoichiometry notwithstanding, the fact is that the C:N:P stoichiometry of phytoplankton is not at all constant and shows very systematic variations as a function of growth rate (Goldman et al. 1979; Terry et al. 1985) and between algal taxa (Arrigo 2005). Phytoplankton that are growing rapidly allocate more of their carbon to ribosomes, which contain relatively large amounts of both N and P. Phytoplankton that are growing relatively slowly because of resource limitation tend to allocate more carbon to “resource-acquisition machinery,” which includes proteins associated with nutrient uptake and chloroplasts, both of which contain N but little or no P (Klausmeier et al. 2004). The result is that the N:P requirement ratio of phytoplankton tends to be negatively correlated with their growth rates (Terry et al. 1985). Furthermore, there are very systematic differences in the elemental composition of the major taxa of phytoplankton (Quigg et al. 2003). Green algae (which contain chlorophyll *b* in addition to chlorophyll *a*), for example, evidence higher C:P and N:P atomic ratios, roughly 200 and 27, respectively, than red algae (which contain chlorophyll *c* in addition to chlorophyll *a*), whose C:P and N:P atomic ratios are roughly 70 and 10, respectively (Arrigo 2005). These considerations suggest that the answer to the question “What is limiting?” may be more complicated than would be the case if the elemental stoichiometry of phytoplankton were the same for all species and under all growth conditions.

Realizing the relative requirements of plants for the essential nutrients listed in Table 2.1, one may ask which of these elements is most likely to limit phytoplankton biomass. Carbon, hydrogen, and oxygen are needed in the largest amounts, but these elements are readily obtained from H<sub>2</sub>O (hydrogen) and CO<sub>2</sub> (carbon and oxygen). Obviously there is no lack of H<sub>2</sub>O in an aquatic environment. Carbon dioxide is a gas that is found in the atmosphere and dissolves in water, reaching at equilibrium a concentration proportional to its concentration in the

atmosphere. The chemistry of the oceans is such that there is invariably an abundance of inorganic carbon to support photosynthesis, although under certain conditions the supply of  $\text{CO}_2$  may limit the production of some species (Riebesell et al. 1993), and deliberate increases of  $\text{CO}_2$  concentrations in experimental systems to simulate the anticipated impacts of continued fossil fuel burning have typically resulted in a stimulation of phytoplankton photosynthesis (Riebesell et al. 2007; Schippers et al. 2004). In contrast, the inorganic carbon concentration in some freshwater lakes is extremely low, and it has sometimes been argued that photosynthesis in such systems might be limited by a lack of  $\text{CO}_2$ . However, Schindler (1974) has convincingly shown that the exchange of  $\text{CO}_2$  between the atmosphere and the water is sufficiently rapid to provide adequate  $\text{CO}_2$  for the development of large phytoplankton blooms over a time period of no more than a few weeks. In other words, the atmosphere acts as a  $\text{CO}_2$  reservoir for the mixed layer of an aquatic system, and the flux of  $\text{CO}_2$  from the atmosphere into the water may easily provide  $\text{CO}_2$  needed for photosynthesis, even if the ambient  $\text{CO}_2$  concentration in the water is low. We will examine more closely how Schindler arrived at this conclusion later in this chapter. For the moment, suffice it to say that,  $\text{CO}_2$  appears to limit phytoplankton biomass in few if any natural aquatic systems.

Table 2.2 lists the average concentrations of most of the remaining macro- and micronutrient elements in typical river water and seawater. Sulfur (as sulfate,  $\text{SO}_4^{2-}$ ), potassium, magnesium, calcium, chlorine, and sodium are the elements that make up the principal salts in seawater. Their concentrations in seawater range from 10 mM to 0.56 M. There is no evidence that a lack of these elements ever limits photosynthesis in the sea. The concentrations of the same elements in river water are much lower and range from ~40 to 400  $\mu\text{M}$ . Again, however, there is no evidence that such concentrations are limiting to photosynthesis. The micronutrient elements are

**Table 2.2** Average concentrations of selected elements in river water and seawater ( $S=35$ ).<sup>a</sup>

| Element | River water |       | Seawater |         |
|---------|-------------|-------|----------|---------|
| B       | 1           | 0.67  | 416      |         |
| Ca      | 332         |       | 10,300   |         |
| Cl      | 226         |       | 546,000  |         |
| Cu      | 0           | 0.003 | 0        | 0.00002 |
| Co      | 0           | 0.024 | 0        | 0.004   |
| Fe      | 0           | 0.716 | 0        | 0.001   |
| K       | 38          |       | 10,200   |         |
| Mg      | 128         |       | 53,200   |         |
| Mn      | 0           | 0.149 | 0        | 0.0005  |
| Mo      | 0           | 0.005 | 0        | 0.11    |
| Na      | 391         |       | 468,000  |         |
| S       | 116         |       | 28,200   |         |
| Si      | 178         |       | 100      |         |
| V       | 0           | 0.02  | 0        | 0.03    |
| Zn      | 0           | 0.459 | 0        | 0.006   |

*Source:* For seawater, Bruland (1983). For freshwater, Martin and Whitfield (1983) with exception of S, Cl, and Na, which were taken from Riley and Chester (1971).

a) Concentration units are  $\mu\text{M}$ .

for the most part found at much lower concentrations than are any of the macronutrients. Although it is true that most of the micronutrients are required in very small amounts, there is evidence that the availability of certain micronutrients may limit algal biomass in some aquatic systems or at least limit the biomass of certain species of algae. For example, phytoplankton known as **diatoms** build an elaborate skeleton of silica that encloses the rest of the cell. Consequently, diatoms require much more silicate than other classes of phytoplankton, and there is fairly convincing evidence that changes in silicate concentrations may affect the abundance of certain diatoms in freshwater systems (Hutchinson 1967, p. 446–455). There is little evidence that silicate limits photosynthetic rates in the ocean, although the distribution of marine diatoms is undoubtedly influenced by silicate availability. Silicate concentrations in ocean surface waters can easily drop as low as  $1\text{--}2\text{ }\mu\text{M}$  (Karl et al. 2001). The greatest abundance of marine diatoms is found in Antarctic seas, where silicate concentrations as high as  $30\text{--}50\text{ }\mu\text{M}$  have been reported during the austral winter. Molybdenum (Mo) plays a role in the formation of the enzyme nitrate reductase and hence is required for the assimilation of nitrogen in the form of nitrate ( $\text{NO}_3^-$ ). Molybdenum is also required for **nitrogen fixation**, the process by which certain plants and bacteria convert atmospheric nitrogen gas ( $\text{N}_2$ ) into a form that can be used in primary production. There is evidence that the availability of Mo limits nitrate uptake and photosynthetic rates in Castle Lake, California (Axler et al. 1980), and evidence presented by Howarth and Cole (1985) indicates that Mo availability limits nitrogen fixation rates in the ocean. In the latter case limitation may result from competitive interference with Mo uptake by sulfate, which has an effective radius and charge distribution nearly identical to those of molybdate. Similar competitive interference would presumably be insignificant in freshwater, because the sulfate concentration in freshwater is less than 1% of the sulfate concentration in seawater. Howarth and Cole's (1985) hypothesis has been challenged by Paulsen et al. (1991), who could find no evidence of Mo limitation of nitrogen fixation in North Carolina coastal waters. Marino et al. (2003), however, present evidence that the inhibition of molybdate uptake by sulfate is not only real but also nonreversible, that is, not explained by a simple competitive inhibition model.

Nitrogen and phosphorus, the two essential macronutrients not yet discussed, are found in seawater below the euphotic zone in concentrations of  $\sim 20\text{--}40$  and  $1.3\text{--}2.5\text{ }\mu\text{M}$ , respectively. Typical aphotic zone concentrations of these elements in freshwater systems may be 2–3 times lower but can vary greatly from one system to another. However, when there is adequate light to support photosynthesis, it is not unusual for the concentrations of inorganic nitrogen and phosphorus in the euphotic zone of both freshwater and marine systems to be in the range  $10\text{--}100\text{ nM}$  (Edmondson 1972; Moutin et al. 2008; Smith et al. 1986). These concentrations are several orders of magnitude smaller than the average concentrations of the other macronutrients listed in Table 2.1; and of those macronutrients, phytoplankton require N and P in much larger amounts than S, K, Mg, or Ca. Thus, based on observed concentrations, N and P are the most likely of the macronutrients to be limiting photosynthesis. However, because many of the micronutrients are present in extremely low concentrations in the euphotic zone, it is impossible to tell, based simply on measured nutrient concentrations, whether N, P, or one of the micronutrients is limiting photosynthetic rates. As a result phytoplankton ecologists have resorted to a bioassay type of experiment to determine the identity of the nutrient(s) limiting phytoplankton production. These bioassay experiments are commonly referred to as nutrient enrichment experiments.

### Nutrient Enrichment Experiments

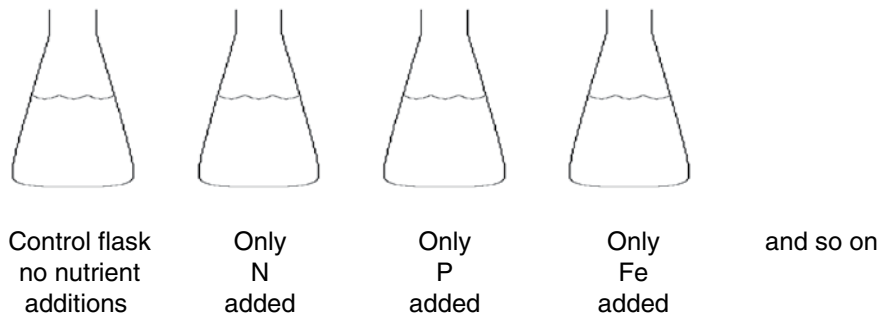
The usual approach in a nutrient enrichment experiment is to fill a series of clear flasks with the water to be assayed and enrich some of the flasks with various nutrients to see whether

these nutrient additions have any effect on phytoplankton production in the flasks. In some cases the water is filtered first to remove the natural phytoplankton and other organisms and then inoculated with a monoculture of a particular phytoplankton species. In other cases the water is not filtered, so that the natural phytoplankton community becomes the test population. Following enrichment, the flasks are incubated under appropriate light and temperature conditions, and the response of the phytoplankton is monitored for a period of time in both the enriched flasks and a control flask, which receives no nutrient additions. The response of the phytoplankton is monitored by normally one of two methods. In the first method the phytoplankton biomass is determined, usually in terms of cell counts, **optical density**, or chlorophyll *a* concentration, and the effect of a given enrichment is measured in terms of the difference in phytoplankton biomass between the enriched flask and the control flask. One generally speaks of such a bioassay as being based on the yield (i.e., biomass) in the enriched flasks. In the second method the actual rate of photosynthesis in each flask is measured, usually after waiting a fixed time interval (approximately 1 day to a week) after the nutrient enrichments. There are pros and cons to both methods. If, as is usually the case, the test population consists of the natural phytoplankton community, one often finds that the composition of the community in the flask changes after several days of incubation. This change results because some species evidently do not grow well under artificial conditions and because nutrient enrichments may not stimulate all species equally. On the one hand, because the biomass in the enriched flasks generally peaks as much as several weeks following enrichment, one can argue that yield-type experiments may misrepresent the nutrient limitation characteristics of the natural phytoplankton assemblage. On the other hand, photosynthetic rates in enriched flasks may vary greatly with time following enrichment, because there may be a lag in the response of phytoplankton to certain enrichments, whereas other enrichments produce a rapid increase in production that subsequently declines. For example, Menzel et al. (1963) were initially led to believe that Sargasso Sea water was iron limited, because after an incubation of a few days photosynthetic rates in flasks enriched with N, P, and Fe were substantially higher than in flasks that received only N and P additions. However, they later discovered that after an incubation of about 1 week, flasks enriched with only N and P showed photosynthetic rates just as high as the flasks enriched with N, P, and Fe had shown after a few days. They concluded that N and P were the principal limiting nutrients and that addition of Fe simply speeded up the response of the phytoplankton to N and P additions. The effect of the added Fe is perhaps not surprising, because Menzel et al. (1963) added N in the form of nitrate, and iron is required to synthesize nitrate reductase, the enzyme that mediates the reduction of nitrate to nitrite, the first step in the process of making nitrate-N available for the production of organic nitrogen compounds. This example illustrates why nutrient enrichment experiments must be interpreted cautiously and carefully to avoid jumping to unwarranted conclusions.

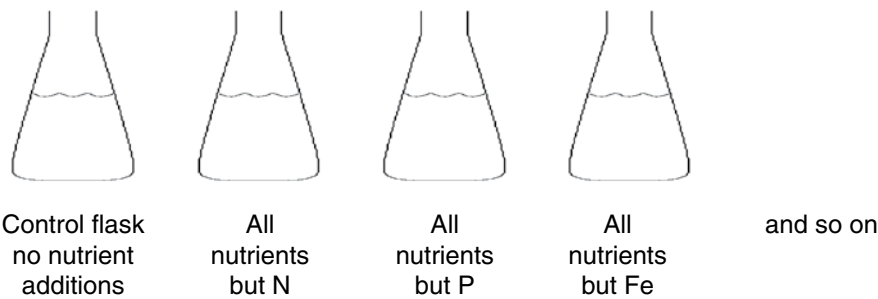
Figure 2.4 illustrates the methodology and interpretation of so-called single-nutrient and multiple-nutrient enrichment experiments. In a single-nutrient enrichment experiment, each of a series of experimental flasks receives an enrichment with only one nutrient. In the multiple-nutrient enrichment experiment, each of a series of experimental flasks is enriched with all essential plant nutrients except one. In both cases the productivity or yield in the experimental flasks is compared with that of the control flasks.

The rationale behind the interpretation of the results is as follows: if the water being studied contains an abundance of all essential nutrients except one, then addition of that single nutrient should greatly stimulate production. If addition of a single nutrient does not greatly stimulate production, then some other nutrient(s) is (are) limiting. Because several nutrients may be co-limiting (i.e., there is very little of each of several nutrients in the water to support additional growth), it is impossible to say in the case where production is not stimulated whether the

Single-nutrient enrichments



Multiple-nutrient enrichments



Results –productivity or yield

|                 | Negative – same or little different from control                              | Positive – much more than control                                                       |
|-----------------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|
| Only X added    | Other nutrients limiting. X may be co-limiting (multi-nutrient co-limitation) | X limiting. Other nutrients may be co-limiting (biochemical or community co-limitation) |
| All but X added | X limiting. Other nutrients may be co-limiting                                | X not limiting                                                                          |

Figure 2.4 Single- and multiple-nutrient enrichment experiments and interpretation of results.

single nutrient added was one of the limiting nutrients or not. We only know that there is at least one limiting nutrient other than the one tested.

In the case of multiple-nutrient enrichments, production little different from the control flask indicates that the nutrient omitted is limiting, because all other nutrients were added in the enrichment. It is impossible to tell, without doing additional experiments, whether other



nutrients are co-limiting. However, if production is much greater than that of the control flask, then the omitted nutrient must not have been limiting. Figure 2.4 summarizes the possible results and conclusions to be reached from the two types of nutrient enrichment experiments.

Unfortunately the simple interpretability of the four outcomes indicated at the bottom of Figure 2.4 is not always encountered in practice. It is not uncommon, for example, in **oligotrophic** aquatic systems, for more than one essential nutrient to be co-limiting. There are three possible **co-nutrient limitation** scenarios (Saito et al. 2008). First, there may be a very low concentration of two or more essential nutrients in the water, in which case only the simultaneous addition of all the co-limiting nutrients produces a result significantly different from the control culture. This type of co-limitation is referred to as **multi-nutrient co-limitation**. For example, Seppala et al. (1999) found that only simultaneous addition of N and P stimulated the growth of phytoplankton in the oligotrophic waters of the Baltic Sea. Addition of only N or only P produced no response.

In other cases of co-limitation, addition of one nutrient, A, stimulates phytoplankton growth, but addition of another nutrient, B, also stimulates phytoplankton growth. There are two scenarios that can explain such results. First, it is possible that addition of one nutrient facilitates uptake or assimilation of a second nutrient. For example, many species of phytoplankton can use dissolved organic phosphorus (**DOP**) as a source of P, but exploitation of many forms of DOP requires an enzyme, alkaline phosphatase, to cleave phosphate groups from DOP, and alkaline phosphatase requires zinc as a cofactor. The ability of phytoplankton to exploit DOP can be enhanced either by adding DOP, which increases the rate at which the DOP is cleaved, or by adding zinc, which enables the phytoplankton to produce more alkaline phosphatase and more rapidly cleave DOP at ambient DOP concentrations (Shaked et al. 2006). This type of co-limitation is referred to as **biochemical co-limitation**. Second, because of the variable physiology of phytoplankton, it is possible that one component of the phytoplankton community is limited by A and another component is limited by B. Addition of A stimulates the growth of the first component, and addition of B stimulates the growth of the second component. This type of co-limitation is referred to as **community co-limitation**. A scenario for community co-limitation is that there are two forms of each of two essential nutrients. Essential nutrient  $\alpha$  can exist in the forms  $\alpha_A$  and  $\alpha_B$ , and essential nutrient  $\beta$  can exist as  $\beta_A$  and  $\beta_B$ . Species A can use  $\alpha_A$  but not  $\alpha_B$ , whereas species B can use  $\beta_B$  but not  $\beta_A$ . Now suppose that the only forms of  $\alpha$  and  $\beta$  available are  $\alpha_B$  and  $\beta_A$ . In that case species A is  $\alpha$ -limited, and species B is  $\beta$ -limited. Addition of  $\alpha_A$  stimulates the growth of A but has no effect on B, which is still  $\beta$ -limited. Addition of  $\beta_B$  stimulates the growth of B but has no effect on A, which is still  $\alpha$ -limited. An example of such a scenario would be a cyanobacterium (species A) that can fix nitrogen but cannot exploit DOP, and a eukaryotic alga (species B) that can exploit DOP but cannot fix nitrogen. If the water contains virtually no inorganic nitrogen or phosphate, then species A is P-limited, and species B is N-limited. Addition of phosphate will stimulate the growth of species A, and addition of inorganic nitrogen will stimulate the growth of species B. This would be an example of community co-limitation.

We have now seen that nutrient enrichment experiments may be complicated by the following factors:

1. Possible changes in the species composition of the culture in the enrichment flask with time
2. Variability over time in the response of the same population to different nutrient additions
3. Co-limitation by multiple nutrients

Such complications need not be serious problems if the enrichment experiments are designed carefully and if the enrichment flasks are monitored frequently. In fact such “complications” may provide useful insights for the experimentalist (e.g., Menzel et al. 1963). Keeping in mind

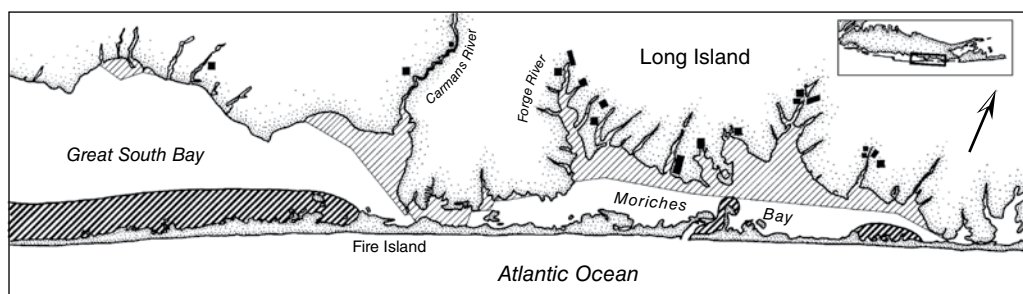
these observations, let us examine several cases in which nutrient enrichment experiments have been used to study nutrient limitation questions.

### Long Island Bays

The release of organic wastes from duck farms began to cause noticeable water pollution problems in certain bays and tributary streams along the southern side of Long Island as the Long Island duckling industry developed in the 1940s. The affected area is shown in Figure 2.5. Most apparent among these problems was the development of massive phytoplankton blooms in the waters of the tributary streams along which the duck farms were located. These blooms extended downstream from the duck farms and into the bays along the coast, where the demise of the once productive oyster and hard-shell clam fishery closely coincided with the development of the phytoplankton blooms (Ryther and Dunstan 1971). Oysters, which feed by filtering water through their gills, were unable to feed or respire effectively, because their gills became coated with the phytoplankton cells (Wagner 1971). Although clams thrived in the phytoplankton-rich waters, the clams were so contaminated with bacteria that they were often commercially unusable. Studies by the Woods Hole Oceanographic Institution between 1950 and 1955 showed that the algal concentrations in the bay water dropped off steadily with increasing distance from the mouths of the principal tributary streams in Moriches Bay in a manner similar to what would be expected from dilution by coastal water. In other words, there was little indication that the dense phytoplankton populations in the bays were actively growing, but rather that they had simply been washed into the bays from tributary streams and subsequently dispersed by tidal currents.

Nutrient analyses performed on the bay and tributary stream waters showed that phosphate and phytoplankton concentrations were closely correlated, with the maximum phosphate concentrations in Moriches Bay of about  $7\mu\text{M}$  dropping off to about  $0.25\mu\text{M}$  at the eastern and western ends of the affected area. Similar analyses for nitrogen in the form of nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), ammonium ( $\text{NH}_4^+$ ), and uric acid (ducks excrete uric acid) revealed virtually no detectable nitrogen in any of these forms except in the immediate vicinity of the duck farms. It was tentatively concluded that nitrogen was the principal nutrient limiting phytoplankton production in the study area, that nitrogenous wastes from the duck farms were stimulating the massive algal blooms in the tributary streams, and that phosphate, being present in excess in the duck farm wastes, simply acted as a tracer of the water and phytoplankton from the tributary streams.

To see whether nitrogen was in fact the nutrient limiting phytoplankton biomass in the system, a series of nutrient enrichment experiments was performed on water samples taken from

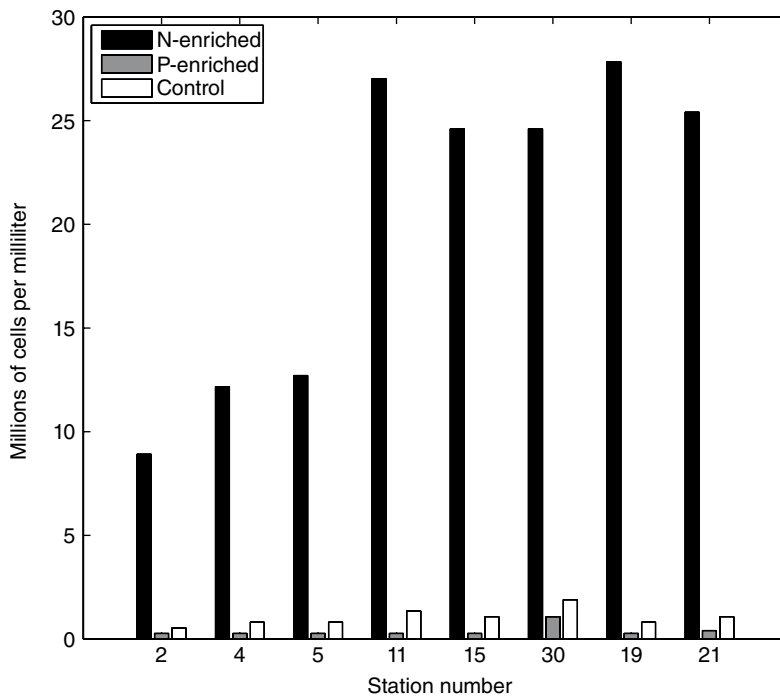


**Figure 2.5** Shellfishing areas affected by duck farm wastes along the south shore of Long Island. Solid blocks along tributary streams indicate duck farms in 1966. Hatched regions indicate shellfishing areas. Lightly hatched shellfishing areas were closed to shellfishing due to pathogen contamination. Source: Redrawn from US Department of the Interior (1966).

Moriches Bay, Great South Bay, and the Forge River, a Moriches Bay tributary on which several duck farms were located. Each water sample was filtered and then poured into three flasks, one of which served as a control and received no nutrient additions. A second flask was enriched with N, and the third flask with P. No other nutrients were added. The experimental setup therefore conformed to the single-nutrient enrichment design of Figure 2.4. All three flasks at each station were inoculated with a pure culture of the phytoplankter *Nannochloris atomus*, the dominant algal species in the phytoplankton blooms, and were incubated for 1 week, at which time the number of cells in each flask was counted. Figure 2.6 shows the results of the experiments. Cell counts in the N-enriched flasks were an order of magnitude or more greater than counts in the control flasks after 1-week incubations. The fact that cell counts were actually lower in the P-enriched flasks than in the control flasks suggests that the phosphate reagent may have contained something that inhibited the growth of the phytoplankton. The fact that counts in the control flasks increased by factors of about 2–4 indicated that the inoculum possessed a moderate potential for growth even without additional nutrients. The order-of-magnitude difference in cell numbers between the N-enriched flasks and the controls indicates that phytoplankton biomass in the system was clearly limited by nitrogen.

### Canadian Experimental Lakes

In the 1960s and early 1970s, the Canadian government authorized a series of nutrient enrichment experiments on whole lakes in the Experimental Lakes Area of western Ontario. The



**Figure 2.6** Cell counts after a 1-week incubation in nutrient enrichment flasks at indicated stations. At each station, the left-hand, middle, and right-hand vertical bars represent the N-enriched flask, the P-enriched flask, and the control flask, respectively. Stations 2, 4, and 5 were located in Great South Bay; station 11 was located between Great South Bay and Moriches Bay; stations 15, 19, and 21 were located in Moriches Bay; and station 30 was located in the Forge River. Source: Redrawn from Ryther and Dunstan (1971). Copyright 1971 by the American Association for the Advancement of Science.

nutrient additions were made directly to the lakes rather than to water samples taken from the lakes to make the experiments as realistic as possible. Of particular concern was the importance of CO<sub>2</sub> exchange between the air and water. In laboratory flasks no mechanism such as stirring or shaking is usually provided to simulate mixing effects and encourage gaseous exchange with the atmosphere. Thus water taken from a lake with a low CO<sub>2</sub> content might be CO<sub>2</sub> limited if incubated in a flask in the laboratory. In the real world CO<sub>2</sub> exchange with the atmosphere, stimulated by wind-generated turbulence and mixing, might be more than adequate to provide the phytoplankton population with CO<sub>2</sub>.

As a test of the effectiveness of CO<sub>2</sub> exchange with the atmosphere, Lake 227, a lake having an extremely low dissolved CO<sub>2</sub> content, was enriched with N and P. Within weeks a massive bloom of phytoplankton had developed, with algal concentrations roughly 100 times greater than in other lakes of the area (Schindler 1974). Gas exchange studies revealed that some of the CO<sub>2</sub> to support the phytoplankton bloom had come from the atmosphere. Considering the results of this experiment and the fact that most lakes (and the oceans) have a much higher CO<sub>2</sub> content than Lake 227, Schindler (1974) concluded that CO<sub>2</sub> probably does not limit phytoplankton biomass in most bodies of water.

To determine the nutrient limiting photosynthetic rates in the experimental lakes, multiple-nutrient enrichments were made to a second lake, Lake 226. This lake consisted of two similar basins separated by a shallow neck. A divider consisting of a sea curtain made from vinyl reinforced with nylon was sealed into the sediments and fastened to the bedrock of the shallow neck (Schindler 1974). The two basins were therefore physically separated. Beginning in May 1973, additions of inorganic carbon and nitrogen were made to one basin, and inorganic carbon, nitrogen, and phosphorus to the other basin. The phytoplankton population in the basin that received only carbon and nitrogen additions was little different from the population before nutrient additions, but a massive algal bloom developed in the basin that received added phosphorus. This experiment clearly showed phosphorus to be a limiting nutrient in the lake.

In a third series of experiments, phosphorus, nitrogen, and inorganic carbon additions were made in 1971 and 1972 to Lake 304. As expected, a large phytoplankton crop developed in response to the nutrient additions. In 1973, although additions of nitrogen and inorganic carbon continued, no phosphorus was added. As a result the phytoplankton population declined dramatically, reaching typical pre-1971 levels. Table 2.3 shows the mean annual phytoplankton biomass in Lake 304 as measured by the mean chlorophyll *a* concentration in the water. Most of the phosphorus added to the lake in 1971 and 1972 was evidently trapped on the bottom of the lake, in the form of either inorganic solids or microbial biomass, and was hence unavailable to support a phytoplankton bloom in 1973. This experiment showed convincingly not only that phosphorus was limiting photosynthetic rates in Lake 304 but also that little of

**Table 2.3** Mean chlorophyll *a* concentrations in Lake 304.

| Year | Chlorophyll <i>a</i> (mg m <sup>-3</sup> ) |
|------|--------------------------------------------|
| 1969 | 6.5                                        |
| 1970 | 11.0                                       |
| 1971 | 21.5                                       |
| 1972 | 24.3                                       |
| 1973 | 8.9                                        |

Source: Data derived from figures reported by Schindler (1974).

the phosphorus added to the lake in 1 year was recycled in the next year. This latter result suggested that lakes having undesirably high phytoplankton populations might be effectively treated by reducing phosphorus inputs. In Chapter 4 we will see how well this idea has worked in practice.

### Nitrogen versus Phosphorus Limitation

Ryther and Dunstan (1971) found convincing evidence that nitrogen limited photosynthetic rates in the Long Island bays, whereas Schindler (1974) found phosphorus to be limiting in the Canadian experimental lakes. These results are rather typical of findings reported in freshwater and marine systems; that is, in freshwater systems, phosphorus is often found to be the principal limiting nutrient, and in marine systems, nitrogen is most commonly found to be limiting (e.g., Thomas 1969). Why would phosphorus tend to be limiting in freshwater systems and nitrogen in marine systems?

A number of papers have been written on this subject, and Howarth (1988) has given an excellent review and discussion of the issues. Which nutrient limits photosynthetic rates depends on the N/P ratio of the external inputs to the system and on the biogeochemical processes that alter the availability of N and P within the system. In the 1960s domestic sewage typically had an N/P ratio of about 9 by atoms (Weibel 1969), which is about one-third to one-half the values typically associated with benthic algae and phytoplankton, respectively. The use of polyphosphates as a component of laundry detergents undoubtedly accounted for the low N/P ratio of domestic wastewater at that time (see Chapter 6). However, it is clear from Ryther and Dunstan's (1971) work in the Long Island bays that wastewater from the duck farms also contained a low N/P ratio relative to phytoplankton needs. A consequence of the low N/P ratio in domestic wastewater and sewage in the 1960s was that systems artificially enriched with such water almost invariably become nitrogen limited. Ryther and Dunstan's (1971) results cannot be attributed so much to the fact that the systems contained seawater but rather to the fact that the water was enriched with wastewater having a low N/P ratio relative to the needs of the phytoplankton.

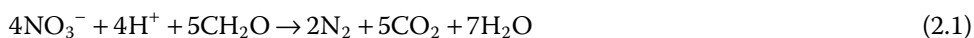
The biogeochemical processes that occur within many freshwater systems tend to create phosphorus limitation. One of the most important such process is nitrogen fixation, of which many species of cyanobacteria are capable. As a result, several experimental lakes deliberately enriched by Schindler (1977) with fertilizer containing a low N/P ratio developed large populations of cyanobacteria. The algae were able to make up for the nitrogen deficiency in the fertilizer by fixing atmospheric nitrogen. Thus a mechanism exists for providing needed nitrogen from the atmosphere (nitrogen fixation), even if nitrogen is limiting in the external inputs to a lake. The atmosphere thus serves as a source both of inorganic carbon (by means of  $\text{CO}_2$  exchange at the air–water interface) and of nitrogen. Phosphorus has no such atmospheric reservoir, however, and all essential phosphorus must come from external inputs or from recycling within a body of water.

In contrast, N fixation by cyanobacteria appears to be of comparatively small importance in most parts of the ocean. The principal reason appears to be the lower availability of iron and perhaps molybdenum in the ocean compared to most freshwaters (Howarth et al. 1988a). Both metals are required for nitrogen fixation. The concentration of Fe in the ocean is orders of magnitude lower than the Fe concentration in typical freshwaters (Table 2.2). There is no doubt that at some times and in some places, N-fixing cyanobacteria are an important source of allochthonous nitrogen in the ocean (Karl et al. 1997; Karl 2000). However, in general N fixation is much less important as a source of allochthonous nitrogen in the ocean than is the case in lakes (Howarth et al. 1988b).

An important factor in the phosphorus limitation question is the fact that the phosphate ion forms insoluble compounds with several cations, including aluminum ( $\text{Al}^{3+}$ ), calcium ( $\text{Ca}^{2+}$ ), and iron ( $\text{Fe}^{3+}$ ). In freshwater systems the most important mechanism of phosphate removal typically involves its adsorption to oxides and oxyhydroxides of iron such as  $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$ . The solid compound sinks to the bottom of a lake, effectively trapping phosphate in the sediments. This mechanism may have been partly responsible for the rapid recovery of Lake 304 in 1973. If the oxygen concentration in the water is very low, however, ferric iron,  $\text{Fe}^{3+}$ , is spontaneously converted to ferrous iron,  $\text{Fe}^{2+}$ . Ferrous iron does not effectively bind phosphate. Thus, if the bottom waters of a lake become anoxic, phosphate trapped in the sediments may be released and circulate back into the water column. In his work on the Canadian experimental lakes, however, Schindler found that in some cases phosphate was efficiently trapped in the sediments even though the bottom waters were anoxic for periods of several months. He reported that uptake of the phosphate by microorganisms in the bottom waters and subsequent sedimentation explained the failure of the phosphate to return to the water column. Nevertheless, the bottom waters of many lakes do remain oxidizing throughout the year, and in such cases the formation and sedimentation of ferric phosphate compounds may be a significant mechanism for removing phosphate from the water column. Nitrogen does not form insoluble chemical precipitates, and there is no mechanism analogous to phosphate adsorption to ferric iron to trap nitrogen in the sediments of either marine or freshwater systems.

Because the average depth of the ocean is roughly 4 km, particulate materials that sink out of the surface mixed layer are essentially lost from the euphotic zone. Upwelling of water from below the **nutricline** does occur at a slow rate in almost all parts of the ocean and at a rapid rate in certain **upwelling** areas. However, with the exception of shallow coastal regions, recycling of nutrients from below the nutricline and from the sediments is a very slow process in most parts of the ocean. Thus recycling of nutrients within the surface mixed layer takes on special importance in most marine food chains. The principal mechanisms for recycling nutrients within the mixed layer are direct excretion (e.g., zooplankton excrete ammonia) and regeneration from detritus. Evidence to date suggests that both animal excretion and regeneration of nutrients from detritus tend to create N-limited conditions. Nutrient release from particulate detritus must be rapid if the nutrients are to be recycled before the particles sink out of the euphotic zone. Phosphorus seems to be released more rapidly from detritus than N, presumably because phosphate ester bonds are more easily cleaved than the covalent bonds of organic nitrogen (Howarth 1988). As a result, fecal material and sedimenting detritus tend to be enriched in N relative to P (Knauer et al. 1979; Lehman 1984). For example, the studies of Knauer et al. (1979) revealed that material that settled into sediment traps near the base of the euphotic zone in the North Pacific Subtropical Gyre contained N and P in an atomic ratio of 29, about twice the Redfield ratio of 16 typically associated with oceanic particulate matter (Copin-montegut and Copin-montegut 1983). Corresponding ratios in coastal areas were 22 and 27 under upwelling and non-upwelling conditions, respectively. With respect to excretion, studies summarized by Lehman (1984) indicate that the soluble compounds released by zooplankton are enriched in P relative to N. Studies by Le Borgne (1982) have clearly shown that the net growth efficiencies of zooplankton are higher for N than P, that is, the zooplankton excrete a higher percentage of the P than of the N in the food they assimilate. Clark et al. (1998) found that the N/P ratios of dissolved organic matter (**DOM**) in the South Pacific increased dramatically with depth, the indication being that phosphorus was being preferentially regenerated from the DOM. Hence biological processes that occur within and below the surface mixed layer tend to create N-limited conditions, and this fact in part accounts for the tendency of open-ocean systems to be N-limited.

**Denitrification** and **anammox** are processes that convert biologically available forms of nitrogen such as nitrate and ammonium into nitrogen gas,  $N_2$ , which can be used as a source of nitrogen only by cyanobacteria that can fix nitrogen. Biologically available forms of nitrogen (i.e., **fixed nitrogen**) include nitrate and ammonium, which can be taken up and assimilated by virtually all photosynthetic organisms.<sup>1</sup> Denitrification is a process by which bacteria use the oxygen in nitrate to oxidize organic matter under anoxic or **hypoxic** conditions. Equation (2.1) is a simple representation of the denitrification process:



The net result of denitrification is that nitrate ( $NO_3^-$ ) is reduced to  $N_2$ , and at the same time organic matter, represented by  $CH_2O$  in Eq. (2.1), is oxidized to  $CO_2$ .

Anammox (anaerobic ammonium oxidation) is a process that was first discovered in wastewater treatment facilities in the 1980s and involves the oxidation of ammonium using nitrite as the oxidant. The reaction proceeds as follows:



The product once again is  $N_2$ , which accounts for 78% of Earth's atmosphere but is biologically unavailable to organisms other than species of bacteria that can fix  $N_2$ . The bacteria responsible for mediating the anammox reaction in wastewater treatment systems were later discovered in parts of the ocean, including the Black Sea, the oxygen minimum zone off the west coast of South America, and the Benguela upwelling system (Arrigo 2005). Remarkably, in the case of the Benguela upwelling system, it appears that very little  $N_2$  is actually produced by denitrifying bacteria. Instead, the principal role of the denitrifiers seems to be to convert  $NO_3^-$  to  $NO_2^-$ , which is then used by anammox bacteria to produce  $N_2$  (Kuypers et al. 2005).

Denitrification and anammox obviously tend to create N-limited conditions, because  $N_2$  is unavailable to aquatic plants other than nitrogen-fixing cyanobacteria. Because of the requirement for low oxygen concentrations, denitrification and anammox are restricted to only certain portions of aquatic habitats. Sediments are usually anoxic below the surface layer, particularly when the overlying water column is highly productive. According to Seitzinger (1988, p. 702), "During the mineralization of organic matter in sediments, a major portion of the mineralized nitrogen is lost from the ecosystem via denitrification," and "The loss of nitrogen via denitrification exceeds the input of nitrogen via  $N_2$  fixation in almost all river, lake, and coastal marine ecosystems in which both processes have been measured."

Denitrification and anammox are not confined to sediments. Both processes may occur in the water column when the oxygen concentrations drops below  $\sim 0.2 \text{ g m}^{-3}$ , a condition that is quite common in some lakes and certain parts of the ocean. Furthermore, even though the concentration of oxygen in a bulk water sample may be well above  $0.2 \text{ g m}^{-3}$ , very low  $O_2$  concentrations may exist in microzones associated with particles. Such microzones may be sites of denitrification and anammox. Studies summarized by Hattori (1983) indicate that the low-oxygen intermediate waters of the Tropical Eastern Pacific Ocean account for a major fraction of the denitrification that occurs in the water column of the ocean and that substantial amounts of denitrification also occur in the low-oxygen intermediate waters of the Arabian Sea, the bottom waters of the southwest African shelf, and perhaps in the Bay of Bengal. Following their

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<sup>1</sup> Organisms that lack the enzyme nitrate reductase cannot make use of nitrate nitrogen, which must be reduced to the oxidation state of ammonium nitrogen before it can be incorporated into organic matter. However, such organisms are the exception rather than the rule.

formation, oceanic bottom waters do not return to the surface again for times of typically 500–1000 years. It is reasonable to expect that denitrification and anammox would cause these subsurface waters to become depleted in nitrogen. The loss of fixed nitrogen via denitrification and anammox from bottom and intermediate waters is probably the major factor that causes subsequently upwelled marine surface waters to be N-limited.

The general picture that emerges from this analysis is that freshwater systems tend to be P-limited because of the sedimentation and burial of phosphate in the sediments, particularly in association with ferric oxides or oxyhydroxides. This mechanism is of much less consequence in the marine P cycle because of the very low Fe concentrations in seawater. The tendency of marine waters to be N-limited reflects the low iron concentration in seawater, the fact that P is recycled more efficiently than N by biological processes in the euphotic zone, and the long time during which denitrification and anammox may act to deplete subsurface waters of fixed nitrogen.

Although these generalizations are useful for understanding the role of nutrients in limiting photosynthetic rates in aquatic systems, it is important to realize that not all lakes and rivers are P-limited, nor are all marine waters N-limited. The magnitude and elemental composition of external nutrient inputs and the relative importance of various biogeochemical processes occurring within the system all combine to determine which nutrient or nutrients limit photosynthetic rates. The relative importance of these inputs and processes will vary from one system to another. Examples of exceptions to the general picture include the apparent limitation by iron of photosynthetic rates in the Pacific equatorial upwelling system, the offshore waters of the Antarctic, and the Northeast Pacific Subarctic Gyre. In those areas the concentrations of phosphate and nitrate in the euphotic zone are well above the levels associated with nutrient limitation, and nutrient enrichment studies conducted by Martin and Fitzwater (1988) as well as numerous *in situ* iron fertilization experiments (Blain et al. 2007; Boyd et al. 2000; Coale et al. 1996; de Baar et al. 2005; Kolber et al. 1994; Tsuda et al. 2003) have clearly shown that Fe is the single nutrient limiting primary production in these so-called high-nutrient, low-chlorophyll (HNLC) regions of the ocean. The explanation seems to be that the Fe/N ratio of intermediate depth ocean waters is low compared to the needs of phytoplankton (Martin and Gordon 1988). In the absence of external Fe inputs, these waters become Fe-limited when upwelled into the euphotic zone, for example, the Pacific equatorial upwelling system (Landry et al. 1997). In coastal waters the input of Fe from land runoff and release from sediments is apparently more than adequate to supply the needed iron, and in the large subtropical gyres that account for about 40% of the ocean's surface area, upwelling is so slow that atmospheric fallout of Fe from dust and rainfall is sufficient to provide the Fe required for photosynthesis. However, in the offshore waters of the Antarctic and northeast Pacific Oceans (Cassar et al. 2007; Tsuda et al. 2003) and in the Pacific equatorial upwelling system (Landry et al. 1997), atmospheric inputs and lateral transport of Fe are insufficient to keep pace with the upward movement of N into the euphotic zone. As a result phytoplankton strip the water of Fe long before the supply of N is exhausted.

There are, however, several places in the ocean where the dichotomy of nitrogen versus iron limitation does not hold. Empirical evidence, including the results of nutrient enrichment experiments, indicates that phosphorus limits photosynthetic rates in some marine waters, particularly parts of the Mediterranean Sea (Krom et al. 1991; Thingstad et al. 1998; Thingstad et al. 2005; Zohary and Robarts 1998), the Central and North Atlantic Ocean (Ammerman et al. 2003; Mills et al. 2004; Sanudo-Wilhelmy et al. 2001; Wu et al. 2000; Zubkov et al. 2007), and perhaps parts of the subtropical North Pacific Ocean (Karl et al. 2001). In the former two cases, these observations likely reflect high inputs of aeolian iron (Husar et al. 1997) that in turn stimulates nitrogen fixation and algal growth, which depletes the surface waters of phosphorus (Sanudo-Wilhelmy et al. 2001; Wu et al. 2000). It may also be responsible for removal of phosphate via adsorption to iron-rich dust (Krom et al. 1991).



## Questions

- 2.1** At the present time Earth's atmosphere contains about  $7.5 \times 10^{17}$  g of inorganic carbon in the form of  $\text{CO}_2$ . The concentration of dissolved inorganic carbon in the ocean is about  $28 \text{ g m}^{-3}$ . The volume of the ocean is about  $1.4 \times 10^{18} \text{ m}^3$ . What is the ratio of the total amount of dissolved inorganic carbon in the ocean to the total amount of inorganic carbon in the atmosphere?
- 2.2** Assume that you work for the United Nations and that a group of scientists comes to you with a proposal to reduce the concentration of  $\text{CO}_2$  in the atmosphere. The proposal is to fertilize the surface waters of the ocean to stimulate the fixation of about  $7.5 \times 10^{16}$  g of carbon, that is, about 10% of the  $\text{CO}_2$  in the atmosphere. They rationalize that the uptake of this much carbon from the surface waters of the ocean will cause an equivalent amount of inorganic carbon to enter the ocean from the atmosphere (recall Lake 227) and thereby reduce the concentration of  $\text{CO}_2$  in the atmosphere by about 10%. They propose to fertilize with either nitrogen (N), phosphorus (P), or iron (Fe). Assuming that the organic matter contains C, N, and P in the Redfield ratio, calculate the amount of N and P that would be required to stimulate the fixation of  $7.5 \times 10^{16}$  g of carbon. Compare these amounts of N and P with present global production of N and P for fertilizer use,  $7 \times 10^7$  tonnes of N and  $3.5 \times 10^7$  tonnes of P per year. How many years of fertilizer production would it take the world to produce enough N and P to stimulate the uptake of  $7.5 \times 10^{16}$  g of carbon by marine phytoplankton? The ratio of carbon to iron in marine phytoplankton is about  $10^4$  g of C per gram of Fe. How many grams of iron would be required to stimulate the uptake of  $7.5 \times 10^{16}$  g of carbon? Global iron production is presently about  $5.5 \times 10^{14} \text{ g y}^{-1}$ . How many days would it take the world to produce enough Fe to stimulate the uptake of  $7.5 \times 10^{16}$  g of carbon by marine phytoplankton?
- 2.3** After some discussion, the scientists decide that fertilization with iron would be the most practical way to stimulate the uptake of  $7.5 \times 10^{16}$  g of carbon. They propose to fertilize the surface waters of the Southern Ocean over a wide area where studies have shown that production is iron limited. In the Southern Ocean excess inorganic nitrogen is present in the surface waters at a concentration of about  $20 \mu\text{M}$ . What concentration of iron should be added to the surface waters to stimulate the uptake of this much inorganic nitrogen, assuming that the carbon-to-nitrogen ratio in the phytoplankton equals the Redfield ratio of 106:16 by atoms? Assume that this much iron is mixed into the euphotic zone, which is 50 m deep. Over what area of the ocean would the iron additions have to be made? How does this figure compare to the surface area of the ocean, which is  $3.6 \times 10^8 \text{ km}^2$ ? Suppose that the area of the Southern Ocean the scientists plan to fertilize is about the size of Alaska, which has an area of  $1.5 \times 10^6 \text{ km}^2$ . How many times would an area the size of Alaska have to be fertilized as described above to stimulate an uptake of  $7.5 \times 10^{16}$  g of carbon? Assume that a ship fertilizing the ocean with iron can fertilize about  $75 \text{ km}^2 \text{ d}^{-1}$ . How many ship-days would be required to fertilize an area the size of Alaska this many times?
- 2.4** A second group of scientists comes to you with another proposal for drawing down the  $\text{CO}_2$  concentration in the atmosphere. The second group of scientists points out that almost all the organic matter that sinks into the aphotic zone of the ocean decomposes completely. As a result the nitrogen and phosphorus incorporated into the organic matter

are released as inorganic nitrogen and inorganic phosphorus, respectively, in deep-ocean water. They argue that pumping this deep-ocean water to the surface would stimulate the synthesis of organic carbon by marine phytoplankton and cause an equivalent amount of  $\text{CO}_2$  to enter the ocean from the atmosphere. What is the flaw in their reasoning?

Wastewater with a nitrogen/phosphorus (N/P) ratio of 8 by atoms is being discharged into a lake. The N/P ratio of the algae in the lake is 16 by atoms. Assume that the wastewater is the only significant source of nitrogen and phosphorus for the lake and that either N or P limits algal biomass in the lake. What will happen to the algal biomass in the lake if.

- 2.5 The N in the wastewater is reduced by a factor of 10?
  - (a) No change
  - (b) Reduced by a factor of 2
  - (c) Reduced by a factor of 5
  - (d) Reduced by a factor of 10
- 2.6 The P in the wastewater is reduced by a factor of 10?
  - (a) No change
  - (b) Reduced by a factor of 2
  - (c) Reduced by a factor of 5
  - (d) Reduced by a factor of 10
- 2.7 The N in the wastewater is increased by a factor of 10?
  - (a) No change
  - (b) Increased by a factor of 2
  - (c) Increased by a factor of 5
  - (d) Increased by a factor of 10
- 2.8 The P in the wastewater is increased by a factor of 10?
  - (a) No change
  - (b) Increased by a factor of 2
  - (c) Increased by a factor of 5
  - (d) Increased by a factor of 10
- 2.9 The optical depth is a dimensionless number defined as  $\ln(I_0/I)$ , where  $I$  is the irradiance at a particular depth and  $I_0$  is the irradiance at the surface. The base of the euphotic zone is now commonly taken to be the depth at which  $I$  equals 0.1% of  $I_0$ . What is the optical depth associated with the base of the euphotic zone?

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## 3

## Physical Factors Affecting Production

Although the availability of light and nutrients most directly influences photosynthetic rates, purely physical processes such as upwelling, vertical mixing, and currents may greatly affect the availability of light and nutrients to aquatic plants. This chapter examines the physical properties of water relevant to these effects. Seasonal production cycles and the susceptibility of aquatic systems to cultural eutrophication stress are then examined using the physical and chemical concepts developed in the first two chapters. Estuaries are singled out for special consideration because of their importance in the life history of many aquatic organisms and because of their susceptibility to pollution stress.

### Physical Properties of Water

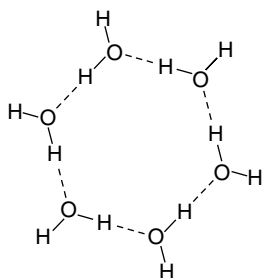
One of the most peculiar properties of pure water is the fact that its density maximum occurs at a temperature (4°C) above the freezing point (0°C). Thus, either heating or cooling pure water initially at a temperature of 4°C causes its density to decrease. On the other hand, the density of typical seawater with a **salinity** of 35 steadily increases as the water is cooled, no matter what the initial temperature is. What is there about pure water that causes it to have a density maximum at 4°C?

First of all, water is, chemically speaking, a polar molecule. The fact that the oxygen atom in the water molecule is more **electronegative** than the hydrogen atoms causes the distribution of negative electrons in the molecule to be shifted slightly toward the oxygen atom. As a result of this shift, the oxygen atom has a local partial negative charge, designated  $2\delta^-$ , and each of the two hydrogen atoms has a local partial positive charge, designated  $\delta^+$ . Figure 3.1 shows a water molecule in its equilibrium configuration and the polarization of charge associated with that structure. Note that the molecule is not linear. The H—O—H angle is about 105°. In the liquid and solid phases, individual water molecules interact with one another. Since positive and negative charges attract each other, the molecules tend to become oriented with their positive and negative ends close together. Figure 3.2 shows the hexagonal arrangement of water molecules in ice I, the most common crystalline form of ice. The hexagonal pattern of the molecules actually extends in three dimensions, although only a single hexagonal unit is shown in Figure 3.2.

The bridge between two adjacent oxygen atoms formed by the hydrogen atom attached to one of the oxygen atoms is called a **hydrogen bond**. Hydrogen bonds are indicated by dashed lines in Figure 3.2. Hydrogen bonds are caused by the attraction of a positively charged hydrogen atom for a negatively charged atom, in this case oxygen. Although the strength of hydrogen



**Figure 3.1** Simple chemical representation of a water molecule. Lines between the oxygen atom (O) and each hydrogen atom (H) represent electron-pair bonds, which hold the atoms in the molecule together.  $\delta^+$  and  $\delta^-$  signs indicate partial polarization of charge.



**Figure 3.2** Hexagonal arrangement of water molecules in ice. Each hydrogen atom is joined by an electron-pair bond to the nearest oxygen atom and by a hydrogen bond to the next closest oxygen atom.

bonds is small compared to that of normal electron-pair bonds,<sup>1</sup> it is the hydrogen bonds that largely serve to orient the water molecules in ice into structures such as ice I.<sup>2</sup> Each water molecule in the three-dimensional structure of ice I is hydrogen bonded to four nearest-neighbor water molecules. An important feature of this type of structure is its high degree of porosity. When ice melts, about 10% of the hydrogen bonds in the ice crystal are broken, and this breakage causes some of the structural units to collapse totally or partially. As these structural units collapse, the density of the water increases, because some of the gaps in the original ice structure are filled. Thus the density of liquid water at 0°C is greater than that of ice at 0°C, and ice therefore floats on water.

Although at any given time most of the water molecules in liquid water are hydrogen bonded,<sup>3</sup> the hydrogen bonds break and reform about  $10^{10}$  times per second. As the temperature of the water is further raised above 0°C, more hydrogen bonds break than form, and the structural units collapse even more. As a result the density of the water is further increased as more gaps in the structure are filled in with smaller collapsed units or individual molecules. However, the increase in temperature is accompanied by another effect that tends to reduce the density. As the water is heated, the individual molecules and structural units move about at faster speeds, just as the translational speed of the atoms or molecules in a gas increases as the temperature of the gas rises. The higher speed of the molecules and structural units in the water causes the water to expand slightly and become less dense, just as a gas expands and becomes less dense when it is heated. Hot air balloon enthusiasts routinely take advantage of the latter phenomenon. As pure water is warmed from 0 to 4°C, the density of the water increases because the effect of the collapsing structural units on the water's density more than offsets the reduction in density caused by the increased translational speed of the water molecules and structural units. However, the latter effect becomes more important above 4°C, and as a result the density of water steadily decreases as the temperature of the water rises above 4°C. Hence the maximum density of pure water occurs at 4°C.

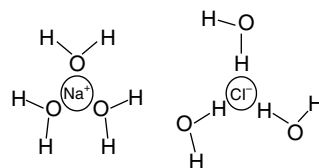
1 The hydrogen bonds in liquid water have a bond energy of about  $4.5 \text{ kcal mol}^{-1}$ . The covalent O—H bond in liquid water has a bond energy of  $110 \text{ kcal mol}^{-1}$ .

2 We now know that the bonding between neighboring water molecules is augmented by some covalent bonding (Helleman 1999), but hydrogen bonds are the principal mechanism that orients neighboring water molecules.

3 Most of the molecules in liquid water are hydrogen bonded even at 100°C, as evidenced by the high heat of vaporization of water.



**Figure 3.3** Qualitative arrangement of water molecules around a positive sodium ( $\text{Na}^+$ ) ion and a negative chlorine ( $\text{Cl}^-$ ) ion. Note that the negative (oxygen) end of the water molecule is closest to the positive  $\text{Na}^+$ , while the positive (hydrogen) end of the water molecule is closest to the negative  $\text{Cl}^-$ .



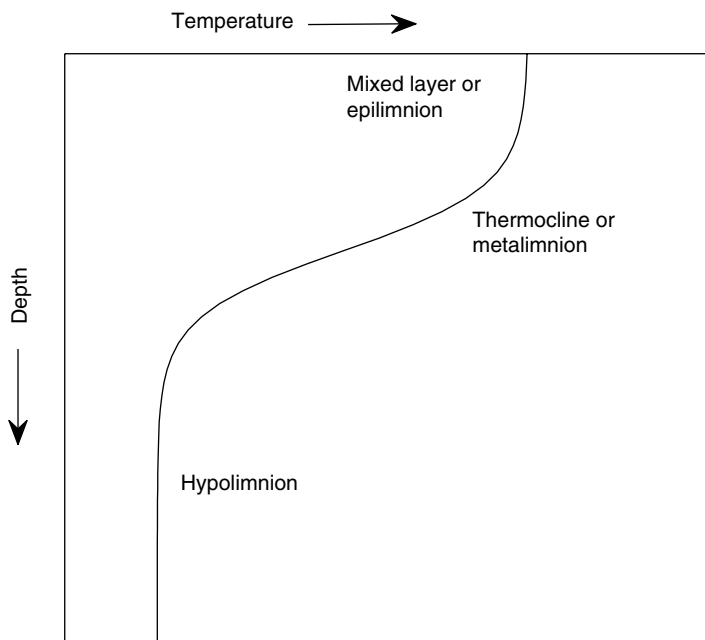
Substances dissolved in water disrupt to a certain degree the arrangement of the structural units. If the dissolved substances are ionic or polar themselves, water molecules become oriented about them with positive and negative ends in close proximity. Figure 3.3 shows how water molecules would be expected to orient themselves around a positive sodium ion and a negative chloride ion.

The concentration of dissolved ions in seawater with a salinity greater than about 24.7 is high enough to significantly disrupt the porous structure of pure water. As a result, changes in structure associated with heating or cooling are never great enough to override the effect on the water's density of changes in the translational speed of the molecules and structural units in the seawater. Thus, the density of seawater with a salinity greater than 24.7 steadily decreases as the water is warmed above the freezing point.

## Water Column Stability and Overturning

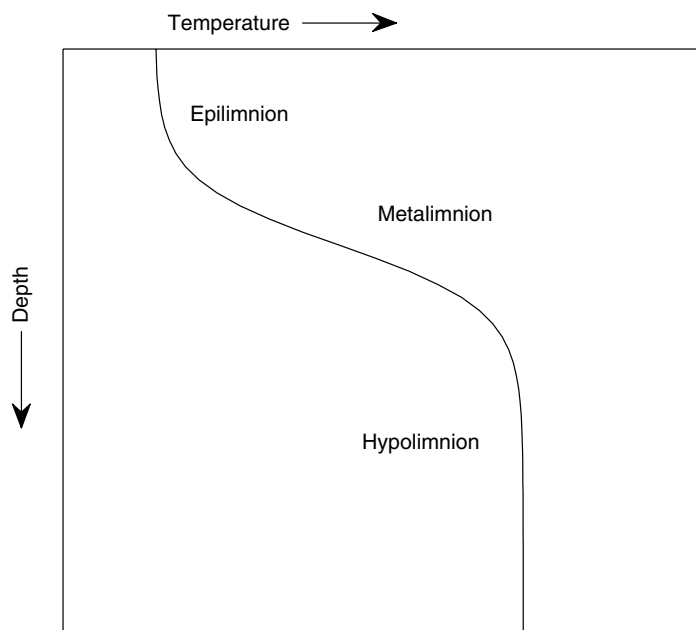
A column of water is resistant to vertical mixing (i.e., stable) if the **potential density** of the water increases steadily with increasing depth. Simplistically, the densest water is found on the bottom, and the least dense water is on the top. If the densest water is on the top, the water column is "top heavy" and will spontaneously mix vertically if slightly disturbed. In a freshwater system, the temperature in a stable water column will decrease steadily with depth if the temperature of the water is everywhere greater than  $4^\circ\text{C}$ . In the ocean the temperature of a stable water column will almost always decrease with increasing depth. However, because changes in salinity also affect density (the higher the salinity, the higher the density), it is possible that in a stable water column the temperature may increase with depth if the salinity also increases. The water column will be stable if the effect of the salinity increase on the density more than offsets the effect of the temperature increase. The warm salt brines at the bottom of the Red Sea, for example, remain at the bottom of the water column because their high salinity makes them denser than the cooler overlying waters. In most parts of the ocean, however, the temperature, or more correctly the **potential temperature**, decreases steadily with increasing depth.

Figure 3.4 shows the characteristic variation of temperature with depth in a hypothetical body of water. The water column is being heated from above by radiant energy, and hence the temperature is highest at the surface. Waves and turbulence generated by winds have created a region of almost constant temperature near the surface. This region is called the mixed layer, or, in strictly limnological work, the **epilimnion**. The depth of the mixed layer may vary greatly, depending on the strength of the winds and the stability of the water column. The mixed layer in a lake may be only a meter or so deep during parts of the summer, but perhaps a hundred or more meters deep at certain times during the fall or winter when the water column is destabilized. The region of relatively rapid temperature change below the mixed layer is called the **thermocline**, or, in limnological work, the **metalimnion**. Below the thermocline is a region of relatively constant temperature referred to as the **hypolimnion** by limnologists. Oceanographers have coined no special name for the corresponding region of the ocean, which we will therefore refer to as sub-thermocline water. The decrease of temperature with depth shown in Figure 3.4

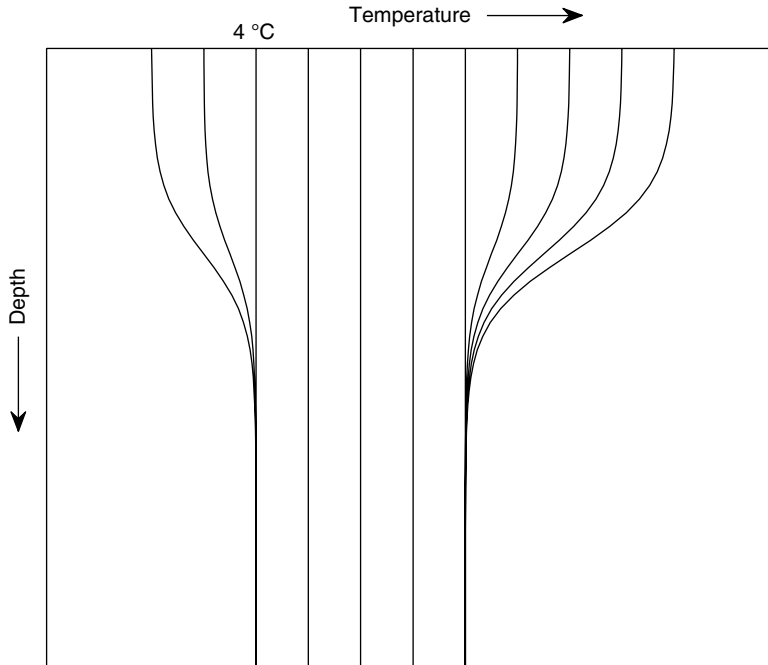


**Figure 3.4** Variation of temperature with depth in a thermally stable marine water column or in a stable column of freshwater in which the temperature is everywhere  $>4^{\circ}\text{C}$ .

would stabilize any water column of constant salinity in the ocean and would stabilize any column of freshwater if the temperature were everywhere  $>4^{\circ}\text{C}$ . Figure 3.5 shows the variation of



**Figure 3.5** Variation of temperature with depth in a thermally stable freshwater system in which the temperature is everywhere  $<4^{\circ}\text{C}$ .



**Figure 3.6** Temperature profiles in a hypothetical freshwater lake in a temperate climate from the end of summer (right-hand side) until the end of winter (left-hand side).

temperature with depth in a stable freshwater system in which the temperature is everywhere  $<4^{\circ}\text{C}$ . In this case the water column is being cooled from above, so that the lowest temperature is found at the surface. The water column is nevertheless stable because the density of freshwater increases with increasing temperature at temperatures below  $4^{\circ}\text{C}$ .

Now let us consider what happens to the temperature structure in a freshwater lake located in a temperate climate as the temperature of the atmosphere and the amount of radiant heating change seasonally. Figure 3.6 shows the sequence of temperature profiles that might be observed in the lake from the middle of summer until the middle of winter. As the atmosphere cools in the fall, heat fluxes from the surface waters of the warmer lake into the atmosphere, causing the temperature of the surface water to drop. As the surface water cools, it becomes denser and sinks. Consequently the mixed layer becomes deeper, and the thermocline begins to break down, as indicated in Figure 3.6. After sufficient cooling, the water column becomes **isothermal**, and any further cooling of the surface water causes the water column to mix from top to bottom. This period of downward mixing of surface waters caused by surface cooling is called the **fall overturn**. If the temperature of the atmosphere becomes sufficiently low, the lake water will be cooled and will remain isothermal until the temperature of the water reaches  $4^{\circ}\text{C}$ . At that point any further cooling of the surface water causes the water column to stratify, with the coldest water being at the top and the warmest water on the bottom. If the lake eventually freezes, the water temperature near the surface will be  $0^{\circ}\text{C}$ , and the temperature of the bottom water will be somewhere between 0 and  $4^{\circ}\text{C}$ .

Between the end of winter and the end of summer, the sequence of temperature profiles follows a pattern similar to the mirror image of Figure 3.6. In the early spring warming of the surface water causes it to become denser and hence induces downward mixing. The water column becomes isothermal at some temperature  $<4^{\circ}\text{C}$  and mixes to the bottom until the

temperature reaches 4°C. This period of water column mixing is called the **spring overturn**. Once the water temperature has reached 4°C, any further warming at the surface causes the water column to stratify. The highest temperature is now found at the surface, and the lowest temperature at the bottom. Thus any further warming at the surface leads to a typical summer temperature profile such as that in Figure 3.4.

Bodies of water that have two overturning periods per year separated by periods of **stratification** are called **dimictic** (twice-mixing). Most lakes in temperate climates in which the summer water temperature is >4°C and the winter water temperature is <4°C are dimictic. Bodies of water that overturn only once per year are termed **monomictic** (once-mixing). Warm lakes in which the winter water temperature never drops below 4°C may be monomictic, as may be cold lakes in which the summer water temperature never rises above 4°C. In the former case overturning occurs during the winter while the surface waters are being cooled; in the latter case overturning occurs during the summer when the surface waters are being warmed. Temperate marine waters with a salinity >24.7 never thermally stratify during the winter while the surface water is being cooled because the density of the water increases steadily all the way to the freezing point. In such waters overturning may occur throughout the winter, and the mixed layer at such times may be hundreds of meters deep.

### The Importance of Overturning

Overturning of the water column serves two highly important functions. First, downward mixing of oxygen-rich surface waters below the thermocline introduces oxygen into the bottom waters of aquatic systems. Without this mechanism of oxygen recharge, the hypolimnia of many lakes would become anoxic, since the simple downward diffusion of gases through a stratified water column is quite slow. For the hypolimnion to remain oxygenated, the respiratory consumption of oxygen by organisms living below the thermocline must not be rapid enough to consume all the oxygen between overturning periods.

The oxygen concentration in the bottom waters of the deep ocean, at depths of several kilometers or more, is almost everywhere unaffected by winter overturning in the waters directly above, since overturning in the oceans rarely occurs to depths as great as several kilometers. Exceptions to this rule are found in the Atlantic Ocean near Greenland and near Antarctica in the Weddell Sea. In the North Atlantic, evaporation causes the salinity of the surface waters to increase to roughly 35, and loss of heat to the atmosphere causes this water to sink to depths of 1.5–4.0 km when its temperature reaches 2–4°C. In the Weddell Sea, surface water temperatures during the winter drop to the freezing point of seawater, roughly –2°C. The formation of sea ice at such times leaves the surrounding waters enriched in dissolved salts, because sea ice has a relatively low salt content. The high salinity and very low temperature of these surface waters cause them to sink (with some mixing) all the way to the bottom. The Weddell Sea is the only area of the ocean where bottom water is formed. Deep-ocean currents transport this bottom water to all the major ocean basins, where mixing and very slow upwelling gradually bring the water back to the surface after a period of approximately 500 years. Despite the long **residence time** of this bottom water, only a very few areas of the ocean are **anoxic** at the bottom. The respiratory consumption of oxygen by organisms in the bottom waters of the ocean is very slow due to the cold temperatures (see discussion of  $Q_{10}$  in Chapter 8) and low rate of food supply. Consequently, the bottom waters remain oxygenated despite being out of contact with the atmosphere for hundreds of years. The only exceptions to this rule are found in places such as the Black Sea and Cariaco Trench, where the fallout of organic matter is exceptionally high and/or the bottom waters are unusually stagnant.

The second important function of overturning is the recharging of surface waters with nutrients. Inorganic nutrients regenerated by excretion or detrital decay below the mixed layer diffuse at only a slow rate upward through the thermocline. Thus in a lake at the end of the summer stratification period, one frequently finds very high nutrient concentrations in the hypolimnion and very low nutrient concentrations in the epilimnion. The low epilimnetic nutrient concentrations of course reflect uptake by the phytoplankton community. The breakdown of the thermocline and the mixing of epilimnetic and hypolimnetic waters return regenerated nutrients to the surface waters. A similar process occurs in the ocean. In aquatic systems where overturning is a weak phenomenon, biomass in the surface waters is low throughout the year due to the lack of an efficient mechanism for bringing nutrients from below the thermocline into the euphotic zone. The large oceanic subtropical gyres are illustrative of such systems.

## Seasonal Production Cycles

With this information one may explain, at least in a qualitative way, the seasonal production cycle found in many temperate aquatic systems. Table 3.1 lists nutrient, light, and photosynthetic characteristics during each of the four seasons in a hypothetical temperate system. During the summer the water column is highly stratified, with a shallow mixed layer whose depth is well above the critical depth. However, the concentration of nutrients in the mixed layer is quite low, and because no efficient mechanism exists for returning nutrients trapped below the thermocline to the mixed layer, photosynthetic rates are also low.

As the surface waters begin to cool in the fall, vertical mixing brings nutrient-rich waters into the euphotic zone. The surface light intensity is decreasing at this time, and the increasing depth of the mixed layer further reduces the average light intensity in the mixed layer. However, the bottom of the mixed layer is well above the critical depth, at least initially. With abundant nutrients and adequate light to support photosynthesis, a phytoplankton bloom frequently occurs at this time. The bloom is terminated when the declining surface light intensity and increasing mixed layer depth cause the bottom of the mixed layer to descend below the critical depth, or at least become close enough to the critical depth that net community production in the mixed layer is quite low.

During the winter nutrient levels in the mixed layer remain high, even if the water column stratifies, because the lack of light prevents any significant phytoplankton uptake of nutrients. Photosynthetic rates during this time are severely limited by the lack of light in the mixed layer.

Following the winter or spring overturning period, warming of surface waters causes the water column to stratify, and the depth of the mixed layer is therefore reduced. At the same

**Table 3.1** Nutrient, light, and photosynthetic characteristics during each of the four seasons in a typical temperate aquatic system in which the mixed layer does not extend to the bottom.

| Season | Nutrients  | Light      | Photosynthesis                                                                          |
|--------|------------|------------|-----------------------------------------------------------------------------------------|
| Summer | Low        | High       | Low and limited by lack of nutrients                                                    |
| Autumn | Increasing | Decreasing | An autumn bloom occurs and is terminated by decreasing light                            |
| Winter | High       | Low        | Low and limited by lack of light                                                        |
| Spring | Decreasing | Increasing | Vernal bloom occurs and is terminated by decreasing nutrient concentrations and grazing |

time the average surface light intensity is increasing, and the shallow winter critical depth begins to deepen. The combination of increasing surface light intensity and decreasing mixed layer depth obviously increases the light available to phytoplankton in the mixed layer. By utilizing the high nutrient concentrations in the mixed layer left over from the fall and perhaps winter mixing periods, the phytoplankton population begins to multiply. A bloom develops when the mixed layer extends no deeper than the upper region of the euphotic zone, where photosynthetic rates are uniformly high (Smetacek and Passow 1990). A combination of herbivore grazing and the exhaustion of nutrient reserves in the mixed layer usually terminates the spring phytoplankton bloom. Production during the rest of the summer remains at a low level, because much of the nutrient reserve used to set off the spring bloom has been temporarily lost below the thermocline as detritus or is tied up in higher trophic level biomass.

## Trophic Status

This admittedly simplified picture of photosynthetic seasonality in a temperate aquatic system underlines the importance of vertical mixing processes and water column stratification in determining the availability of light and nutrients for photosynthesis. Vertical mixing stimulates the recycling of nutrients from deep water but at the same time reduces the amount of light available to the phytoplankton by increasing the mixed layer depth. How then do aquatic systems become highly productive (i.e., eutrophic) for more than the short periods of time typical of spring or fall blooms? The answer is that in shallow systems the mixed layer may extend all the way or most of the way to the bottom during much of the year. In such systems recycling of nutrients is highly efficient, because there is little or no part of the system into which detritus may sink and regenerated nutrients become trapped. Because the system is shallow, it is impossible for the mixed layer to extend to great depths, and in fact the entire water column may be in the euphotic zone during much of the year. In contrast, in a very deep system, recycling of nutrients from detritus that has fallen far below the euphotic zone is extremely inefficient. In fact, in most parts of the ocean and in some deep lakes, overturning of the water column may never extend to the bottom. Furthermore, in deep systems, the mixed layer may extend to great depths during overturning periods, so that production is brought to a halt due to the lack of light in the mixed layer. Thus barring unusual circumstances (e.g., sewage disposal, upwelling), deep aquatic systems are inherently less productive than shallow aquatic systems. Recalling that the eutrophication process involves a gradual reduction in the depth of an aquatic system, it should not be surprising to learn that annual production in a system undergoing eutrophication is an accelerating function of time. The rate of increase of production is small at first but becomes progressively larger over the course of years as the system both accumulates nutrients and recycles them more efficiently. Relatively deep, unproductive systems are often referred to as being **oligotrophic** (few nutrients), whereas highly productive, usually shallow systems are called **eutrophic** (many nutrients or nourishing). The term **mesotrophic** is sometimes applied to systems with intermediate characteristics. One should not get the impression that all aquatic systems are initially oligotrophic. A lake, for example, may be shallow from its inception and therefore tend toward an initial high rate of production. The present trophic status of a body of water is determined both by its original characteristics and by its history since formation. In all cases, however, the natural tendency of aquatic systems is to become shallower and more productive, that is, to undergo eutrophication.

## Susceptibility of Systems to Oxygen Depletion

The aphotic zone of a body of water will become anoxic if the consumption of oxygen by biological or chemical processes exceeds the rate of resupply by vertical mixing and diffusion. With the exception of some species of bacteria, virtually all aquatic organisms require oxygen for respiration. It is therefore generally considered desirable for all parts of the water column to remain oxygenated. From our discussion of trophic status, it is obvious that depth is an important determinant of productivity in an aquatic system, and depth obviously influences the percentage of the water column that is impacted by vertical mixing and overturning. Consequently, depth plays an important role in determining the susceptibility of an aquatic system to oxygen depletion.

Deep oligotrophic systems are the least likely of aquatic systems to develop oxygen depletion problems. This conclusion is based on the following two considerations:

- 1) With the exception of allochthonous inputs such as stream runoff, virtually all the organic carbon that is metabolized by aphotic zone organisms must have been produced in the euphotic zone. Consequently, the respiratory activity of aphotic zone organisms is directly related to the productivity in the euphotic zone. Because oligotrophic systems are by definition unproductive systems, the amount of food available to aphotic zone organisms is small, and the numbers of these organisms and their overall respiratory rate are also small.
- 2) In a deep aquatic system, the volume of water below the thermocline is large relative to the volume of the mixed layer. Therefore the total amount of oxygen potentially available for respiration in a deep system is quite large relative to the small part of the system that is used for production. Thus the productivity of the surface waters would have to be exceptionally high for respiration to significantly reduce the average deep-water oxygen concentration. If the deep waters are reoxygenated regularly by means of overturning, it is virtually impossible for a deep oligotrophic system to become anoxic at any depth.

Shallow systems that are mixed to the bottom at all times obviously do not develop seasonal oxygen depletion problems. If there is a sufficiently vigorous mixing of the water column and exchange of gases with the atmosphere, the oxygen concentration in such systems is likely to remain near the saturation level at all times. If the wind dies down, however, so that oxygen exchange with the atmosphere is sluggish, the oxygen concentration in a highly productive, shallow system may drop to almost zero within a few days or even a few hours. The lowest concentrations are of course observed at night, when there is no photosynthetic production of oxygen. The shallow western basin of Lake Erie, with an average depth of only about 7.4 m, provides a good example of a shallow, productive system that may develop serious oxygen depletion problems after several days of calm weather. Aquaculture ponds, which are typically only about 1.0 m deep and receive large inputs of allochthonous organic matter in the form of feeds, are illustrative of the more extreme cases in which the respiratory activity of organisms in the system may strip the water of oxygen within a few hours on a calm night.

Seasonal oxygen depletion problems are undoubtedly most common in bodies of water having somewhat intermediate depths, that is, shallow enough to be highly productive, yet deep enough so that the mixed layer does not extend to the bottom except during overturning periods. In lakes of this sort, the hypolimnion may be rather small compared with the epilimnion. Hence even a moderate amount of production in the epilimnion may result in enough food being consumed and respired in the hypolimnion to reduce the hypolimnetic oxygen concentration to virtually zero between overturning events. The central basin of Lake Erie, with a mean depth of 18.5 m, is a good example of such a system. The disappearance from Lake Erie's

central basin of certain fish species that normally inhabit cold, deep waters and that function efficiently only when oxygen concentrations are near saturation levels is undoubtedly explained in part by the periodic low oxygen concentrations that characterize the central basin's hypolimnion. We will study the conditions in Lake Erie in more detail in Chapter 4. For the moment, suffice it to say that the development of low oxygen concentrations below the thermocline in any aquatic system is frequently associated with an undesirable change in the type and abundance of organisms living in the water.

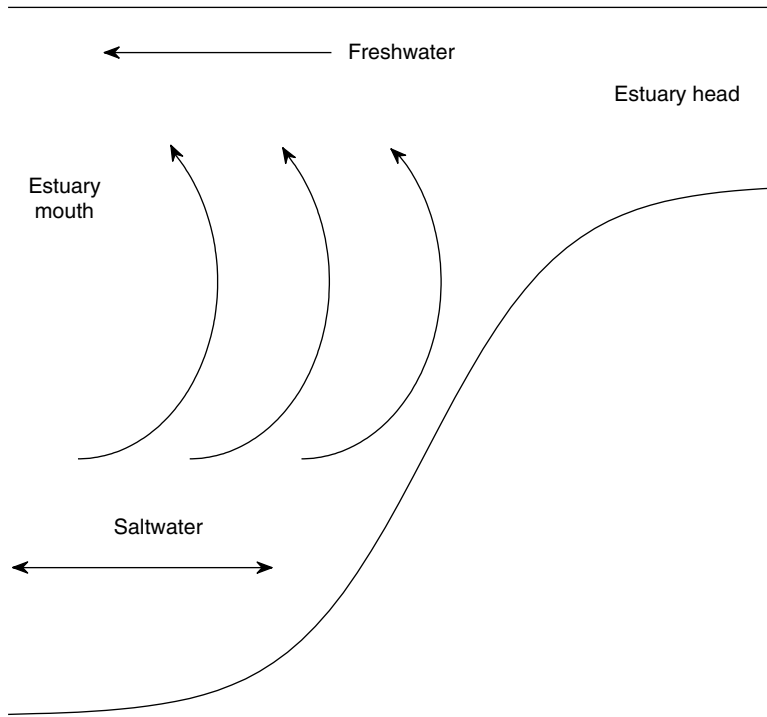
Large-scale fish kills, in some cases involving hundreds of thousands or even millions of fish, are probably the most dramatic and most highly publicized results of oxygen depletion problems associated with eutrophication. Seasonal fluctuations of oxygen levels are unlikely to be associated with the sudden killing of large numbers of organisms, because seasonal declines in oxygen concentration are gradual. In such cases organisms are more likely to be eliminated from the system due to their inability to function efficiently (e.g., to escape predators, obtain food, or reproduce) than to suffocation. It is possible, however, in extremely productive systems, for oxygen levels to fluctuate from saturating or supersaturating conditions during the day to virtually zero at night. The aforementioned aquaculture ponds are examples of systems with the potential for this sort of behavior, but similar problems may develop in more natural systems seriously impacted by eutrophication. If the concentration of phytoplankton in the water is very dense, one can expect that the abundance of herbivores, primary carnivores, and higher trophic level organisms will also be high, because organisms are naturally attracted to a source of food. If this situation should develop in a fairly open system, and if the oxygen level does drop dangerously low at night, all motile organisms will rapidly try to leave the area and for the most part will be successful as long as there are wide avenues of escape. Large-scale kills of aquatic organisms do, however, sometimes occur in bodies of water that have only restricted escape routes. In such an isolated and highly eutrophic body of water, large numbers of organisms may be attracted by the abundance of food during the day when the oxygen concentration is high. At night, however, the respiration of all these organisms may consume the oxygen in the water, and organisms that are unable to find their way out of the system will suffocate. A system must be highly eutrophic for such a situation to develop, but there is no doubt that large-scale kills of the sort described do occur from time to time in some systems.

## Estuaries: A Special Case

An **estuary** is defined as a semi-enclosed coastal body of water having a free connection with the open ocean and within which seawater is measurably diluted by freshwater derived from land drainage (Lauff 1967). Estuaries may be formed by the drowning of river valleys (Chesapeake Bay), by glacial scouring (Puget Sound), by the formation of barrier islands or sand spits (Pamlico Sound), or by tectonic processes (San Francisco Bay).

Regardless of their mode of formation, estuaries tend to be highly productive systems because of the nature of the **estuarine circulation** pattern that characterizes these systems. Because freshwater is less dense than saltwater of comparable temperature, there is a natural tendency in estuarine systems for the freshwater from land runoff to flow from the head to the mouth of the estuary along the surface, whereas seawater moves in and out with the tides along the bottom. Figure 3.7 depicts the general pattern of water movement in an estuary. As the curved arrows in Figure 3.7 indicate, there is invariably some upward mixing of seawater into the freshwater, so that some of the seawater that enters the estuary near the bottom flows back out near the surface. As a result there is a net outflow of water (freshwater mixed with some saltwater) at the mouth of the estuary in the upper water column, and a net inflow of seawater in





**Figure 3.7** Simplified estuarine circulation pattern.

the lower water column. If the flux of freshwater into the estuary at the head is large compared with the tidal in-and-out flux of seawater, there is generally a sharp demarcation between the freshwater at the top of the water column and the saltwater below. Due to the mixing of saltwater and freshwater, this sharp transition region gradually blurs as one approaches the mouth of the estuary. Such an estuary is commonly referred to as a **salt wedge estuary**, because of the shape of the saltwater “wedge” in the lower part of the water column when the estuary is viewed in profile (Fig. 3.8).

If the in-and-out flux of the tides is large compared with the flux of freshwater, then freshwater and seawater tend to be thoroughly mixed together throughout the estuary, except of course in the immediate vicinity of the head. Such an estuary is commonly referred to as a well-mixed estuary. Undoubtedly many estuaries are best classified as having circulation patterns intermediate between those of typical salt wedge and well-mixed estuaries. The important point to bear in mind, however, is that there is a net outflow of water near the surface and a net inflow near the bottom at the mouth of all estuaries, regardless of whether the details of the circulation pattern correspond most closely to those of a salt wedge, well-mixed, or intermediate-type situation.

Because there is a net inflow and upward mixing of seawater at the bottom of an estuary, detritus that has sunk out of the mixed layer at the surface and regenerated nutrients from the deeper water are constantly being carried back into the estuary and mixed up into the surface waters. Suspended organic matter that drifts out of the estuary on the surface current and that subsequently sinks offshore or is eaten and then excreted offshore tends to be swept back into the estuary by the net influx of bottom water. Figure 3.9 depicts the cycling of nutrients and organic matter in an estuary as influenced by the estuarine circulation pattern. Thus the physical circulation pattern in estuaries provides a natural mechanism for recycling food and

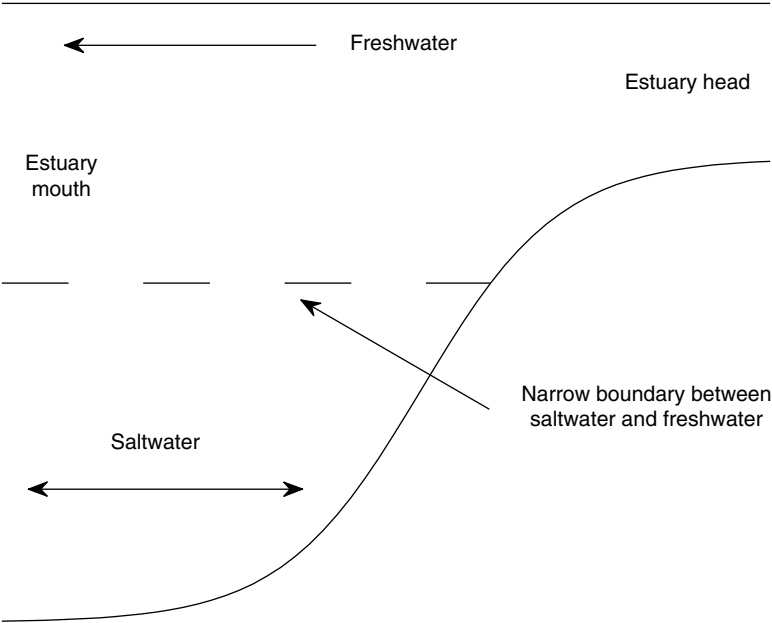


Figure 3.8 Profile of a salt wedge estuary.

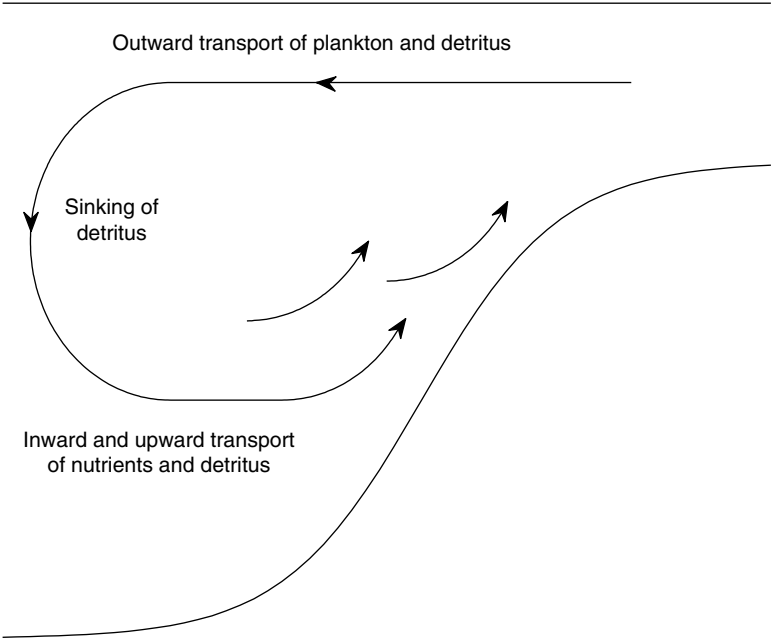


Figure 3.9 Cycling of nutrients and organic matter in a typical estuary.

inorganic nutrients and thereby maintains a high level of production in the system. Unfortunately, pollutants introduced into an estuary tend to be recycled by the same circulation mechanism. From this standpoint alone, estuaries are one of the last places one would

choose to discharge pollutants, because the pollutants will not be conveniently washed out to sea and dispersed. Rather they will tend to be recycled over and over within the estuarine system. Admittedly there will be leakage to the open ocean, and some pollutants will tend to be trapped in the sediments rather than recycled in the water column. However, as a general rule, the estuarine circulation pattern can be expected to exacerbate the impact of pollutants discharged into the estuary. Estuaries are particularly susceptible to problems associated with cultural eutrophication, because the estuarine circulation pattern tends to recycle discharged nutrients and hence magnify their impact on production and biomass.

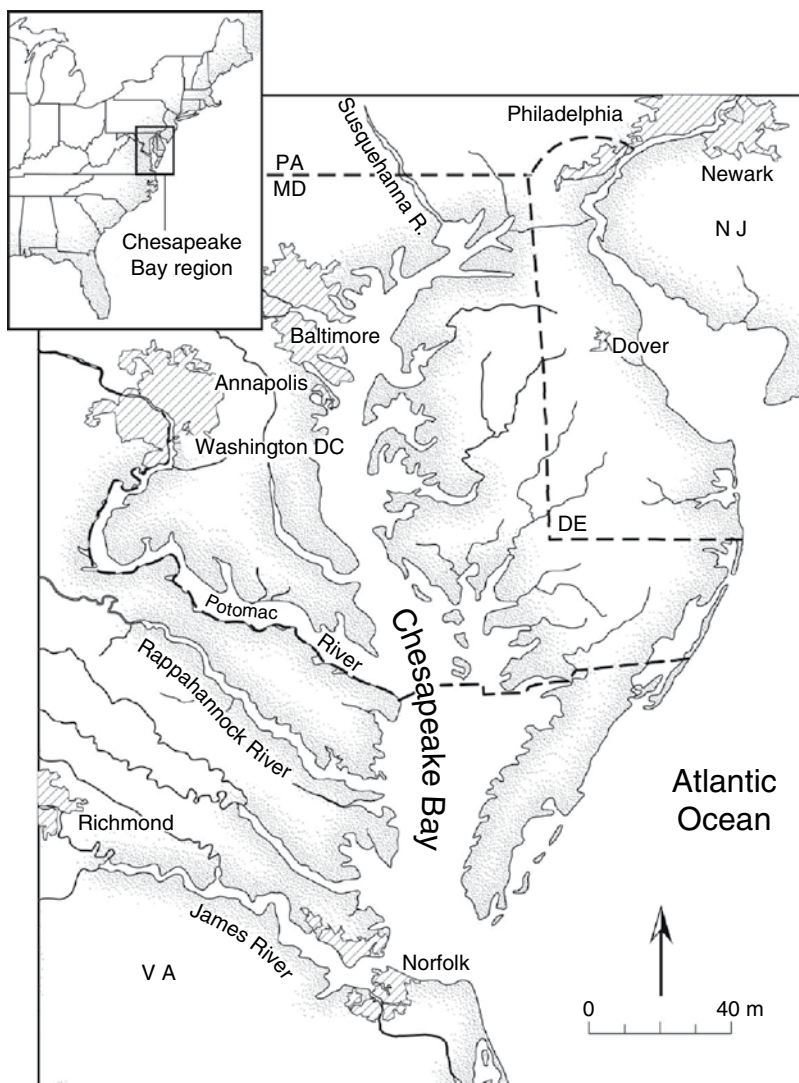
Estuaries are naturally eutrophic systems because of the high efficiency with which the estuarine circulation pattern recycles nutrients. Because of their high productivity, estuaries such as those found along the coastline of the United States account for some important coastal fisheries. Furthermore, estuaries serve as breeding and/or nursery grounds for many organisms that one usually associates with the open ocean, such as sharks and whales. Finally, estuaries are traversed by a number of migratory species that breed either in freshwater (e.g., salmon) or in saltwater (e.g., the American eel). Contamination of estuaries by any sort of pollution may therefore have much graver consequences for aquatic systems than would perhaps be apparent from a casual examination of the abundance and kinds of organisms present in the estuary at any one time. Many large population and industrial centers have developed adjacent to estuaries because of the easy access to both the ocean and inland river systems for water transportation. Unfortunately, the wastes from these large population/industrial centers have often been discharged carelessly into estuarine waters, with little or no awareness of the biological importance of the estuary or of the tendency of pollutants to be recycled within the system. The following two examples are particularly good illustrations of the role of physical processes in determining the impact of pollutant discharges on estuarine systems.

## Chesapeake Bay

The Chesapeake Bay is the largest estuary in the United States. It was formed as a result of the rise of sea level following the last glaciation and is basically the drowned lower course of the Susquehanna River (Fig. 3.10). The Bay has an area of about 11,400 km<sup>2</sup>, but its average depth is only 6–7 m. The Susquehanna and Potomac rivers account for about 70% of the freshwater flow into the Bay. Historically the Chesapeake Bay has been a highly productive ecosystem. It still supports several thousand full-time commercial seafood harvesters, and it produces roughly 27% of the US commercial catch of menhaden, 38% of blue crabs, and 63% of striped bass (NOAA 2015). Nevertheless, the Chesapeake Bay is not well.

Between 1965 and 1985 the Bay lost 80–90% of its benthic grass beds, which provided critical habitat for many fish and aquatic birds. During roughly the same period, there were dramatic declines in the populations of fish such as striped bass, shad, yellow perch, alewife, blueback herring, and white perch. The oyster populations are estimated to be about 1% of what they were in 1900 (Baker and Horton 1990). Their decline has been attributed to a combination of overfishing, pollution, and disease.

Oxygen depletion in the bottom waters of the Chesapeake Bay during the summer has been a common occurrence for many years (Newcombe and Horne 1938), but some studies have suggested that the problem has become much more severe in recent years (Hagy et al. 2004; Officer et al. 1984). The most obvious culprit has been eutrophication, and with this in mind a serious effort to reduce nutrient loading to the Bay began in 1987. The effort was part of a larger program to restore and protect the Bay, formally set forth in mutual agreements between



**Figure 3.10** Chesapeake Bay and its major tributary streams.

the Environmental Protection Agency (EPA), the Chesapeake Bay Commission, and the states of Virginia, Maryland, Pennsylvania, and the District of Columbia in 1983, 1987, 2000, 2010, and 2014 (CBP 2015). The history of the so-called Chesapeake Bay Program (CBP) is discussed in the following text.

The 1983 agreement was a one-page document that recognized that a cooperative approach was necessary to solve the Bay's pollution problems. The 1987 agreement established goals for the reduction of pollutant loading to the Bay, goals that were to be met by the year 2000. Among the goals was a 40% reduction in the loading of N and P to the Bay. Amendments to the 1987 agreement in 1992 targeted nutrient reduction at upstream sources and called for an evaluation of the CBP's Basinwide Toxics Reduction Strategy to determine the impact of toxic substances on the Bay's biota. The year 2000 marked the signing of Chesapeake 2000, a very comprehensive agreement that established 102 goals to upgrade the condition of the Bay and,