

7 WATER POLLUTION

7.1. NATURE AND TYPES OF WATER POLLUTANTS

Throughout history, the quality of drinking water has been a factor in determining human welfare. Fecal pollution of drinking water has frequently caused waterborne diseases that have decimated the populations of whole cities. Unwholesome water polluted by natural sources has caused great hardship for people forced to drink it or use it for irrigation.

Although there are still occasional epidemics of bacterial and viral diseases caused by infectious agents carried in drinking water, waterborne diseases have in general been well controlled, and drinking water in technologically advanced countries is now remarkably free of the disease-causing agents that were very common water contaminants only a few decades earlier.

Currently, waterborne toxic chemicals pose the greatest threat to the safety of water supplies in industrialized nations. This is particularly true of groundwater in the U.S., which exceeds in volume the flow of all U.S. rivers, lakes, and streams. In some areas, the quality of groundwater is subject to a number of chemical threats. There are many possible sources of chemical contamination. These include wastes from industrial chemical production, metal plating operations, and pesticide runoff from agricultural lands. Some specific pollutants include industrial chemicals such as chlorinated hydrocarbons; heavy metals, including cadmium, lead, and mercury; saline water; bacteria, particularly coliforms; and general municipal and industrial wastes.

Since World War II there has been a tremendous growth in the manufacture and use of synthetic chemicals. Many of the chemicals have contaminated water supplies. Two examples are insecticide and herbicide runoff from agricultural land, and industrial discharge into surface waters. Also, there is a threat to groundwater from waste chemical dumps and landfills, storage lagoons, treating ponds, and other facilities. These threats are discussed in more detail in Chapter 19.

It is clear that water pollution should be a concern of every citizen. Understanding the sources, interactions, and effects of water pollutants is essential for

controlling pollutants in an environmentally safe and economically acceptable manner. Above all, an understanding of water pollution and its control depends upon a basic knowledge of aquatic environmental chemistry. That is why this text covers the principles of aquatic chemistry prior to discussing pollution. Water pollution may be studied much more effectively with a sound background in the fundamental properties of water, aquatic microbial reactions, sediment-water interactions, and other factors involved with the reactions, transport, and effects of these pollutants.

Water pollutants can be divided among some general categories, as summarized in [Table 7.1](#). Most of these categories of pollutants, and several subcategories, are discussed in this chapter. An enormous amount of material is published on this subject each year, and it is impossible to cover it all in one chapter. In order to be up to date on this subject the reader may want to survey journals and books dealing with water pollution, such as those listed in the Supplementary References section at the end of this chapter.

Table 7.1. General Types of Water Pollutants

Class of pollutant	Significance
Trace Elements	Health, aquatic biota, toxicity
Heavy metals	Health, aquatic biota, toxicity
Organically-bound metals	Metal transport
Radionuclides	Toxicity
Inorganic pollutants	Toxicity, aquatic biota
Asbestos	Human health
Algal nutrients	Eutrophication
Acidity, alkalinity, salinity (in excess)	Water quality, aquatic life
Trace organic pollutants	Toxicity
Polychlorinated biphenyls	Possible biological effects
Pesticides	Toxicity, aquatic biota, wildlife
Petroleum wastes	Effect on wildlife, esthetics
Sewage, human and animal wastes	Water quality, oxygen levels
Biochemical oxygen demand	Water quality, oxygen levels
Pathogens	Health effects
Detergents	Eutrophication, wildlife, esthetics
Chemical carcinogens	Incidence of cancer
Sediments	Water quality, aquatic biota, wildlife
Taste, odor, and color	Esthetics

7.2. ELEMENTAL POLLUTANTS

Trace element is a term that refers to those elements that occur at very low levels of a few parts per million or less in a given system. The term **trace substance** is a more general one applied to both elements and chemical compounds.

Table 7.2 summarizes the more important trace elements encountered in natural waters. Some of these are recognized as nutrients required for animal and plant life, including some that are essential at low levels but toxic at higher levels. This is typical behavior for many substances in the aquatic environment, a point that must be

Table 7.2. Important Trace Elements in Natural Waters

Element	Sources	Effects and Significance
Arsenic	Mining byproduct, chemical waste	Toxic ¹ , possibly carcinogenic
Beryllium	Coal, industrial wastes	Toxic
Boron	Coal, detergents, wastes	Toxic
Chromium	Metal plating	Essential as Cr(III), toxic as Cr(VI)
Copper	Metal plating, mining, industrial waste	Essential trace element, toxic to plants and algae at higher levels
Fluorine (F ⁻)	Natural geological sources, wastes, water additive	Prevents tooth decay at around 1 mg/L, toxic at higher levels
Iodine (I ⁻)	Industrial wastes, natural brines, seawater intrusion	Prevents goiter
Iron	Industrial wastes, corrosion, acid mine water, microbial action	Essential nutrient, damages fixtures by staining
Lead	Industrial waste, mining, fuels	Toxic, harmful to wildlife
Manganese	Industrial wastes, acid mine water, microbial action	Toxic to plants, damages fixtures by staining
Mercury	Industrial waste, mining, coal	Toxic, mobilized as methyl mercury compounds by anaerobic bacteria
Molybdenum	Industrial wastes, natural sources	Essential to plants, toxic to animals
Selenium	Natural sources, coal	Essential at lower levels, toxic at higher levels
Zinc	Industrial waste, metal plating, plumbing	Essential element, toxic to plants at higher levels

¹ Toxicities of these elements are discussed in Chapter 23.

kept in mind in judging whether a particular element is beneficial or detrimental. Some of these elements, such as lead or mercury, have such toxicological and environmental significance that they are discussed in detail in separate sections.

Some of the **heavy metals** are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to humans. These elements are in general the transition metals, and some of the representative elements, such as lead and tin, in the lower right-hand corner of the periodic table. Heavy metals include essential elements like iron as well as toxic metals like cadmium and mercury. Most of them have a tremendous affinity for sulfur and disrupt enzyme function by forming bonds with sulfur groups in enzymes. Protein carboxylic acid ($-\text{CO}_2\text{H}$) and amino ($-\text{NH}_2$) groups are also chemically bound by heavy metals. Cadmium, copper, lead, and mercury ions bind to cell membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate biocompounds or catalyze their decomposition. The biochemical effects of metals are discussed in Chapter 23.

Some of the **metalloids**, elements on the borderline between metals and non-metals, are significant water pollutants. Arsenic, selenium, and antimony are of particular interest.

Inorganic chemicals manufacture has the potential to contaminate water with trace elements. Among the industries regulated for potential trace element pollution of water are those producing chlor-alkali, hydrofluoric acid, sodium dichromate (sulfate process and chloride ilmenite process), aluminum fluoride, chrome pigments, copper sulfate, nickel sulfate, sodium bisulfate, sodium hydrosulfate, sodium bisulfite, titanium dioxide, and hydrogen cyanide.

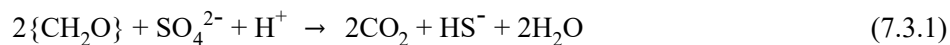
7.3. HEAVY METALS

Cadmium

Pollutant **cadmium** in water may arise from industrial discharges and mining wastes. Cadmium is widely used in metal plating. Chemically, cadmium is very similar to zinc, and these two metals frequently undergo geochemical processes together. Both metals are found in water in the +2 oxidation state.

The effects of acute cadmium poisoning in humans are very serious. Among them are high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells. It is believed that much of the physiological action of cadmium arises from its chemical similarity to zinc. Specifically, cadmium may replace zinc in some enzymes, thereby altering the stereostructure of the enzyme and impairing its catalytic activity. Disease symptoms ultimately result.

Cadmium and zinc are common water and sediment pollutants in harbors surrounded by industrial installations. Concentrations of more than 100 ppm dry weight sediment have been found in harbor sediments. Typically, during periods of calm in the summer when the water stagnates, the anaerobic bottom layer of harbor water has a low soluble Cd concentration because microbial reduction of sulfate produces sulfide,



which precipitates cadmium as insoluble cadmium sulfide:



Mixing of bay water from outside the harbor and harbor water by high winds during the winter results in desorption of cadmium from harbor sediments by aerobic bay water. This dissolved cadmium is carried out into the bay where it is absorbed by suspended solid materials, which then become incorporated with the bay sediments. This is an example of the sort of complicated interaction of hydraulic, chemical solution-solid, and microbiological factors involved in the transport and distribution of a pollutant in an aquatic system.

Lead

Inorganic **lead** arising from a number of industrial and mining sources occurs in water in the +2 oxidation state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually entered natural water systems. In addition to pollutant sources, lead-bearing limestone and galena (PbS) contribute lead to natural waters in some locations.

Despite greatly increased total use of lead by industry, evidence from hair samples and other sources indicates that body burdens of this toxic metal have decreased during recent decades. This may be the result of less lead used in plumbing and other products that come in contact with food or drink.

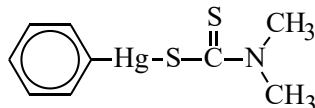
Acute lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver, and the brain and central nervous system. Sickness or death results. Lead poisoning from environmental exposure is thought to have caused mental retardation in many children. Mild lead poisoning causes anemia. The victim may have headaches and sore muscles, and may feel generally fatigued and irritable.

Except in isolated cases, lead is probably not a major problem in drinking water, although the potential exists in cases where old lead pipe is still in use. Lead used to be a constituent of solder and some pipe-joint formulations, so that household water does have some contact with lead. Water that has stood in household plumbing for some time may accumulate significant levels of lead (along with zinc, cadmium, and copper) and should be drained for a while before use.

Mercury

Because of its toxicity, mobilization as methylated forms by anaerobic bacteria, and other pollution factors, **mercury** generates a great deal of concern as a heavy-metal pollutant. Mercury is found as a trace component of many minerals, with continental rocks containing an average of around 80 parts per billion, or slightly less, of this element. Cinnabar, red mercuric sulfide, is the chief commercial mercury ore. Fossil fuel coal and lignite contain mercury, often at levels of 100 parts per billion or even higher, a matter of some concern with increased use of these fuels for energy resources.

Metallic mercury is used as an electrode in the electrolytic generation of chlorine gas, in laboratory vacuum apparatus, and in other applications. Significant quantities of inorganic mercury(I) and mercury(II) compounds are used annually. Organic mercury compounds used to be widely applied as pesticides, particularly fungicides. These mercury compounds include aryl mercurials such as phenyl mercuric dimethyldithiocarbamate



(formerly used in paper mills as a slimicide and as a mold retardant for paper), and alkyl-mercurials such as ethylmercuric chloride, C_2H_5HgCl , that was used as a seed fungicide. Because of their resistance to degradation and their mobility, the alkyl mercury compounds are generally considered to be more of an environmental threat than either the aryl or inorganic compounds.

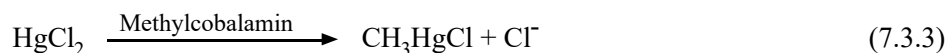
Mercury enters the environment from a large number of miscellaneous sources related to human use of the element. These include discarded laboratory chemicals, batteries, broken thermometers, amalgam tooth fillings, and formerly lawn fungicides and pharmaceutical products. Taken individually, each of these sources may not contribute much of the toxic metal, but the total effect can be substantial. Sewage effluent sometimes contains up to 10 times the level of mercury found in typical natural waters.

The toxicity of mercury was tragically illustrated in the Minamata Bay area of Japan during the period 1953-1960. A total of 111 cases of mercury poisoning and 43 deaths were reported among people who had consumed seafood from the bay that had been contaminated with mercury waste from a chemical plant that drained into Minamata Bay. Congenital defects were observed in 19 babies whose mothers had consumed seafood contaminated with mercury. The level of metal in the contaminated seafood was 5-20 parts per million.

Among the toxicological effects of mercury are neurological damage, including irritability, paralysis, blindness, or insanity; chromosome breakage; and birth defects. The milder symptoms of mercury poisoning such as depression and irritability have a psychopathological character. Because of the resemblance of these symptoms to common human behavior, mild mercury poisoning may escape detection. Some forms of mercury are relatively nontoxic and were formerly used as medicines, for example, in the treatment of syphilis. Other forms of mercury, particularly organic compounds, are highly toxic.

Because there are few major natural sources of mercury, and since most inorganic compounds of this element are relatively insoluble, it was assumed for some time that mercury was not a serious water pollutant. However, in 1970, alarming mercury levels were discovered in fish in Lake Saint Clair located between Michigan and Ontario, Canada. A subsequent survey by the U.S. Federal Water Quality Administration revealed a number of other waters contaminated with mercury. It was found that several chemical plants, particularly caustic chemical manufacturing operations, were each releasing up to 14 or more kilograms of mercury in wastewaters each day.

The unexpectedly high concentrations of mercury found in water and in fish tissues result from the formation of soluble monomethylmercury ion, CH_3Hg^+ , and volatile dimethylmercury, $(\text{CH}_3)_2\text{Hg}$, by anaerobic bacteria in sediments. Mercury from these compounds becomes concentrated in fish lipid (fat) tissue and the concentration factor from water to fish may exceed 10^3 . The methylating agent by which inorganic mercury is converted to methylmercury compounds is methylcobalamin, a vitamin B_{12} analog:



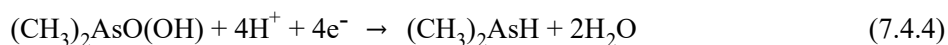
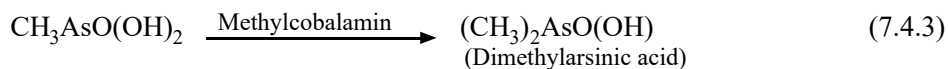
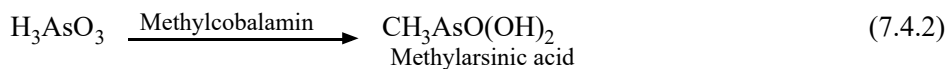
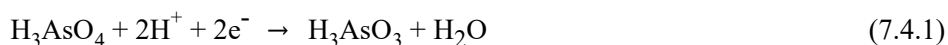
It is believed that the bacteria that synthesize methane produce methylcobalamin as an intermediate in the synthesis. Thus, waters and sediments in which anaerobic decay is occurring provide the conditions under which methylmercury production occurs. In neutral or alkaline waters, the formation of dimethylmercury, $(\text{CH}_3)_2\text{Hg}$, is favored. This volatile compound can escape to the atmosphere.

7.4. METALLOIDS

The most significant water pollutant metalloid element is arsenic, a toxic element that has been the chemical villain of more than a few murder plots. Acute arsenic poisoning can result from the ingestion of more than about 100 mg of the element. Chronic poisoning occurs with the ingestion of small amounts of arsenic over a long period of time. There is some evidence that this element is also carcinogenic.

Arsenic occurs in the Earth's crust at an average level of 2-5 ppm. The combustion of fossil fuels, particularly coal, introduces large quantities of arsenic into the environment, much of it reaching natural waters. Arsenic occurs with phosphate minerals and enters into the environment along with some phosphorus compounds. Some formerly-used pesticides, particularly those from before World War II, contain highly toxic arsenic compounds. The most common of these are lead arsenate, $\text{Pb}_3(\text{AsO}_4)_2$; sodium arsenite, Na_3AsO_3 ; and Paris Green, $\text{Cu}_3(\text{AsO}_3)_2$. Another major source of arsenic is mine tailings. Arsenic produced as a by-product of copper, gold, and lead refining exceeds the commercial demand for arsenic, and it accumulates as waste material.

Like mercury, arsenic may be converted to more mobile and toxic methyl derivatives by bacteria, according to the following reactions:



7.5. ORGANICALLY BOUND METALS AND METALLOIDS

An appreciation of the strong influence of complexation and chelation on heavy metals' behavior in natural waters and wastewaters may be gained by reading Sections 3.10-3.17, which deal with that subject. Methylmercury formation is discussed in Section 7.3. Both topics involve the combination of metals and organic entities in water. It must be stressed that the interaction of metals with organic compounds is of utmost importance in determining the role played by the metal in an aquatic system.

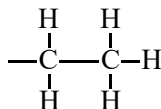
There are two major types of metal-organic interactions to be considered in an aquatic system. The first of these is complexation, usually chelation when organic ligands are involved. A reasonable definition of complexation by organics applicable to natural water and wastewater systems is a system in which a species is present that reversibly dissociates to a metal ion and an organic complexing species as a function of hydrogen ion concentration:



In this equation, M^{2+} is a metal ion and H_2L is the acidic form of a complexing—frequently chelating—ligand, L^{2-} , illustrated here as a compound that has two ionizable hydrogens.

Organometallic compounds, on the other hand, contain metals bound to organic entities by way of a carbon atom and do not dissociate reversibly at lower pH or greater dilution. Furthermore, the organic component, and sometimes the particular oxidation state of the metal involved, may not be stable apart from the organometallic compound. A simple way to classify organometallic compounds for the purpose of discussing their toxicology is the following:

1. Those in which the organic group is an alkyl group such as ethyl in tetraethyllead, $Pb(C_2H_5)_4$:

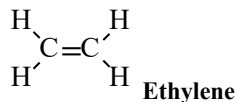


2. **Carbonyls**, some of which are quite volatile and toxic, having carbon monoxide bonded to metals:



(In the preceding Lewis formula of CO each dash, —, represents a pair of bonding electrons, and each pair of dots, :, represents an unshared pair of electrons.)

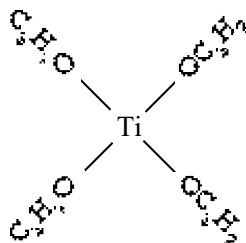
3. Those in which the organic group is a π electron donor, such as ethylene or benzene.



Combinations exist of the three general types of compounds outlined above, the most prominent of which are arene carbonyl species in which a metal atom is bonded to both an aryl entity such as benzene and to several carbon monoxide molecules.

A large number of compounds exist that have at least one bond between the metal and a C atom on an organic group, as well as other covalent or ionic bonds between the metal and atoms other than carbon. Because they have at least one metal-carbon bond, as well as properties, uses, and toxicological effects typical of organometallic compounds, it is useful to consider such compounds along with organometallic compounds. Examples are monomethylmercury chloride, CH_3HgCl , in which the organometallic CH_3Hg^+ ion is ionically bonded to the chloride anion. Another example is phenyldichloroarsine, $\text{C}_6\text{H}_5\text{AsCl}_2$, in which a phenyl group is covalently bonded to arsenic through an As-C bond, and two Cl atoms are also covalently bonded to arsenic.

A number of compounds exist that consist of organic groups bonded to a metal atom through atoms other than carbon. Although they do not meet the strict definition thereof, such compounds can be classified as organometallics for the discussion of their toxicology and aspects of their chemistry. An example of such a compound is isopropyl titanate, $\text{Ti}(i\text{-OC}_3\text{H}_7)_4$, also called titanium isopropylate,



a colorless liquid melting at 14.8°C and boiling at 104°C . Its behavior is more that of an organometallic compound than that of an inorganic compound, and by virtue of its titanium content it is not properly classified as an organic compound. The term “organometal” is sometimes applied to such a compound, which for environmental considerations may be regarded as an organometallic compound.

The interaction of trace metals with organic compounds in natural waters is too vast an area to cover in detail in this chapter; however, it may be noted that metal-organic interactions may involve organic species of both pollutant (such as EDTA) and natural (such as fulvic acids) origin. These interactions are influenced by, and sometimes play a role in, redox equilibria; formation and dissolution of precipitates; colloid formation and stability; acid-base reactions; and microorganism-mediated reactions in water. Metal-organic interactions may increase or decrease the toxicity of metals in aquatic ecosystems, and they have a strong influence on the growth of algae in water.

Organotin Compounds

Of all the metals, tin has the greatest number of organometallic compounds in commercial use, with global production on the order of 40,000 metric tons per year.

In addition to synthetic organotin compounds, methylated tin species can be produced biologically in the environment. Figure 7.1 gives some examples of the many known organotin compounds.

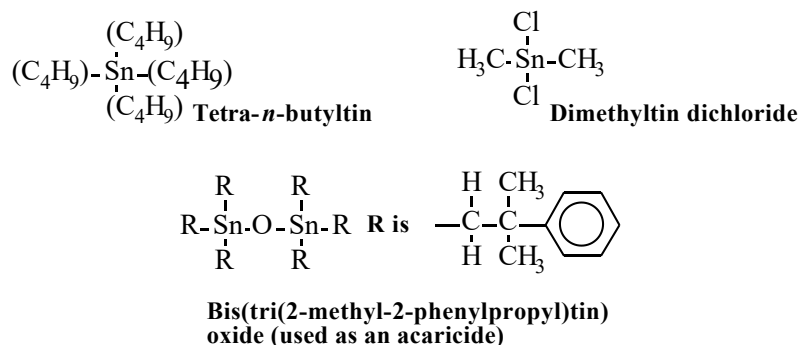


Figure 7.1. Examples of organotin compounds.

Major industrial uses of organotin compounds include applications of tin compounds in fungicides, acaricides, disinfectants, antifouling paints, stabilizers to lessen the effects of heat and light in PVC plastics, catalysts, and precursors for the formation of films of SnO_2 on glass. Tributyl tin chloride and related tributyl tin (TBT) compounds have bactericidal, fungicidal, and insecticidal properties and are of particular environmental significance because of their use as industrial biocides. In addition to tributyl tin chloride, other tributyl tin compounds used as biocides include the hydroxide, the naphthenate, bis(tributyltin) oxide, and tris(tributylstannyl) phosphate. TBT has been widely used in boat and ship hull coatings to prevent the growth of fouling organisms. Other applications include preservation of wood, leather, paper, and textiles. Antifungal TBT compounds have been used as slimicides in cooling tower water.

Obviously the many applications of organotin compounds for a variety of uses poses a significant potential for environmental pollution. Because of their applications near or in contact with bodies of water, organotin compounds are potentially significant water pollutants and have been linked to endocrine disruption in shellfish, oysters, and snails. Because of such concerns, several countries, including the U.S., England, and France, prohibited TBT application on vessels smaller than 25 meters in length during the 1980s. In response to concerns over water pollution, in 1998 the International Maritime Organization agreed to ban organotin antifouling paints on all ships by 2003.

7.6. INORGANIC SPECIES

Some important inorganic water pollutants were mentioned in Sections 7.2-7.4 as part of the discussion of pollutant trace elements. Inorganic pollutants that contribute acidity, alkalinity, or salinity to water are considered separately in this chapter. Still another class is that of algal nutrients. This leaves unclassified, however, some important inorganic pollutant species, of which cyanide ion, CN^- , is probably the most important. Others include ammonia, carbon dioxide, hydrogen sulfide, nitrite, and sulfite.

Cyanide

Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid, K_a of 6×10^{-10} . The cyanide ion has a strong affinity for many metal ions, forming relatively less-toxic ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$, with iron(II), for example. Volatile HCN is very toxic and has been used in gas chamber executions in the U.S.

Cyanide is widely used in industry, especially for metal cleaning and electroplating. It is also one of the main gas and coke scrubber effluent pollutants from gas works and coke ovens. Cyanide is widely used in certain mineral-processing operations. In August of 1995 approximately 2.7 billion liters of cyanide-contaminated water mixed with red clay from mine tailings spilled into the Essequibo River from a breached dam at a gold mining operation in the South American country of Guyana. The water contained cyanide at a level of approximately 25 parts per million, which killed all the fish in the small Omai Creek leading from the breached dam to the Essequibo River. No human fatalities or confirmed health effects were reported, however.

Ammonia and Other Inorganic Pollutants

Excessive levels of ammoniacal nitrogen cause water-quality problems. **Ammonia** is the initial product of the decay of nitrogenous organic wastes, and its presence frequently indicates the presence of such wastes. It is a normal constituent of low-pE groundwaters and is sometimes added to drinking water, where it reacts with chlorine to provide residual chlorine (see Section 8.11). Since the $\text{p}K_a$ of ammonium ion, NH_4^+ , is 9.26, most ammonia in water is present as NH_4^+ rather than as NH_3 .

Hydrogen sulfide, H_2S , is a product of the anaerobic decay of organic matter containing sulfur. It is also produced in the anaerobic reduction of sulfate by microorganisms (see Chapter 6) and is evolved as a gaseous pollutant from geothermal waters. Wastes from chemical plants, paper mills, textile mills, and tanneries may also contain H_2S . Its presence is easily detected by its characteristic rotten-egg odor. In water, H_2S is a weak diprotic acid with $\text{p}K_{a1}$ of 6.99 and $\text{p}K_{a2}$ of 12.92; S^{2-} is not present in normal natural waters. The sulfide ion has tremendous affinity for many heavy metals, and precipitation of metallic sulfides often accompanies production of H_2S .

Free **carbon dioxide**, CO_2 , is frequently present in water at high levels due to decay of organic matter. It is also added to softened water during water treatment as part of a recarbonation process (see Chapter 8). Excessive carbon dioxide levels may make water more corrosive and may be harmful to aquatic life.

Nitrite ion, NO_2^- , occurs in water as an intermediate oxidation state of nitrogen over a relatively narrow pE range. Nitrite is added to some industrial process water as a corrosion inhibitor. However, it rarely occurs in drinking water at levels over 0.1 mg/L.

Sulfite ion, SO_3^{2-} , is found in some industrial wastewaters. Sodium sulfite is commonly added to boiler feedwaters as an oxygen scavenger:



Since pK_{a1} of sulfurous acid is 1.76 and pK_{a2} is 7.20, sulfite exists as either HSO_3^- or SO_3^{2-} in natural waters, depending upon pH. It may be noted that hydrazine, N_2H_4 , also functions as an oxygen scavenger:



Asbestos in Water

The toxicity of inhaled asbestos is well established. The fibers scar lung tissue and cancer eventually develops, often 20 or 30 years after exposure. It is not known for sure whether asbestos is toxic in drinking water. This has been a matter of considerable concern because of the dumping of taconite (iron ore tailings) containing asbestos-like fibers into Lake Superior. The fibers have been found in drinking waters of cities around the lake. After having dumped the tailings into Lake Superior since 1952, the Reserve Mining Company at Silver Bay on Lake Superior solved the problem in 1980 by constructing a 6-square-mile containment basin inland from the lake. This \$370-million facility keeps the taconite tailings covered with a 3-meter layer of water to prevent escape of fiber dust.

7.7. ALGAL NUTRIENTS AND EUTROPHICATION

The term **eutrophication**, derived from the Greek word meaning “well-nourished,” describes a condition of lakes or reservoirs involving excess algal growth. Although some algal productivity is necessary to support the food chain in an aquatic ecosystem, excess growth under eutrophic conditions may eventually lead to severe deterioration of the body of water. The first step in eutrophication of a body of water is an input of plant nutrients ([Table 7.3](#)) from watershed runoff or sewage. The nutrient-rich body of water then produces a great deal of plant biomass by photosynthesis, along with a smaller amount of animal biomass. Dead biomass accumulates in the bottom of the lake, where it partially decays, recycling nutrient carbon dioxide, phosphorus, nitrogen, and potassium. If the lake is not too deep, bottom-rooted plants begin to grow, accelerating the accumulation of solid material in the basin. Eventually a marsh is formed, which finally fills in to produce a meadow or forest.

Eutrophication is often a natural phenomenon; for instance, it is basically responsible for the formation of huge deposits of coal and peat. However, human activity can greatly accelerate the process. To understand why this is so, refer to [Table 7.3](#), which shows the chemical elements needed for plant growth. Most of these are present at levels more than sufficient to support plant life in the average lake or reservoir. Hydrogen and oxygen come from the water itself. Carbon is provided by CO_2 from the atmosphere or from decaying vegetation. Sulfate, magnesium, and calcium are normally present in abundance from mineral strata in contact with the water. The micronutrients are required at only very low levels (for example, approximately 40 ppb for copper). Therefore, the nutrients most likely to be limiting are the “fertilizer” elements: nitrogen, phosphorus, and potassium. These are all present in sewage and are, of course, found in runoff from heavily fertilized

fields. They are also constituents of various kinds of industrial wastes. Each of these elements can also come from natural sources—phosphorus and potassium from mineral formations, and nitrogen fixed by bacteria, cyanobacteria, or discharge of lightning in the atmosphere.

Table 7.3. Essential Plant Nutrients: Sources and Functions

Nutrient	Source	Function
<i>Macronutrients</i>		
Carbon (CO ₂)	Atmosphere, decay	Biomass constituent
Hydrogen	Water	Biomass constituent
Oxygen	Water	Biomass constituent
Nitrogen (NO ₃ ⁻)	Decay, pollutants, atmosphere (from nitrogen-fixing organisms)	Protein constituent
Phosphorus (phosphate)	Decay, minerals, pollutants	DNA/RNA constituent
Potassium	Minerals, pollutants	Metabolic function
Sulfur (sulfate)	Minerals	Proteins, enzymes
Magnesium	Minerals	Metabolic function
Calcium	Minerals	Metabolic function
<i>Micronutrients</i>		
B, Cl, Co, Cu, Fe, Mo, Mn, Na, Si, V, Zn	Minerals, pollutants	Metabolic function and/or constituent of enzymes

In most cases, the single plant nutrient most likely to be limiting is phosphorus, and it is generally named as the culprit in excessive eutrophication. Household detergents are a common source of phosphate in wastewater, and eutrophication control has concentrated upon eliminating phosphates from detergents, removing phosphate at the sewage treatment plant, and preventing phosphate-laden sewage effluents (treated or untreated) from entering bodies of water. (See Chapter 3 for additional details regarding phosphates and detergent phosphate substitutes in water.)

In some cases, nitrogen or even carbon may be limiting nutrients. This is particularly true of nitrogen in seawater.

The whole eutrophication picture is a complex one, and continued research is needed to solve the problem. It is indeed ironic that in a food-poor world, nutrient-rich wastes from overfertilized fields or from sewage are causing excessive plant growth in many lakes and reservoirs. This illustrates a point that in many cases pollutants are resources (in this case, plant nutrients) gone to waste.

7.8. ACIDITY, ALKALINITY, AND SALINITY

Aquatic biota are sensitive to extremes of pH. Largely because of osmotic effects, they cannot live in a medium having a salinity to which they are not adapted. Thus, a fresh-water fish soon succumbs in the ocean, and sea fish normally cannot live in fresh water. Excess salinity soon kills plants not adapted to it. There are, of course, ranges in salinity and pH in which organisms live. As shown in Figure 7.2, these ranges frequently may be represented by a reasonably symmetrical curve, along the fringes of which an organism may live without really thriving. These curves do not generally exhibit a sharp cutoff at one end or the other, as does the high-temperature end of the curve representing the growth of bacteria as a function of temperature (Figure 6.7).

The most common source of **pollutant acid** in water is acid mine drainage. The sulfuric acid in such drainage arises from the microbial oxidation of pyrite or other sulfide minerals as described in Chapter 6. The values of pH encountered in acid-polluted water may fall below 3, a condition deadly to most forms of aquatic life except the culprit bacteria mediating the pyrite and iron(II) oxidation, which thrive under very low pH conditions. Industrial wastes frequently have the potential to contribute strong acid to water. Sulfuric acid produced by the air oxidation of pollutant sulfur dioxide (see Chapter 11) enters natural waters as acidic rainfall. In cases where the water does not have contact with a basic mineral, such as limestone, the water pH may become dangerously low. This condition occurs in some Canadian lakes, for example.

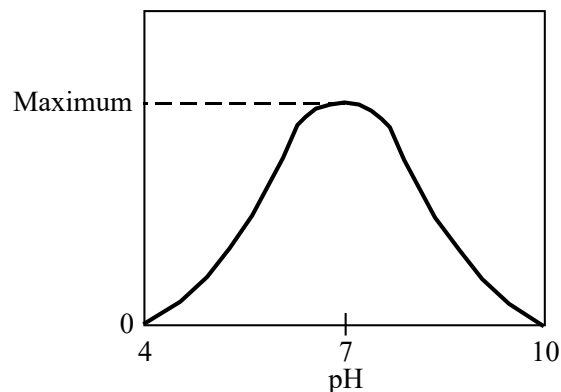


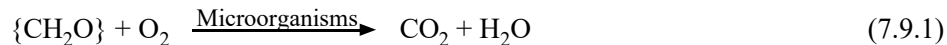
Figure 7.2. A generalized plot of the growth of an aquatic organism as a function of pH.

Excess **alkalinity**, and frequently accompanying high pH, generally are not introduced directly into water from anthropogenic sources. However, in many geographic areas, the soil and mineral strata are alkaline and impart a high alkalinity to water. Human activity can aggravate the situation—for example, by exposure of alkaline overburden from strip mining to surface water or groundwater. Excess alkalinity in water is manifested by a characteristic fringe of white salts at the edges of a body of water or on the banks of a stream.

Water **salinity** may be increased by a number of human activities. Water passing through a municipal water system inevitably picks up salt from a number of processes; for example, recharging water softeners with sodium chloride is a major contributor to salinity in municipal wastewater. Salts can leach from spoil piles. One of the major environmental constraints on the production of shale oil, for example, is the high percentage of leachable sodium sulfate in piles of spent shale. Careful control of these wastes is necessary to prevent further saline pollution of water in areas where salinity is already a problem. Irrigation adds a great deal of salt to water, a phenomenon responsible for the Salton Sea in California, and is a source of conflict between the United States and Mexico over saline contamination of the Rio Grande and Colorado rivers. Irrigation and intensive agricultural production have caused saline seeps in some of the Western states. These occur when water seeps into a slight depression in tilled, sometimes irrigated, fertilized land, carrying salts (particularly sodium, magnesium, and calcium sulfates) along with it. The water evaporates in the dry summer heat, leaving behind a salt-laden area which no longer supports much plant growth. With time, these areas spread, destroying the productivity of crop land.

7.9. OXYGEN, OXIDANTS, AND REDUCTANTS

Oxygen is a vitally important species in water (see Chapter 2). In water, oxygen is consumed rapidly by the oxidation of organic matter, $\{\text{CH}_2\text{O}\}$:

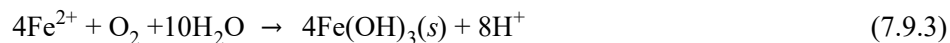


Unless the water is re-aerated efficiently, as by turbulent flow in a shallow stream, it rapidly loses oxygen and will not support higher forms of aquatic life.

In addition to the microorganism-mediated oxidation of organic matter, oxygen in water may be consumed by the biooxidation of nitrogenous material,



and by the chemical or biochemical oxidation of chemical reducing agents:



All these processes contribute to the deoxygenation of water.

The degree of oxygen consumption by microbially-mediated oxidation of contaminants in water is called the **biochemical oxygen demand** (or biological oxygen demand), **BOD**. This parameter is commonly measured by determining the quantity of oxygen utilized by suitable aquatic microorganisms during a five-day period. Despite the somewhat arbitrary five-day period, this test remains a respectable measure of the short-term oxygen demand exerted by a pollutant.¹

The addition of oxidizable pollutants to streams produces a typical oxygen sag curve as shown in [Figure 7.3](#). Initially, a well-aerated, unpolluted stream is relatively

free of oxidizable material; the oxygen level is high; and the bacterial population is relatively low. With the addition of oxidizable pollutant, the oxygen level drops because reaeration cannot keep up with oxygen consumption. In the decomposition zone, the bacterial population rises. The septic zone is characterized by a high bacterial population and very low oxygen levels. The septic zone terminates when the oxidizable pollutant is exhausted, and then the recovery zone begins. In the recovery zone, the bacterial population decreases and the dissolved oxygen level increases until the water regains its original condition.

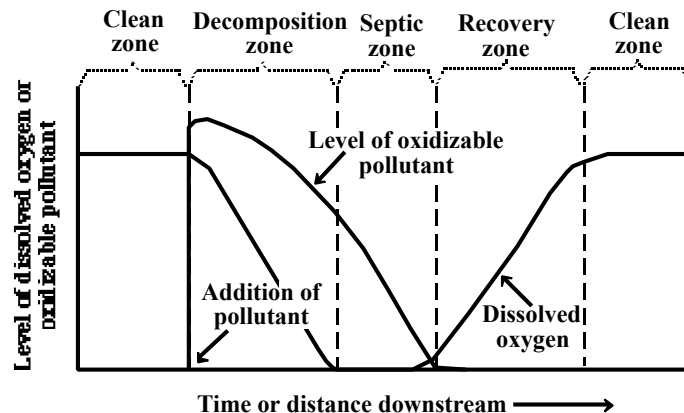


Figure 7.3. Oxygen sag curve resulting from the addition of oxidizable pollutant material to a stream.

Although BOD is a reasonably realistic measure of water quality insofar as oxygen is concerned, the test for determining it is time-consuming and cumbersome to perform. Total organic carbon (TOC), is frequently measured by catalytically oxidizing carbon in the water and measuring the CO_2 that is evolved. It has become popular because TOC is readily determined instrumentally.

7.10. ORGANIC POLLUTANTS

Sewage

As shown in [Table 7.4](#), sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants, including organic pollutants. Some of these pollutants, particularly oxygen-demanding substances (see Section 7.9)—oil, grease, and solids—are removed by primary and secondary sewage-treatment processes. Others, such as salts, heavy metals, and refractory (degradation-resistant) organics, are not efficiently removed.

Disposal of inadequately treated sewage can cause severe problems. For example, offshore disposal of sewage, once commonly practiced by coastal cities, results in the formation of beds of sewage residues. Municipal sewage typically contains about 0.1% solids, even after treatment, and these settle out in the ocean in a typical pattern, illustrated in [Figure 7.4](#). The warm sewage water rises in the cold hypolimnion and is carried in one direction or another by tides or currents. It does not

Table 7.4. Some of the Primary Constituents of Sewage from a City Sewage System

Constituent	Potential sources	Effects in water
Oxygen-demanding substances	Mostly organic materials, particularly human feces	Consume dissolved oxygen
Refractory organics	Industrial wastes, household products	Toxic to aquatic life
Viruses	Human wastes	Cause disease (possibly cancer); major deterrent to sewage recycle through water systems
Detergents	Household detergents	Esthetics, prevent grease and oil removal, toxic to aquatic life
Phosphates	Detergents	Algal nutrients
Grease and oil	Cooking, food processing, industrial wastes	Esthetics, harmful to some aquatic life
Salts	Human wastes, water softeners, industrial wastes	Increase water salinity
Heavy metals	Industrial wastes, chemical laboratories	Toxicity
Chelating agents	Some detergents, industrial wastes	Heavy metal ion solubilization and transport
Solids	All sources	Esthetics, harmful to aquatic life

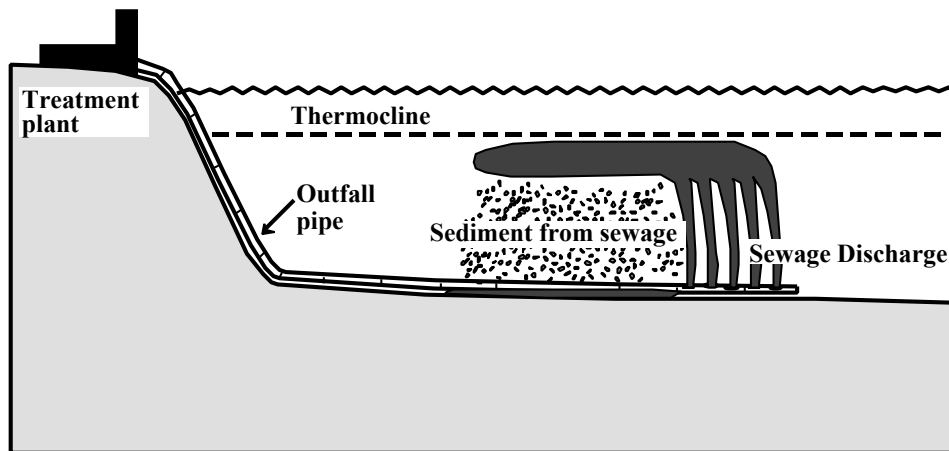


Figure 7.4. Settling of solids from an ocean-floor sewage effluent discharge.

rise above the thermocline; instead, it spreads out as a cloud from which the solids rain down on the ocean floor. Aggregation of sewage colloids is aided by dissolved salts in seawater (see Chapter 5), thus promoting the formation of sludge-containing sediment.

Another major disposal problem with sewage is the sludge produced as a product of the sewage treatment process (see Chapter 8). This sludge contains organic material which continues to degrade slowly; refractory organics; and heavy metals. The amounts of sludge produced are truly staggering. For example, the city of Chicago produces about 3 million tons of sludge each year. A major consideration in the safe disposal of such amounts of sludge is the presence of potentially dangerous components such as heavy metals.

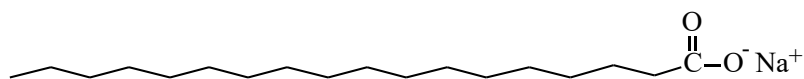
Careful control of sewage sources is needed to minimize sewage pollution problems. Particularly, heavy metals and refractory organic compounds need to be controlled at the source to enable use of sewage, or treated sewage effluents, for irrigation, recycling to the water system, or groundwater recharge.

Soaps, detergents, and associated chemicals are potential sources of organic pollutants. These pollutants are discussed briefly here.

Soaps, Detergents, and Detergent Builders

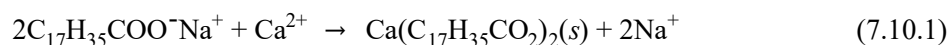
Soaps

Soaps are salts of higher fatty acids, such as sodium stearate, $C_{17}H_{35}COO^-Na^+$. The cleaning action of soap results largely from its emulsifying power and its ability to lower the surface tension of water. This concept may be understood by considering the dual nature of the soap anion. An examination of its structure shows that the stearate ion consists of an ionic carboxyl “head” and a long hydrocarbon “tail”:



In the presence of oils, fats, and other water-insoluble organic materials, the tendency is for the “tail” of the anion to dissolve in the organic matter, whereas the “head” remains in aquatic solution. Thus, the soap emulsifies, or suspends, organic material in water. In the process, the anions form colloidal soap micelles, as shown in [Figure 5.4](#).

The primary disadvantage of soap as a cleaning agent comes from its reaction with divalent cations to form insoluble salts of fatty acids:



These insoluble solids, usually salts of magnesium or calcium, are not at all effective as cleaning agents. In addition, the insoluble “curds” form unsightly deposits on clothing and in washing machines. If sufficient soap is used, all of the divalent cations may be removed by their reaction with soap, and the water containing excess soap will have good cleaning qualities. This is the approach

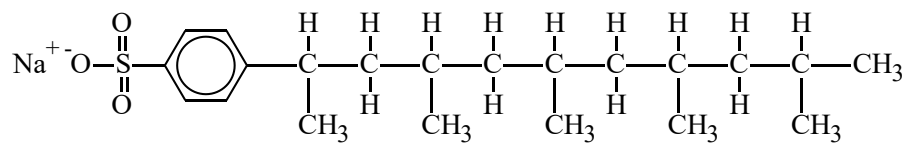
commonly used when soap is employed with unsoftened water in the bathtub or wash basin, where the insoluble calcium and magnesium salts can be tolerated. However, in applications such as washing clothing, the water must be softened by the removal of calcium and magnesium or their complexation by substances such as polyphosphates (see Section 3.16).

Although the formation of insoluble calcium and magnesium salts has resulted in the essential elimination of soap as a cleaning agent for clothing, dishes, and most other materials, it has distinct advantages from the environmental standpoint. As soon as soap gets into sewage or an aquatic system, it generally precipitates as calcium and magnesium salts. Hence, any effects that soap might have in solution are eliminated. With eventual biodegradation, the soap is completely eliminated from the environment. Therefore, aside from the occasional formation of unsightly scum, soap does not cause any substantial pollution problems.

Detergents

Synthetic **detergents** have good cleaning properties and do not form insoluble salts with “hardness ions” such as calcium and magnesium. Such synthetic detergents have the additional advantage of being the salts of relatively strong acids and, therefore, they do not precipitate out of acidic waters as insoluble acids, an undesirable characteristic of soaps. The potential of detergents to contaminate water is high because of their heavy use throughout the consumer, institutional, and industrial markets. It has been projected that by 2004, about 3.0 billion pounds of detergent surfactants will be consumed in the U.S. household market alone, with slightly more consumed in Europe.² Most of this material, along with the other ingredients associated with detergent formulations, is discarded with wastewater.

The key ingredient of detergents is the **surfactant** or surface-active agent, which acts in effect to make water “wetter” and a better cleaning agent. Surfactants concentrate at interfaces of water with gases (air), solids (dirt), and immiscible liquids (oil). They do so because of their **amphiphilic structure**, meaning that one part of the molecule is a polar or ionic group (head) with a strong affinity for water, and the other part is a hydrocarbon group (tail) with an aversion to water. This kind of structure is illustrated below for the structure of alkyl benzene sulfonate (ABS) surfactant:

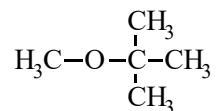


Until the early 1960s, ABS was the most common surfactant used in detergent formulations. However, it suffered the distinct disadvantage of being only very slowly biodegradable because of its branched-chain structure (see Section 6.10). The most objectionable manifestation of the nonbiodegradable detergents, insofar as the average citizen was concerned, was the “head” of foam that began to appear in glasses of drinking water in areas where sewage was recycled through the domestic water supply. Sewage-plant operators were disturbed by spectacular beds of foam which appeared near sewage outflows and in sewage treatment plants. Occasionally,

quently, their effects upon organisms are not known, particularly for long-term exposures at very low levels. The potential of synthetic organics for causing genetic damage, cancer, or other ill effects is uncomfortably high. On the positive side, organic pesticides enable a level of agricultural productivity without which millions would starve. Synthetic organic chemicals are increasingly taking the place of natural products in short supply. Thus it is that organic chemicals are essential to the operation of a modern society. Because of their potential danger, however, acquisition of knowledge about their environmental chemistry must have a high priority.

Biorefractory organics are the organic compounds of most concern in wastewater, particularly when they are found in sources of drinking water. These are poorly biodegradable substances, prominent among which are aryl or chlorinated hydrocarbons. Included in the list of biorefractory organic industrial wastes are benzene, bornyl alcohol, bromobenzene, bromochlorobenzene, butylbenzene, camphor chloroethyl ether, chloroform, chloromethylethyl ether, chloronitrobenzene, chloropyridine, dibromobenzene, dichlorobenzene, dichloroethyl ether, dinitrotoluene, ethylbenzene, ethylene dichloride, 2-ethylhexanol, isocyanic acid, isopropylbenzene, methylbiphenyl, methyl chloride, nitrobenzene, styrene, tetrachloroethylene, trichloroethane, toluene, and 1,2-dimethoxybenzene. Many of these compounds have been found in drinking water, and some are known to cause taste and odor problems in water. Biorefractory compounds are not completely removed by biological treatment, and water contaminated with these compounds must be treated by physical and chemical means, including air stripping, solvent extraction, ozonation, and carbon adsorption.

Methyl *tert*-butyl ether (MTBE),

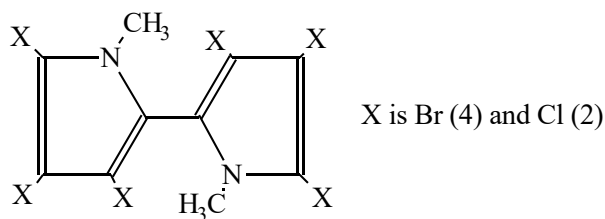


is now showing up as a low-level water pollutant in the U.S. This compound is added to gasoline as an octane booster and to decrease emissions of automotive exhaust air pollutants. A detailed study of the occurrence of MTBE in Donner Lake (California) showed significant levels of this pollutant, which spiked upward dramatically over the July 4 holiday.³ They were attributed largely to emissions of unburned fuel from recreational motorboats and personal watercraft having two-cycle engines that discharge their exhausts directly to the water. In 1999 the U.S. Environmental Protection Agency proposed phasing out the use of MTBE in gasoline, largely because of its potential to pollute water.

Naturally Occurring Chlorinated and Brominated Compounds

Although halogenated organic compounds in water, such as those discussed as pesticides in Section 7.11, are normally considered to be from anthropogenic sources, approximately 2400 such compounds have been identified from natural sources. These are produced largely by marine species, especially some kinds of red algae, probably as chemical defense agents. Some marine microorganisms, worms, sponges, and tunicates are also known to produce organochlorine and organobro-

mine compounds. An interesting observation has been made of the possible bioaccumulation of a class of compounds with the formula $C_{10}H_6N_2Br_4Cl_2$ in several species of sea birds from the Pacific ocean region.⁴ Although the structural formula of the compound could not be determined with certainty, mass spectral data indicate that it is 1,1'-dimethyl-tetrabromodichloro-2,2'-bipyrrrole (below):



7.11. PESTICIDES IN WATER

The introduction of DDT during World War II marked the beginning of a period of very rapid growth in pesticide use. Pesticides are employed for many different purposes. Chemicals used in the control of invertebrates include **insecticides**, **molluscicides** for the control of snails and slugs, and **nematicides** for the control of microscopic roundworms. Vertebrates are controlled by **rodenticides** which kill rodents, **avicides** used to repel birds, and **piscicides** used in fish control. **Herbicides** are used to kill plants. Plant **growth regulators**, **defoliants**, and **plant desiccants** are used for various purposes in the cultivation of plants. **Fungicides** are used against fungi, **bactericides** against bacteria, **slimicides** against slime-causing organisms in water, and **algicides** against algae. As of the mid-1990s, U.S. agriculture used about 365 million kg of pesticides per year, whereas about 900 million kg of insecticides were used in nonagricultural applications including forestry, landscaping, gardening, food distribution, and home pest control. Insecticide production has remained about level during the last three or four decades. However, insecticides and fungicides are the most important pesticides with respect to human exposure in food because they are applied shortly before or even after harvesting. Herbicide production has increased as chemicals have increasingly replaced cultivation of land in the control of weeds and now accounts for the majority of agricultural pesticides. The potential exists for large quantities of pesticides to enter water either directly, in applications such as mosquito control or indirectly, primarily from drainage of agricultural lands.

Natural Product Insecticides, Pyrethrins, and Pyrethroids

Several significant classes of insecticides are derived from plants. These include **nicotine** from tobacco, **rotenone** extracted from certain legume roots, and **pyrethrins** (see structural formulas in [Figure 7.5](#)). Because of the ways that they are applied and their biodegradabilities, these substances are unlikely to be significant water pollutants.

Pyrethrins and their synthetic analogs represent both the oldest and newest of insecticides. Extracts of dried chrysanthemum or pyrethrum flowers, which contain pyrethrin I and related compounds, have been known for their insecticidal properties

for a long time, and may have even been used as botanical insecticides in China almost 2000 years ago. The most important commercial sources of insecticidal pyrethrins are chrysanthemum varieties grown in Kenya. Pyrethrins have several advantages as insecticides, including facile enzymatic degradation, which makes them relatively safe for mammals; ability to rapidly paralyze (“knock down”) flying insects; and good biodegradability characteristics.

Synthetic analogs of the pyrethrins, **pyrethroids**, have been widely produced as insecticides during recent years. The first of these was allethrin, and another common example is fenvalerate (see structures in Figure 7.5).

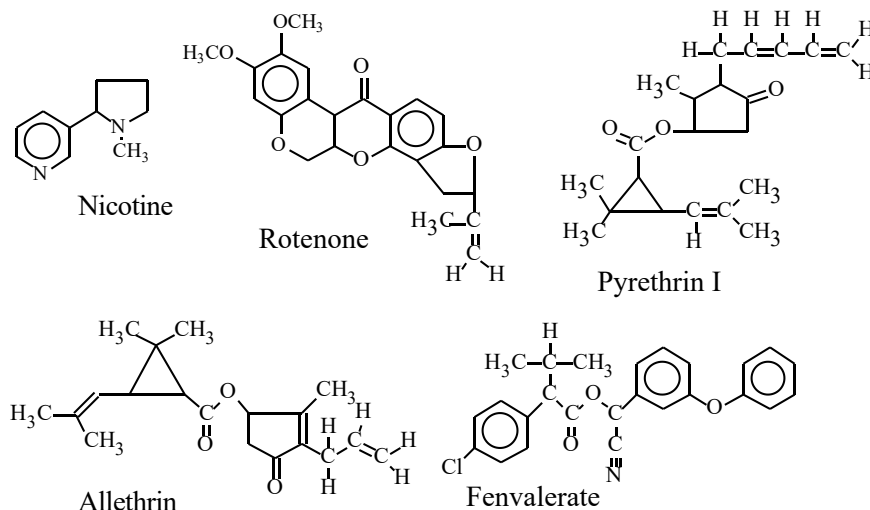


Figure 7.5. Common botanical insecticides and synthetic analogs of the pyrethrins.

DDT and Organochlorine Insecticides

Chlorinated hydrocarbon or organochlorine insecticides are hydrocarbon compounds in which various numbers of hydrogen atoms have been replaced by Cl atoms. The structural formulas of several chlorinated hydrocarbon insecticides are shown in Figure 7.6. It can be seen that the structural formulas of many of these insecticides are very similar; dieldrin and endrin are stereoisomers. The most commonly used insecticides in the 1960s, these compounds have been largely phased out of general use because of their toxicities, and particularly their accumulation and persistence in food chains. They are discussed briefly here, largely because of their historical interest, and because their residues in soils and sediments still contribute to water pollution.

Of the organochlorine insecticides, the most notable has been **DDT** (dichlorodiphenyltrichloroethane or 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane), which was used in massive quantities following World War II. It has a low acute toxicity to mammals, although there is some evidence that it might be carcinogenic. It is a very persistent insecticide and accumulates in food chains. It has been banned in the U.S. since 1972. For some time, **methoxychlor** was a popular DDT substitute, reasonably biodegradable, and with a low toxicity to mammals. Structurally similar **chlordane**, **aldrin**, **dieldrin/endrin**, and **heptachlor**, all now banned for application in the U.S.,

share common characteristics of high persistence and suspicions of potential carcinogenicity. **Toxaphene** is a mixture of up to 177 individual compounds produced by chlorination of camphene, a terpene isolated from pine trees, to give a material that contains about 68% Cl and has an empirical formula of $C_{10}H_{10}Cl_8$. This compound had the widest use of any agricultural insecticide, particularly on cotton. It was employed to augment other insecticides, especially DDT, and in later years methyl parathion. A mixture of five isomers, 1,2,3,4,5,6-hexachlorocyclohexane has been widely produced for insecticidal use. Only the gamma isomer is effective as an insecticide, whereas the other isomers give the product a musty odor and tend to undergo bioaccumulation. A formulation of the essentially pure gamma isomer has been marketed as the insecticide called **lindane**.

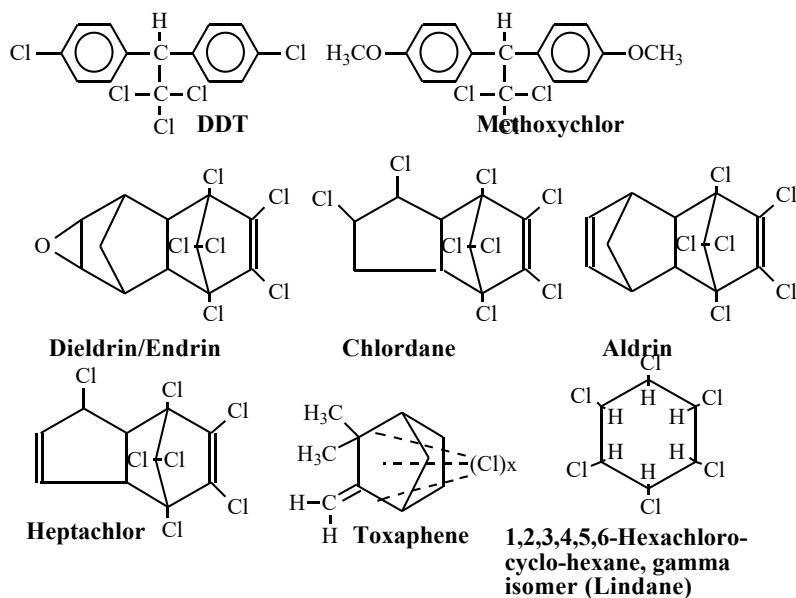
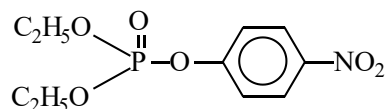


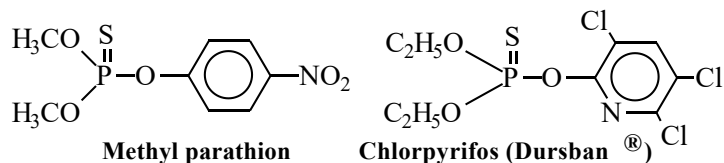
Figure 7.6. Common organochlorine insecticides.

Organophosphate Insecticides

Organophosphate insecticides are insecticidal organic compounds that contain phosphorus, some of which are organic esters of orthophosphoric acid, such as paraoxon:

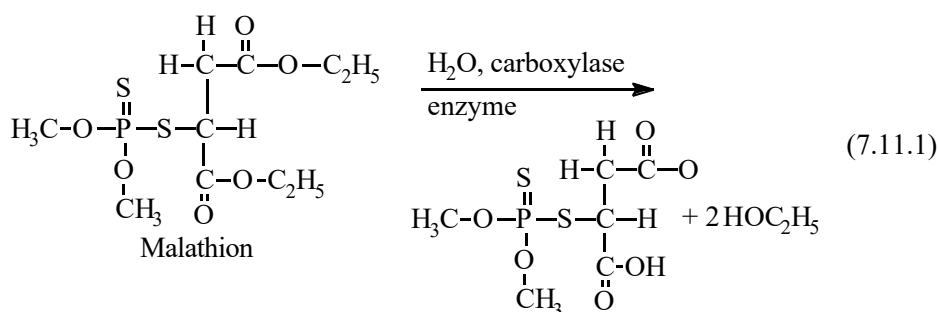


More commonly, insecticidal phosphorus compounds are phosphorothionate compounds, such as parathion or chlorpyrifos,



which have an =S group rather than an =O group bonded to P.

The toxicities of organophosphate insecticides vary a great deal. For example, as little as 120 mg of parathion has been known to kill an adult human, and a dose of 2 mg has killed a child. Most accidental poisonings have occurred by absorption through the skin. Since its use began, several hundred people have been killed by parathion. In contrast, **malathion** shows how differences in structural formula can cause pronounced differences in the properties of organophosphate pesticides. Malathion has two carboxyester linkages which are hydrolyzable by carboxylase enzymes to relatively nontoxic products as shown by the following reaction:



The enzymes that accomplish malathion hydrolysis are possessed by mammals, but not by insects, so mammals can detoxify malathion and insects cannot. The result is that malathion has selective insecticidal activity. For example, although malathion is a very effective insecticide, its LD₅₀ (dose required to kill 50% of test subjects) for adult male rats is about 100 times that of parathion, reflecting the much lower mammalian toxicity of malathion compared to some of the more toxic organophosphate insecticides, such as parathion.

Unlike the organohalide compounds they largely displaced, the organophosphates readily undergo biodegradation and do not bioaccumulate. Because of their high biodegradability and restricted use, organophosphates are of comparatively little significance as water pollutants.

Carbamates

Pesticidal organic derivatives of carbamic acid, for which the formula is shown in [Figure 7.7](#), are known collectively as **carbamates**. Carbamate pesticides have been widely used because some are more biodegradable than the formerly popular organochlorine insecticides, and have lower dermal toxicities than most common organophosphate pesticides.

Carbaryl has been widely used as an insecticide on lawns or gardens. It has a low toxicity to mammals. **Carbofuran** has a high water solubility and acts as a plant

systemic insecticide. As a plant systemic insecticide, it is taken up by the roots and leaves of plants so that insects are poisoned by the plant material on which they feed. **Pirimicarb** has been widely used in agriculture as a systemic aphicide. Unlike many carbamates, it is rather persistent, with a strong tendency to bind to soil.

The toxic effects of carbamates to animals are due to the fact that these compounds inhibit acetylcholinesterase. Unlike some of the organophosphate insecticides, they do so without the need for undergoing a prior biotransformation and are therefore classified as direct inhibitors. Their inhibition of acetylcholinesterase is relatively reversible. Loss of acetylcholinesterase inhibition activity may result from hydrolysis of the carbamate ester, which can occur metabolically.

Herbicides

Herbicides are applied over millions of acres of farmland worldwide and are widespread water pollutants as a result of this intensive use. A 1994 report by the private Environmental Working Group indicated the presence of herbicides in 121 Midwestern U.S. drinking water supplies.⁵ The herbicides named were atrazine, simazine, cyanazine, metolachlor, and alachlor, of which the first three are the most widely used. These substances are applied to control weeds on corn and soybeans, and the communities most affected were in the “Corn Belt” states of Kansas, Nebraska, Iowa, Illinois, and Missouri. The group doing the study applied the EPA’s most strict standard for pesticides in food to water to come up with an estimate of approximately 3.5 million people at additional risk of cancer from these pesticides in drinking water.

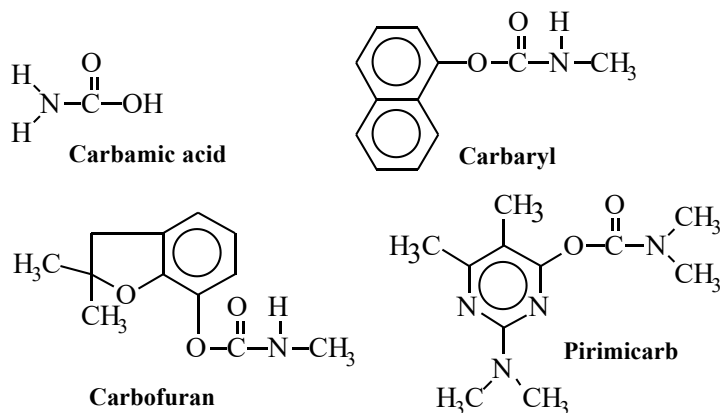


Figure 7.7 Carbamic acid and three insecticidal carbamates.

Bipyridilium Compounds

As shown by the structures in [Figure 7.8](#), a bipyridilium compound contains 2 pyridine rings per molecule. The two important pesticidal compounds of this type are the herbicides **diquat** and **paraquat**, the structural formulas of which are illustrated below:

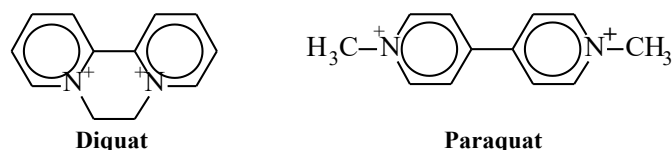


Figure 7.8. The two major bipyridilium herbicides (cation forms).

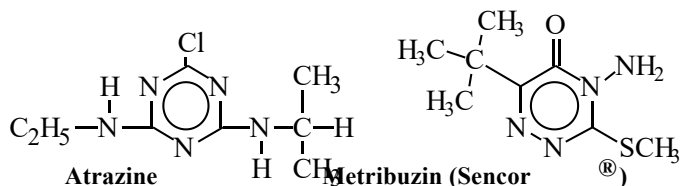
Other members of this class of herbicides include chlormequat, morfamquat, and difenzoquat. Applied directly to plant tissue, these compounds rapidly destroy plant cells and give the plant a frostbitten appearance. However, they bind tenaciously to soil, especially the clay mineral fraction, which results in rapid loss of herbicidal activity so that sprayed fields can be planted within a day or two of herbicide application.

Paraquat, which was registered for use in 1965, has been one of the most used of the bipyridilium herbicides. Highly toxic, it is reputed to have “been responsible for hundreds of human deaths.”⁶ Exposure to fatal or dangerous levels of paraquat can occur by all pathways, including inhalation of spray, skin contact, ingestion, and even suicidal hypodermic injections. Despite these possibilities and its widespread application, paraquat is used safely without ill effects when proper procedures are followed.

Because of its widespread use as a herbicide, the possibility exists of substantial paraquat contamination of food. Drinking water contamination by paraquat has also been observed.

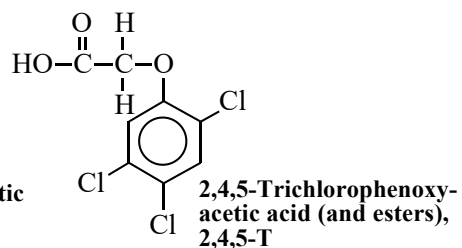
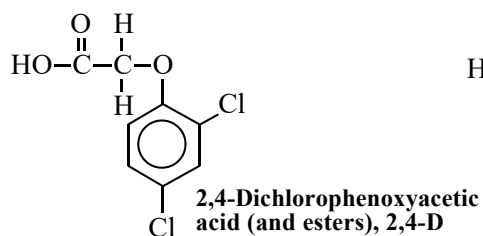
Herbicidal Heterocyclic Nitrogen Compounds

A number of important herbicides contain three heterocyclic nitrogen atoms in ring structures and are therefore called **triazines**. Triazine herbicides inhibit photosynthesis. Selectivity is gained by the inability of target plants to metabolize and detoxify the herbicide. The most long established and common example of this class is atrazine, widely used on corn, and a widespread water pollutant in corn-growing regions. Another member of this class is metribuzin, which is widely used on soybeans, sugarcane, and wheat.



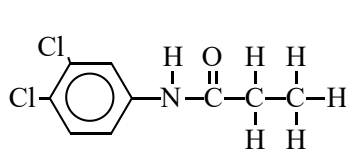
Chlorophenoxy Herbicides

The chlorophenoxy herbicides, including 2,4-D and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) shown below, were manufactured on a large scale for weed and brush control and as military defoliants. At one time the latter was of particular concern because of contaminant TCDD (see below) present as a manufacturing byproduct.

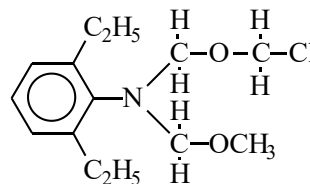


Substituted Amide Herbicides

A diverse group of herbicides consists of substituted amides. Prominent among these are propanil, applied to control weeds in rice fields, and alachlor, marketed as Lasso[®] and widely applied to fields to kill germinating grass and broad-leaved weed seedlings:



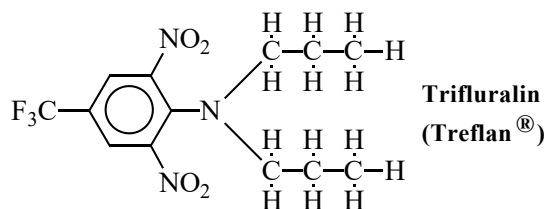
Propanil



Alachlor

Nitroaniline Herbicides

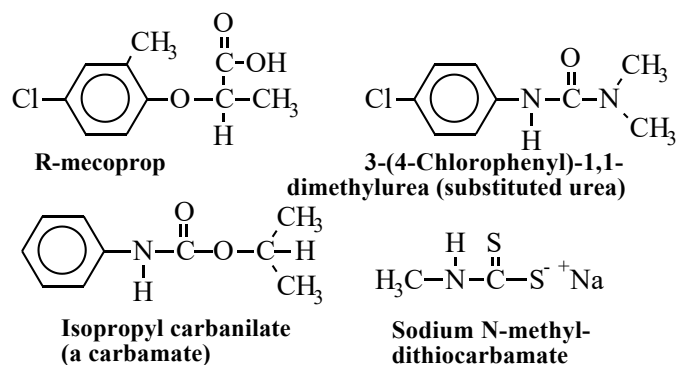
Nitroaniline herbicides are characterized by the presence of NO₂ and a substituted -NH₂ group on a benzene ring as shown for trifluralin:



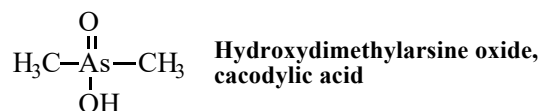
This class of herbicides is widely represented in agricultural applications and includes benefin (Balan[®]), oryzalin (Surflan[®]), pendimethalin (Prowl[®]), and fluchoralin (Basalin[®]).

Miscellaneous Herbicides

A wide variety of chemicals have been used as herbicides, and have been potential water pollutants. One such compound is R-mecoprop. Other types of herbicides include substituted ureas, carbamates, and thiocarbamates:



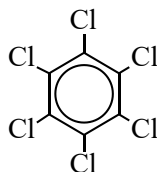
Until about 1960, arsenic trioxide and other inorganic arsenic compounds (see Section 7.4) were employed to kill weeds. Because of the incredibly high rates of application of up to several hundred kilograms per acre, and because arsenic is non-biodegradable, the potential still exists for arsenic pollution of surface water and groundwater from fields formerly dosed with inorganic arsenic. Organic arsenicals, such as cacodylic acid,



have also been widely applied to kill weeds.

Byproducts of Pesticide Manufacture

A number of water pollution and health problems have been associated with the manufacture of organochlorine pesticides. For example, degradation-resistant hexachlorobenzene,



is used as a raw material for the synthesis of other pesticides and has often been found in water.

The most notorious byproducts of pesticide manufacture are **polychlorinated dibenzodioxins**. From 1 to 8 Cl atoms may be substituted for H atoms on dibenzo-*p*-dioxin (Figure 7.9), giving a total of 75 possible chlorinated derivatives. Commonly referred to as “dioxins,” these species have a high environmental and toxicological significance. Of the dioxins, the most notable pollutant and hazardous waste compound is **2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)**, often referred to simply as “**dioxin**.” This compound, which is one of the most toxic of all synthetic substances to some animals, was produced as a low-level contaminant in the manufacture of some aryl, oxygen-containing organohalide compounds such as

chlorophenoxy herbicides (mentioned previously in this section) synthesized by processes used until the 1960s.

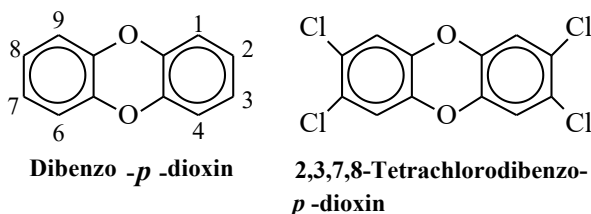
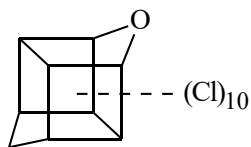


Figure 7.9. Dibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), often called simply “dioxin.” In the structure of dibenzo-*p*-dioxin, each number refers to a numbered carbon atom to which an H atom is bound, and the names of derivatives are based upon the carbon atoms where another group has been substituted for the H atoms, as is seen by the structure and name of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

TCDD has a very low vapor pressure of only 1.7×10^{-6} mm Hg at 25°C, a high melting point of 305°C, and a water solubility of only 0.2 µg/L. It is stable thermally up to about 700°C, has a high degree of chemical stability, and is poorly biodegradable. It is very toxic to some animals, with an LD₅₀ of only about 0.6 µg/kg body mass in male guinea pigs. (The type and degree of its toxicity to humans is largely unknown; it is known to cause a severe skin condition called chloracne). Because of its properties, TCDD is a stable, persistent environmental pollutant and hazardous waste constituent of considerable concern. It has been identified in some municipal incineration emissions, in which it is believed to form when chlorine from the combustion of organochlorine compounds reacts with carbon in the incinerator.

TCDD has been a highly publicized environmental pollutant from improper waste disposal. The most notable case of TCDD contamination resulted from the spraying of waste oil mixed with TCDD on roads and horse arenas in Missouri in the early 1970s. The oil was used to try to keep dust down in these areas. The extent of contamination was revealed by studies conducted in late 1982 and early 1983. As a result, the U.S. EPA bought out the entire TCDD-contaminated town of Times Beach, Missouri, in March 1983, at a cost of \$33 million. Subsequently, permission was granted by the courts to incinerate the soil at Times Beach, as well as TCDD-contaminated soil from other areas at a total estimated cost of about \$80 million. TCDD has been released in a number of industrial accidents, the most massive of which exposed several tens of thousands of people to a cloud of chemical emissions spread over an approximately 3-square-mile area at the Givaudan-La Roche Icmesa manufacturing plant near Seveso, Italy, in 1976. On an encouraging note from a toxicological perspective, no abnormal occurrences of major malformations were found in a study of 15,291 children born in the area within 6 years after the release.⁷

One of the greater environmental disasters ever to result from pesticide manufacture involved the production of Kepone, structural formula



This pesticide has been used for the control of banana-root borer, tobacco wireworm, ants, and cockroaches. Kepone exhibits acute, delayed, and cumulative toxicity in

birds, rodents, and humans, and it causes cancer in rodents. It was manufactured in Hopewell, Virginia, during the mid-1970s. During this time, workers were exposed to Kepone and are alleged to have suffered health problems as a result. The plant was connected to the Hopewell sewage system, and frequent infiltration of Kepone wastes caused the Hopewell sewage treatment plant to become inoperative at times. As much as 53,000 kg of Kepone may have been dumped into the sewage system during the years the plant was operated. The sewage effluent was discharged to the James River, resulting in extensive environmental dispersion and toxicity to aquatic organisms. Decontamination of the river would have required dredging and detoxification of 135 million cubic meters of river sediment at a prohibitively high cost of several billion dollars.

7.12. POLYCHLORINATED BIPHENYLS

First discovered as environmental pollutants in 1966, **polychlorinated biphenyls (PCB compounds)** have been found throughout the world in water, sediments, bird tissue, and fish tissue. These compounds constitute an important class of special wastes. They are made by substituting from 1 to 10 Cl atoms onto the biphenyl aryl structure as shown on the left in [Figure 7.10](#). This substitution can produce 209 different compounds (congeners), of which one example is shown on the right in [Figure 7.10](#).

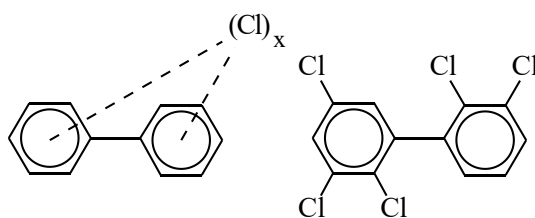


Figure 7.10. General formula of polychlorinated biphenyls (left, where X may range from 1 to 10) and a specific 5-chlorine congener (right).

Polychlorinated biphenyls have very high chemical, thermal, and biological stability; low vapor pressure; and high dielectric constants. These properties have led to the use of PCBs as coolant-insulation fluids in transformers and capacitors; for the impregnation of cotton and asbestos; as plasticizers; and as additives to some epoxy paints. The same properties that made extraordinarily stable PCBs so useful also contributed to their widespread dispersion and accumulation in the environment. By regulations issued in the U.S. under the authority of the Toxic Substances Control Act passed in 1976, the manufacture of PCBs was discontinued in the U.S., and their uses and disposal were strictly controlled.

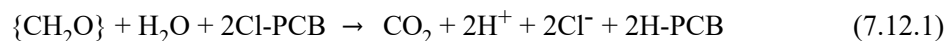
Several chemical formulations have been developed to substitute for PCBs in electrical applications. Disposal of PCBs from discarded electrical equipment and other sources have caused problems, particularly since PCBs can survive ordinary incineration by escaping as vapors through the smokestack. However, they can be destroyed by special incineration processes.

PCBs are especially prominent pollutants in the sediments of the Hudson River as a result of waste discharges from two capacitor manufacturing plants which ope-

rated about 60 km upstream from the southernmost dam on the river from 1950 to 1976. The river sediments downstream from the plants exhibit PCB levels of about 10 ppm, 1-2 orders of magnitude higher than levels commonly encountered in river and estuary sediments.

Biodegradation of PCBs

The biodegradation of PCBs in New York's Hudson River provides an interesting example of microbial degradation of environmental chemicals. As a result of the dumping of PCBs in the Hudson River mentioned above, these virtually insoluble, dense, hydrophobic materials accumulated in the river's sediment, causing serious concern about their effects on water quality as a result of their bioaccumulation in fish. Methods of removal, such as dredging, were deemed prohibitively expensive and likely to cause severe contamination and disposal problems. Although it was well known that aerobic bacteria could degrade PCBs with only one or two Cl atom constituents, most of the PCB congeners discharged to the sediments had multiple chlorine atom constituents, specifically an average of 3.5 Cl atoms per PCB molecule at the time the PCBs were discharged. However, investigations during the late 1980s revealed that the PCBs in the sediments had been largely converted to mono- and dichloro-substituted forms. This conversion had to be due to the action of anaerobic bacteria, a fact later confirmed with laboratory cultures.⁸ Such bacteria do not use PCBs as a carbon source, but rather as electron acceptors in the overall process,



where Cl-PCB represents a site of chlorine substitution on a PCB molecule and H-PCB represents a site of hydrogen substitution. The net result of this process is the replacement of Cl by H on the more highly chlorine-substituted PCB molecules. The circumstances under which this took place in the sediments included anaerobic conditions and very long residence times. These are ideal for the growth of anaerobic bacteria, which tend to carry out their metabolic processes slowly with relatively low efficiency compared to aerobic organisms, and in complex synergistic relationships with other anaerobic bacteria.

The mono- and dichloro substituted PCBs are degraded by aerobic bacteria. Aerobic processes oxidize the molecules and cleave the aryl rings as shown in [Figure 7.11](#). Ultimately, the PCBs are mineralized by conversion to inorganic chloride, carbon dioxide, and water.

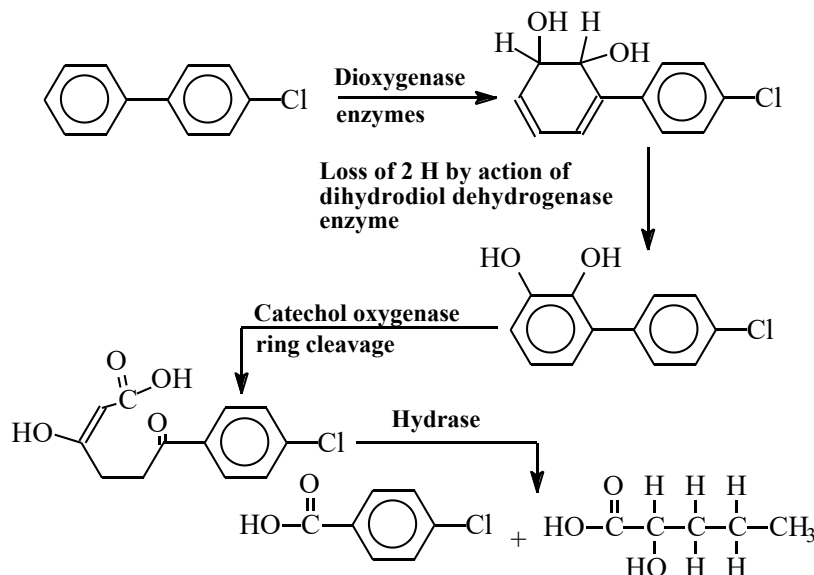


Figure 7.11. Enzymatic processes involved in the initial attack of aerobic bacteria on mono- and dichloro substituted PCBs.

Ideally, in the case of PCBs in sediments, about half of the work of remediation by biodegradation—conversion of highly substituted PCBs to molecules with one or two chlorines—is done by the slow, steady action of anaerobic bacteria without human intervention. Since the PCB products tend to stay in anaerobic surroundings, some assistance is required to provide oxygen to finish the biodegradation aerobically by introducing aerobic bacteria acclimated to PCB biodegradation, along with the oxygen and nutrients required for their growth.⁹

Polybrominated Biphenyls

Polybrominated biphenyl (PBB) is a chemical fire retardant which was accidentally mistaken for magnesium oxide and mixed with cattle feed distributed in Michigan in 1973. As a result, over 30,000 cattle, approximately 6000 hogs, 1500 sheep, 1.5 million chickens, 18,000 pounds of cheese, 2700 pounds of butter, 34,000 pounds of dry milk products, and 5 million eggs had to be destroyed. Farm families eating PBB-contaminated foods had ingested the substance, and it was detected in the blood of many Michigan residents, causing a great deal of anxiety to people who may have been exposed to the substance. Persons who had ingested PBB tended to have less disease resistance and increased incidence of rashes, liver ailments, and headaches. The economic cost of the Michigan PBB incident was very high, with some estimates exceeding \$100 million.

7.13. RADIONUCLIDES IN THE AQUATIC ENVIRONMENT

The massive production of **radionuclides** (radioactive isotopes) by weapons and nuclear reactors since World War II has been accompanied by increasing concern about the effects of radioactivity upon health and the environment. Radionuclides are produced as fission products of heavy nuclei of such elements as uranium or plutonium. They are also produced by the reaction of neutrons with stable nuclei. These phenomena are illustrated in Figure 7.12 and specific examples are given in Table 7.5. Radionuclides are formed in large quantities as waste products in nuclear power generation. Their ultimate disposal is a problem that has caused much controversy regarding the widespread use of nuclear power. Artificially produced radionuclides are also widely used in industrial and medical applications, particularly as “tracers.” With so many possible sources of radionuclides, it is impossible to entirely eliminate radioactive contamination of aquatic systems. Furthermore, radionuclides may enter aquatic systems from natural sources. Therefore, the transport, reactions, and biological concentration of radionuclides in aquatic ecosystems are of great importance to the environmental chemist.

Radionuclides differ from other nuclei in that they emit **ionizing radiation** — alpha particles, beta particles, and gamma rays. The most massive of these emissions is the **alpha particle**, a helium nucleus of atomic mass 4, consisting of two neutrons and two protons. The symbol for an alpha particle is ${}^4_2\alpha$. An example of alpha production is found in the radioactive decay of uranium-238:



This transformation occurs when a uranium nucleus, atomic number 92 and atomic mass 238, loses an alpha particle, atomic number 2 and atomic mass 4, to yield a thorium nucleus, atomic number 90 and atomic mass 234.

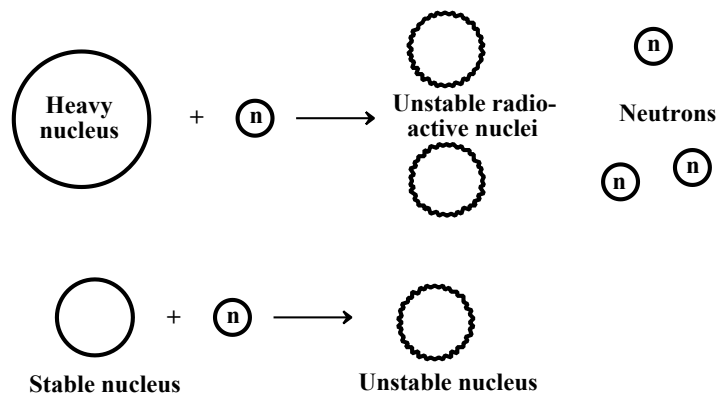


Figure 7.12. A heavy nucleus, such as that of ${}^{235}\text{U}$, may absorb a neutron and break up (undergo fission), yielding lighter radioactive nuclei. A stable nucleus may absorb a neutron to produce a radioactive nucleus.

Beta radiation consists of either highly energetic, negative electrons, which are designated ${}^0_{-1}\beta$, or positive electrons, called positrons, and designated ${}^0_{+1}\beta$. A typical beta emitter, chlorine-38, may be produced by irradiating chlorine with neutrons. The chlorine-37 nucleus, natural abundance 24.5%, absorbs a neutron to produce

chlorine-38 and gamma radiation:



The chlorine-38 nucleus is radioactive and loses a negative **beta particle** to become an argon-38 nucleus:



Since the negative beta particle has essentially no mass and a -1 charge, the stable product isotope, argon-38, has the same mass and a charge 1 greater than chlorine-38.

Gamma rays are electromagnetic radiation similar to X-rays, though more energetic. Since the energy of gamma radiation is often a well-defined property of the emitting nucleus, it may be used in some cases for the qualitative and quantitative analysis of radionuclides.

The primary effect of alpha particles, beta particles, and gamma rays upon materials is the production of ions; therefore, they are called **ionizing radiation**. Due to their large size, alpha particles do not penetrate matter deeply, but cause an enormous amount of ionization along their short path of penetration. Therefore, alpha particles present little hazard outside the body, but are very dangerous when

Table 7.5. Radionuclides in Water

Radionuclide	Half-life	Nuclear reaction, description, source
<i>Naturally occurring and from cosmic reactions</i>		
Carbon-14	5730 y ¹	${}^{14}\text{N}(\text{n},\text{p}){}^{14}\text{C}$, ² thermal neutrons from cosmic or nuclear-weapon sources reacting with N_2
Silicon-32	~300 y	${}^{40}\text{Ar}(\text{p},\text{x}){}^{32}\text{Si}$, nuclear spallation (splitting of the nucleus) of atmospheric argon by cosmic-ray protons
Potassium-40	$\sim 1.4 \times 10^9$ y	0.0119% of natural potassium including potassium in the body
<i>Naturally occurring from ${}^{238}\text{U}$ series</i>		
Radium-226	1620 y	Diffusion from sediments, atmosphere
Lead-210	21 y	${}^{226}\text{Ra} \rightarrow 6 \text{ steps} \rightarrow {}^{210}\text{Pb}$
Thorium-230	75,200 y	${}^{238}\text{U} \rightarrow 3 \text{ steps} \rightarrow {}^{230}\text{Th}$ produced <i>in situ</i>
Thorium-234	24 d	${}^{238}\text{U} \rightarrow {}^{234}\text{Th}$ produced <i>in situ</i>
<i>From reactor and weapons fission³</i>		
Strontium-90 (28 y)	Iodine-131 (8 d)	Cesium-137 (30 y)

Barium-140 (13 d) > Zirconium-95 (65 d) > Cerium-141 (33d) > Strontium-89 (51 d)
 > Ruthenium-103 (40 d) > Krypton-85 (10.3 y)

From nonfission sources

Cobalt-60	5.25 y	From nonfission neutron reactions in reactors
Manganese-54	310 d	From nonfission neutron reactions in reactors
Iron-55	2.7 y	$^{56}\text{Fe}(n,2n)^{55}\text{Fe}$, from high-energy neutrons acting on iron in weapons hardware
Plutonium-239	24,300 y	$^{238}\text{U}(n,\gamma)^{239}\text{Pu}$, neutron capture by uranium

¹ Abbreviations: y, years; d, days

² This notation shows the isotope nitrogen-14 reacting with a neutron, n, giving off a proton, p, and forming the carbon-14 isotope; other nuclear reactions may be deduced from this notation where x represents nuclear fragments from spallation.

³ The first three fission-product radioisotopes listed below as products of reactor and weapons fission are of most significance because of their high yields and biological activity. The other fission products are listed in generally decreasing order of yield.

ingested. Although beta particles are more penetrating than alpha particles, they produce much less ionization per unit path length. Gamma rays are much more penetrating than particulate radiation, but cause much less ionization. Their degree of penetration is proportional to their energy.

The **decay** of a specific radionuclide follows first-order kinetics; that is, the number of nuclei disintegrating in a short time interval is directly proportional to the number of radioactive nuclei present. The rate of decay, $-dN/dt$, is given by the equation,

$$\text{Decay rate} = - \frac{dN}{dt} = \lambda N \quad (7.13.4)$$

where N is the number of radioactive nuclei present and λ is the rate constant, which has units of reciprocal time. Since the exact number of disintegrations per second is difficult to determine in the laboratory, radioactive decay is often described in terms of the **activity**, A, which is proportional to the absolute rate of decay. The first-order decay equation may be expressed in terms of A,

$$A = A_0 e^{-\lambda t} \quad (7.13.5)$$

where A is the activity at time t; A_0 is the activity when t is zero; and e is the natural logarithm base. The **half-life**, $t_{1/2}$, is generally used instead of λ to characterize a radionuclide:

$$t_{1/2} = \frac{0.693}{\lambda} \quad (7.13.6)$$

As the term implies, a half-life is the period of time during which half of a given number of atoms of a specific kind of radionuclide decay. Ten half-lives are required for the loss of 99.9% of the activity of a radionuclide.

Radiation damages living organisms by initiating harmful chemical reactions in tissues. For example, bonds are broken in the macromolecules that carry out life processes. In cases of acute radiation poisoning, bone marrow which produces red blood cells is destroyed and the concentration of red blood cells is diminished. Radiation-induced genetic damage is of great concern. Such damage may not become apparent until many years after exposure. As humans have learned more about the effects of ionizing radiation, the dosage level considered to be safe has steadily diminished. For example, the United States Nuclear Regulatory Commission has dropped the maximum permissible concentration of some radioisotopes to levels of less than one ten-thousandth of those considered safe in the early 1950s. Although it is possible that even the slightest exposure to ionizing radiation entails some damage, some radiation is unavoidably received from natural sources. For the majority of the population, exposure to natural radiation exceeds that from artificial sources.

The study of the ecological and health effects of radionuclides involves consideration of many factors. Among these are the type and energy of radiation emitter and the half-life of the source. In addition, the degree to which the particular element is absorbed by living species and the chemical interactions and transport of the element in aquatic ecosystems are important factors. Radionuclides having very short half-lives may be hazardous when produced but decay too rapidly to affect the environment into which they are introduced. Radionuclides with very long half-lives may be quite persistent in the environment but of such low activity that little environmental damage is caused. Therefore, in general, radionuclides with intermediate half-lives are the most dangerous. They persist long enough to enter living systems while still retaining a high activity. Because they may be incorporated within living tissue, radionuclides of "life elements" are particularly dangerous. Much concern has been expressed over strontium-90, a common waste product of nuclear testing. This element is interchangeable with calcium in bone. Strontium-90 fallout drops onto pasture and crop land and is ingested by cattle. Eventually, it enters the bodies of infants and children by way of cow's milk.

Some radionuclides found in water, primarily radium and potassium-40, originate from natural sources, particularly leaching from minerals. Others come from pollutant sources, primarily nuclear power plants and testing of nuclear weapons. The levels of radionuclides found in water typically are measured in units of picocuries/liter, where a curie is 3.7×10^{10} disintegrations per second, and a picocurie is 1×10^{-12} that amount, or 3.7×10^{-2} disintegrations per second. (2.2 disintegrations per minute).

The radionuclide of most concern in drinking water is **radium**, Ra. Areas in the United States where significant radium contamination of water has been observed include the uranium-producing regions of the western U.S., Iowa, Illinois, Wisconsin, Missouri, Minnesota, Florida, North Carolina, Virginia, and the New England states.

The maximum contaminant level (MCL) for total radium (^{226}Ra plus ^{228}Ra) in drinking water is specified by the U.S. Environmental Protection Agency as 5 pCi/L (picocuries per liter). Perhaps as many as several hundred municipal water supplies

in the U.S. exceed this level and require additional treatment to remove radium. Fortunately, conventional water softening processes, which are designed to take out excessive levels of calcium, are relatively efficient in removing radium from water.

As the use of nuclear power has increased, the possible contamination of water by fission-product radioisotopes has become more of a cause for concern. (If nations continue to refrain from testing nuclear weapons above ground, it is hoped that radioisotopes from this source will contribute only minor amounts of radioactivity to water.) Table 7.5 summarizes the major natural and artificial radionuclides likely to be encountered in water.

Transuranic elements are of growing concern in the oceanic environment. These alpha emitters are long-lived and highly toxic. As their production increases, so does the risk of environmental contamination. Included among these elements are various isotopes of neptunium, plutonium, americium, and curium. Specific isotopes, with half-lives in years given in parentheses, are: Np-237 (2.14×10^6); Pu-236 (2.85); Pu-238 (87.8); Pu-239 (2.44×10^4); Pu-240 (6.54×10^3); Pu-241 (15); Pu-242 (3.87×10^5); Am-241 (433); Am-243 (7.37×10^6); Cm-242 (0.22); and Cm-244 (17.9).

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