Fourth Edition

Aquatic Pollution

An Introductory Text

Edward A. Laws

WILEY

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Contents

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 $842 \, km^2$. The concentration of phosphorus in Onondaga Lake, New York, sometimes characterized as the most polluted lake in the United States, dropped from $730 \, \mu g \, L^{-1}$ in 1970 to less than $20 \, \mu g \, L^{-1}$ 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 $750 \, km^2$ 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[1]; 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^2 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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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 compound**s 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.

$$\text{Energy} + \underset{\text{carbon dioxide}}{6CO_2} + \underset{\text{water}}{6H_2O} \quad \overset{\text{Photosynthesis}}{\underset{\text{Respiration}}{\rightleftarrows}} \quad \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6O_2}$$
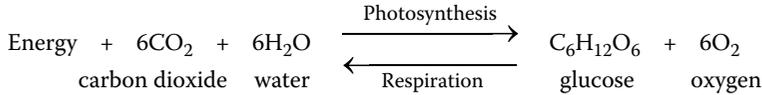
In this case glucose is the organic compound; the term organic means that the compound is found in organisms. If the reaction proceeds from left to right, the energy source is sunlight. Part of this energy is stored chemically in the glucose molecule. If the glucose is then oxidized by burning it with 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**.[1] 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

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1 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 1.1 Diagram of a food chain through trophic level four.
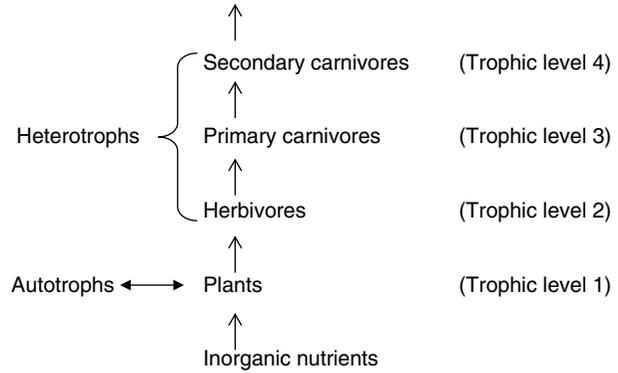
level, primary carnivores the third trophic level, and so forth. Such a food chain is depicted schematically in Figure 1.1.

In most aquatic systems the transfer of food from one trophic level to the next is believed to occur with an efficiency of only about 20%. In other words, the rate at which food is ingested by a trophic level is about five times greater than the rate at which food is passed on to the next trophic level. This efficiency is referred to as an **ecological efficiency**, or more specifically as a trophic level intake efficiency (Odum 1971, p. 76). Ecological efficiencies are generally low, because much of the food ingested by a trophic level is either respired to provide energy or excreted because it cannot be incorporated into new trophic level biomass. However, ecological efficiencies are also reduced when, for example, an organism dies from disease or a female fish releases her eggs into the water. Eggs occupy a trophic level that is always lower than the trophic level of the organism that produced them.

Ecological Pyramids

Because ecological efficiencies are only about 20% in aquatic systems, the flux of food from one trophic level to the next steadily decreases as one moves up the food chain. The result is that the primary production rate is likely to greatly exceed the production of top-level carnivores, the magnitude of the discrepancy depending on the number of trophic levels in the food chain. Ryther (1969) has estimated that there are roughly six trophic levels in typical open-ocean marine food chains. In contrast, some coastal and upwelling areas may have food chains with as few as three trophic levels. This difference stems in part from the fact that the primary producers in open-ocean systems are dominated by very small microscopic plants called **phytoplankton**, whereas in coastal and upwelling areas the individual phytoplankton cells tend to be larger, and the cells tend to form chains and gelatinous masses. In the coastal and upwelling areas, the primary producers can therefore be efficiently grazed by rather large herbivorous crustaceans such as **copepods** or even small fish. However, in the open ocean, most of the phytoplankton are much too small to be consumed by crustaceans and small fish, and several intermediate trophic levels therefore separate these two categories of organisms.

Regardless of the length of the food chain, the steady decrease in the flux of food to higher and higher trophic levels usually results in a decrease in the biomass of organisms on successively higher trophic levels. Thus, if one were to represent the biomass of each trophic level by a bar whose length was proportional to the biomass of organisms in the trophic level and if one were to lay these bars on top of each other, the resulting figure would look qualitatively like Figure 1.2. Arranged in this way the bars of trophic level biomass form a pyramid, often referred to as an ecological pyramid.

| Trophic level 4 |
| Trophic level 3 |
| Trophic level 2 |
| Trophic level 1 |
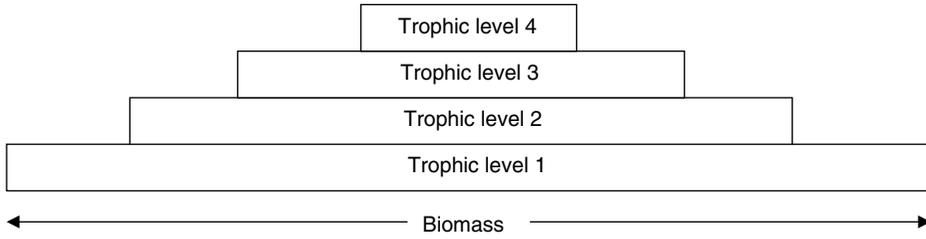
Biomass

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:

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

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

$$\frac{B_3}{B_2} = E \frac{T_2}{T_3} \tag{1.2}$$

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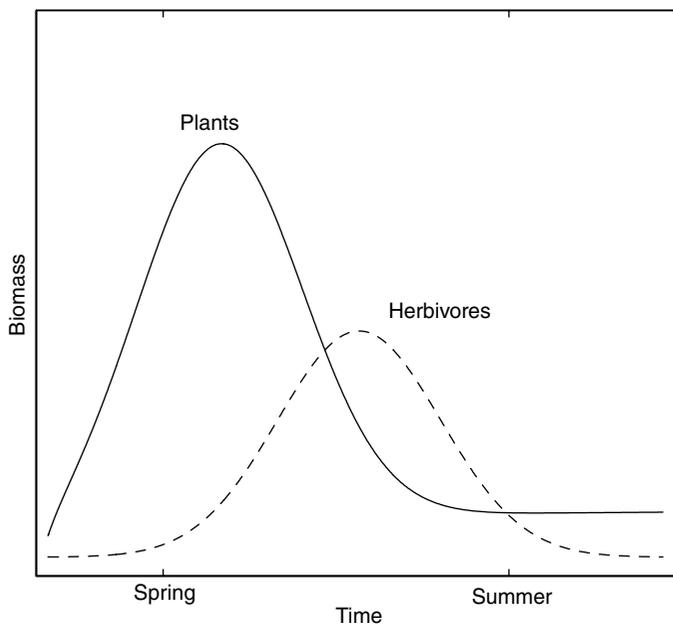
Figure 1.3 Biomass of plants and herbivores during spring and early summer in a hypothetical temperate aquatic ecosystem.

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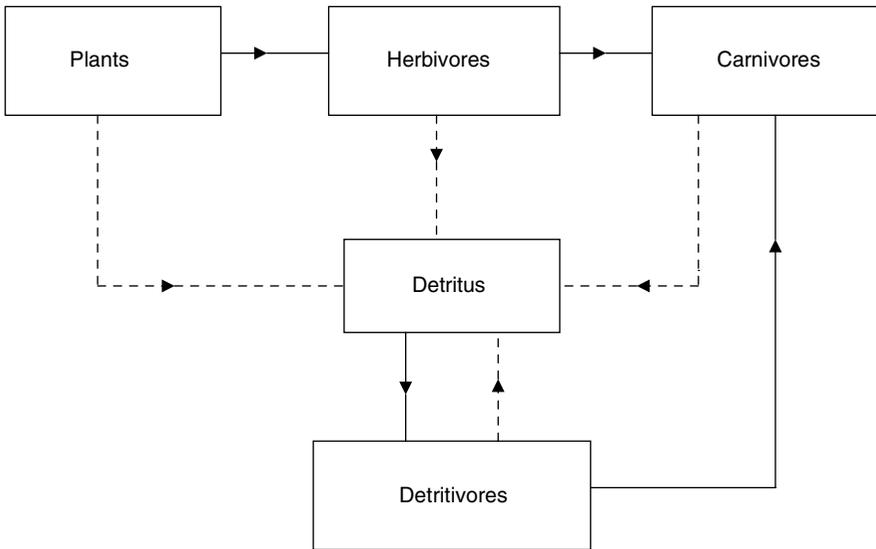
Figure 1.4 Box model of the grazing and detritus food chains and the interactions between the two food chains. Solid lines represent feeding relationships. Dashed lines represent excretion.

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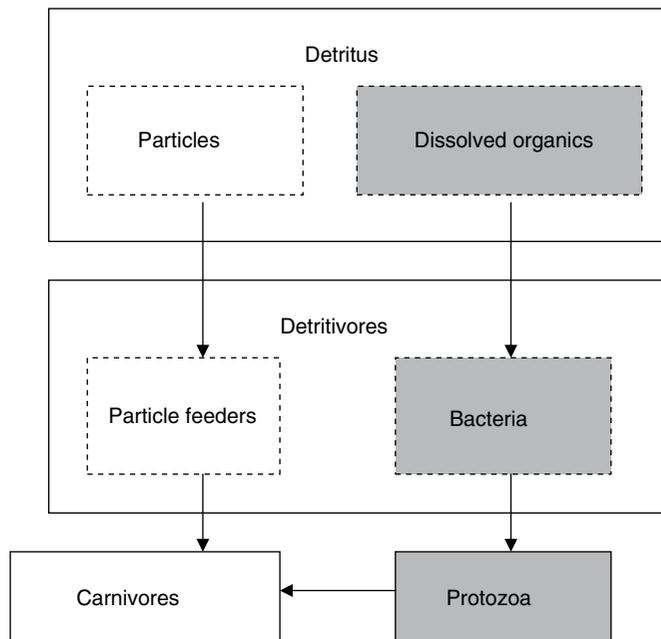
within the system. Such a system cannot persist unless subsidized by an external input of organic compounds, as, for example, from stream runoff.

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.[2] 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)[a]
Water	0.00005
Plankton	0.04
Silverside minnow	0.23
Sheepshead minnow	0.94
Pickerel (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

$$\frac{P_3}{P_2} = E_P \frac{T_{2P}}{T_{3P}} \tag{1.3}$$

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

$$\frac{(P_3 / B_3)}{(P_2 / B_2)} = \left(\frac{P_3}{P_2}\right)\left(\frac{B_2}{B_3}\right) = \frac{E_P\left(\dfrac{T_{2P}}{T_{3P}}\right)}{E\left(\dfrac{T_2}{T_P}\right)} = \frac{E_P}{E} \tag{1.4}$$

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 logicality 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