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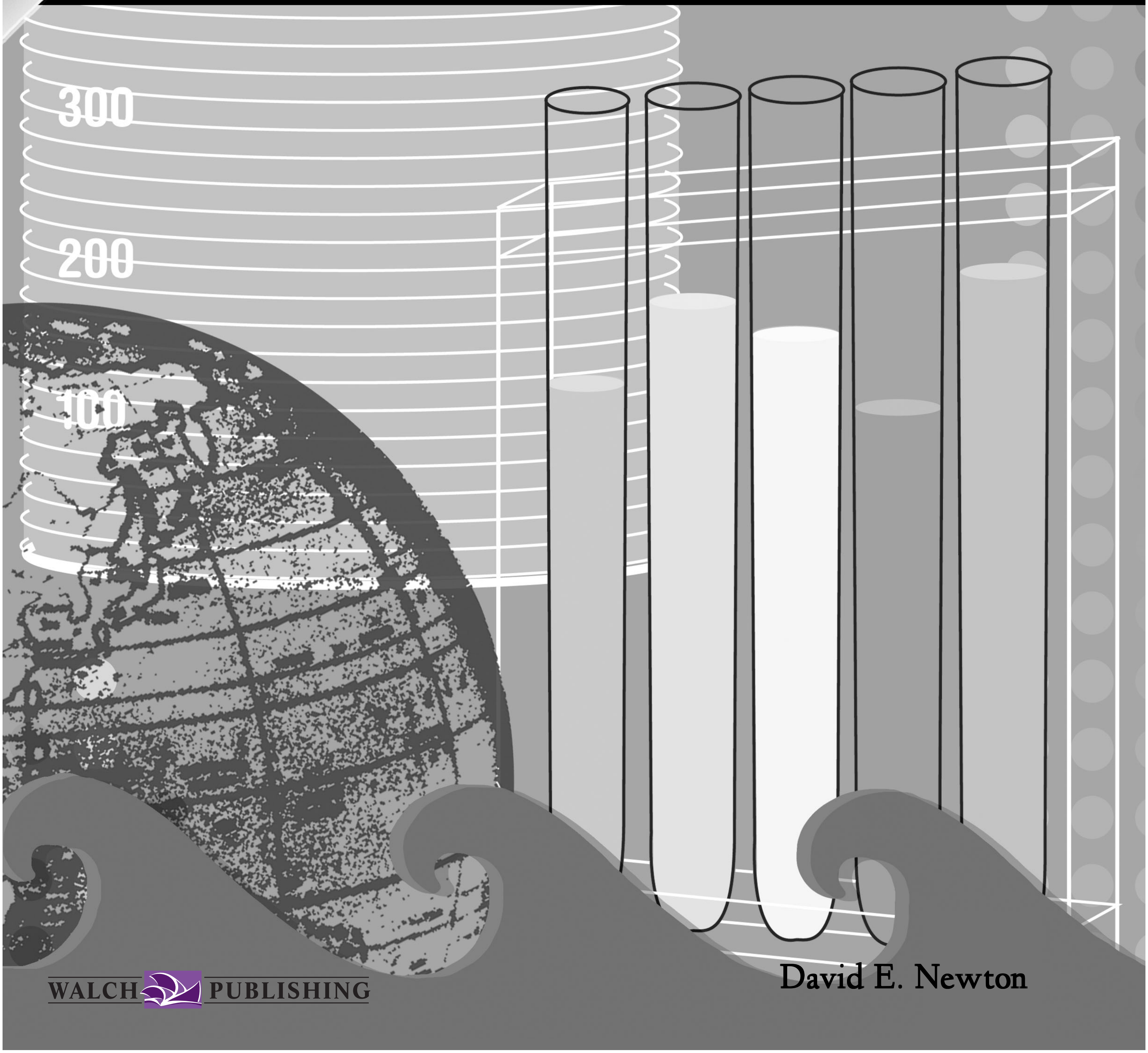
ENVIRONMENTAL CHEMISTRY



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To the Teacher

Strictly speaking, environmental chemistry is the chemistry of the physical and biological environment, as well as the effects human activity has on the environment. A thorough exploration of the subject must address both of these aspects of the field because one cannot understand the *changes* that take place in the environment without first appreciating the environment's fundamental characteristics.

In the limited space available here, we have chosen to focus on the nature of pollution, its sources, its effects on the biotic and abiotic environment, and methods for controlling those effects. This approach seems appropriate because students are likely to be more familiar and more interested in such issues than in the general topic of the chemistry of the natural environment. To broaden students' understanding of more general topics in the field, the teacher is encouraged to become more familiar with and to make use of some of the books and Internet web sites listed in Appendix III.

This book can be used as a supplementary text in a beginning course. You can use specific sections of the text to illustrate concepts you are developing in the classroom, and/or as a source for special assignments, extra credit projects, or motivating devices. The text assumes that students have a basic background in chemistry, as well as limited experience with quantitative problem solving, organic chemistry, and other more advanced topics that may not be covered in introductory chemistry. Teachers may find it necessary to provide background information on topics that are unfamiliar to their students.

The text may also be used as the basis for an advanced course in environmental chemistry. In this case, we recommend that you supplement this text with other texts, references, and Internet sources.

Each chapter concludes with Exploration Activities. These are straightforward exercises that reinforce the basic principles presented in the chapter. The Answer Key is in Appendix II.

Appendix I has Additional Activities designed to be more challenging for students, calling for original research, creative thinking, and use of the Internet and other resources.

The author wishes to thank Professor Don Cass, College of the Atlantic, Bar Harbor, Maine, who read and commented on the first edition of this book. Professor Cass made many helpful comments and suggestions that enhanced the potential value of this book. Any errors that remain in the Second Edition are, however, entirely the responsibility of the author who, as always, appreciates receiving suggestions for changes and improvements in the text.

To the Student

Chemistry! Ugh! I hate the subject. It's all about moles and atomic orbitals and reaction rates. What does it have to do with the real world?

Perhaps you've heard other students make such comments about an introductory chemistry class. These comments may even have passed through your own mind.

But chemistry has many important applications to everyday life. Sometimes those applications do not become obvious until some time—perhaps much too long—after one has begun a study of the subject. But one has only to look through the daily newspaper or watch the evening news to realize the essential role chemistry has in daily events.

The purpose of this book is to show the relevance of chemistry to one very important field: environmental science, the study of human effects on the physical and biological environment. This text illustrates that understanding chemical principles can help you understand environmental changes and how the most harmful of those changes can be controlled.

However, this is only an introduction to environmental chemistry, a large and complex subject. For students interested in the topic, more advanced books, courses, and web sites are available, some of which are listed in Appendix III at the end of this book. But for now, let's begin at the beginning, with an overview of Earth, its environment, and the field of environmental chemistry.

BACKGROUND

The Water Cycle

Water can be found in all three regions of the planet: atmosphere, lithosphere, and hydrosphere. Water vapor, for example, constitutes a small but important fraction of air, a fraction that varies widely from place to place on Earth. Water also occurs in the soil as groundwater. The movement of groundwater is an important process for both living organisms and natural geological events.

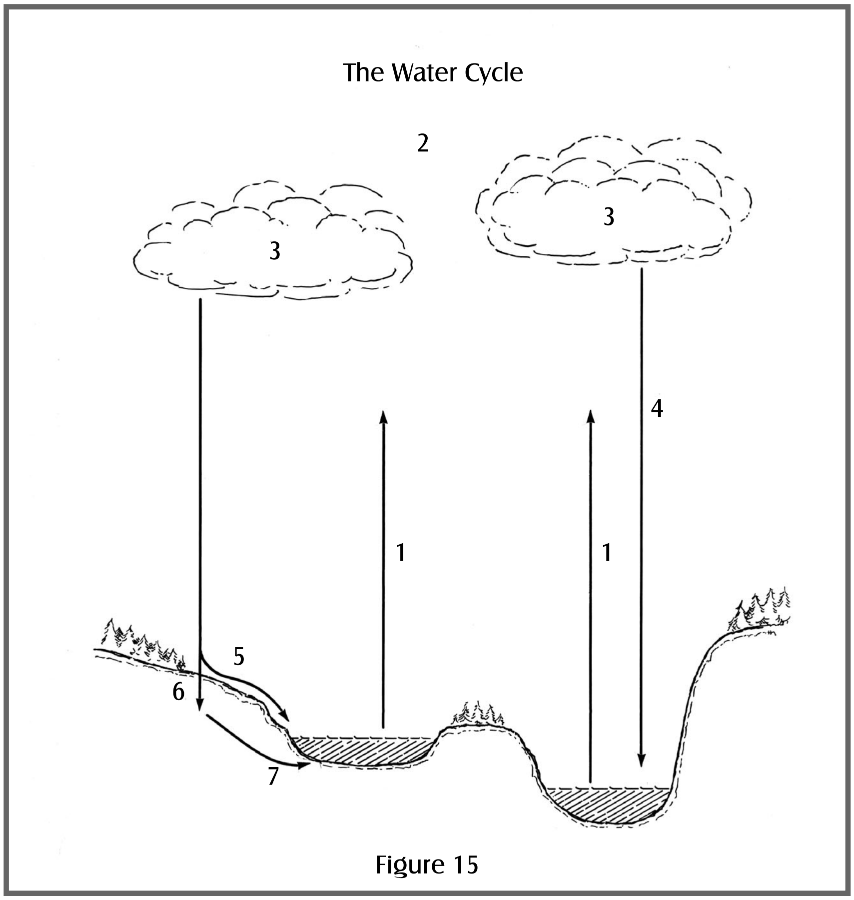

Figure 15

Water moves among the hydrosphere, atmosphere, and lithosphere in a process known as the **water cycle,** shown in Figure 15. At one stage of the cycle, water evaporates from lakes, rivers, oceans, and other parts of the hydrosphere (1). The water vapor becomes part of the atmosphere, either as dispersed water molecules (2) or condensed as tiny droplets of liquid water or ice crystals in clouds (3).

Dispersed water molecules eventually coalesce, condensing on particles of dust or other impurities in the air to form liquid droplets or tiny ice crystals (3). Droplets and crystals grow larger by accretion until they are heavy enough to fall back to Earth as precipitation (4). Precipitation may occur as rain, snow, hail, or sleet, depending on environmental conditions.

Some precipitation returns directly to the hydrosphere (4), completing the water cycle. Other precipitation falls on land (soil, vegetation, buildings, etc.) where it may run off the surface into a river or lake (5) or soak into the ground (6). Water that penetrates the soil becomes groundwater that slowly moves through the earth, returning to the hydrosphere and completing the water cycle (7).

Water is an excellent solvent that dissolves a variety of substances at every stage of the water cycle. All atmospheric gases are soluble to some extent in water. Thus, water that falls as rain is not completely pure but is a complex solution containing oxygen, nitrogen, carbon dioxide, and other trace gases. The pH of rainwater in equilibrium with atmospheric carbon dioxide is about 5.6.

Water in lakes, rivers, streams, and the oceans also dissolves atmospheric gases at the water's surface. Water also dissolves solids where it is in contact with riverbeds and lake and ocean bottoms. A stream that runs through a vein of limestone ($CaCO_3$), for example, will convert some of the calcium carbonate to a more soluble compound, calcium bicarbonate ($Ca(HCO_3)_2$).

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

As limestone dissolves, the stream loses some of its CO_2 and becomes less acidic.

Groundwater is especially efficient in dissolving minerals from the earth.

Groundwater is especially efficient in dissolving minerals from the earth. When the process described in the equation above occurs deep underground, large blocks of limestone may be dissolved over long periods of time, resulting in the formation of caves. Once the cave is formed, groundwater dripping from its ceiling and onto its floor loses CO_2 to the air and water by evaporation. The equation is then driven to the left, calcium bicarbonate decomposes more rapidly, and calcium carbonate precipitates out of solution. The accumulation of $CaCO_3$ results in the formation of stalactites on cave ceilings and stalagmites on cave floors.

Anthropogenic chemicals in the atmosphere or lithosphere may become contaminants in the water cycle. To the extent that they pose a risk to living organisms, they may also be classified as pollutants. One example is the role of anthropogenic sulfur dioxide and nitrogen oxides in the production of acid precipitation. Also, pesticides and fertilizers used in agriculture may be dissolved by runoff or groundwater. We will focus on the most important anthropogenic pollutants found in the hydrosphere.

EXPLORE Exploration Activities

1. Outline the steps in the water cycle.

2. Why is rainwater acidic?

3. Why is groundwater a more efficient solvent of minerals than river water?

BACKGROUND

Types of Water Pollutants

Fouled stream banks, dead fish, oil-covered beaches, ponds filled with weeds, and smelly rivers are all evidence of polluted waters. Some types of water pollutants are obvious to an observer. In some cases, animal wastes can be seen floating down a polluted stream. An oil slick on a lake is visible evidence of an accidental spill or intentional industrial discharge.

Yet, many types of water pollutants are not visible to the naked eye. Some of these pollutants are at least as hazardous to plant and animal life as the more visible forms. Table 9 lists some categories into which water pollutants may be grouped.

Some Types of Water Pollutants

Pollutant	Source(s)	Effects
oxygen-demanding wastes	garbage; human and animal wastes	deprive aquatic organisms of oxygen
pathogens	human and animal wastes	cause disease
nutrients	fertilizers; agricultural and household wastes	lead to eutrophication of waterways
synthetic organic compounds	industry and agriculture; household and commercial detergents	toxic to aquatic and human life
petroleum products	household and industrial wastes	toxic to aquatic life; aesthetically displeasing
heavy metals	industrial and chemical processes	toxic to aquatic and human life
salts	agricultural, household, and industrial wastes	increase salinity; may be toxic
sediments	storm runoff and agricultural wastes	may clog waterways; may be harmful to aquatic organisms
acidity	mine and mine tailing runoffs; acid deposition	toxic to aquatic life
radioactive materials	military, industrial, chemical, and medical wastes	carcinogenic, teratogenic, and mutagenic
heat	power generation and industry	may be harmful to some forms of aquatic life

Table 9

EXPLORE Exploration Activities

1. List six types of water pollutants.

2. What are some indicators of polluted water? What evidence of polluted water have you seen in your community?

BACKGROUND

Oxygen-Demanding Materials

Any body of water contains some waste organic materials. These materials might include dead plants, uneaten food from homes, and animal feces. Bacteria in the water oxidize (decompose) such materials to CO_2 and H_2O.

$$\text{organic material} + O_2 \xrightarrow{\text{bacteria}} CO_2 + H_2O.$$

Nitrogenous compounds in organic wastes, usually in the form of ammonium compounds, are also oxidized with the formation of nitrates.

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

The amount of oxygen present in a sample of water depends on temperature and atmospheric pressure.

Oxidation is possible because of molecular oxygen dissolved in water. The amount of oxygen present in a sample of water depends on temperature and atmospheric pressure—that is, altitude. At sea level and 20°C, pure water holds 9.1 ppm of dissolved oxygen. At an altitude of 900 meters and a temperature of 20°C, the solubility of water is 8.2 ppm. And at the same altitude and a temperature of 40°C, its solubility drops to 5.8 ppm. (Recall that in water solutions, the unit *ppm* is comparable to a concentration expressed in milligrams per liter, or mg/L.)

In an unpolluted river, stream, or lake, sufficient oxygen is available to decompose wastes and supply the needs of aquatic organisms. The water source becomes polluted when wastes accumulate and use up all or most of the dissolved oxygen in water. At that point, little or no dissolved oxygen remains in the water, and fish and other aquatic organisms begin to die.

One measure of the degree of pollution of water, therefore, is its **biochemical oxygen demand** (BOD), the amount of oxygen needed to decompose organic wastes in water. A high BOD value means that a large amount of oxygen is needed to oxidize a large volume of wastes, with little oxygen available to sustain aquatic life. A low BOD value means that only a small amount of oxygen is required to oxidize wastes, leaving sufficient oxygen for aquatic life.

SOME TYPICAL VALUES OF BIOCHEMICAL OXYGEN DEMAND

Sample	BOD (ppm)
pure water	0
naturally occurring water	2–5
polluted water (when most fish begin to die)	>5
municipal sewage after primary and secondary treatment	10–20
untreated municipal sewage	100–400
runoff from barnyards and feedlots	100–10,000
wastes from food-processing plants	100–10,000

Table 10

The standard test for measuring BOD in a sample of water is to incubate the sample for five days at a temperature of 20°C. At the end of that period, the amount of oxygen consumed is measured, giving the BOD for that water sample. Some typical values of BOD are listed in Table 10.

Although BOD is the traditional method for measuring oxygen demand, other tests are also available. A much faster test is the **chemical oxygen demand** (COD) test. To measure COD, a sample of water is titrated against a strong oxidizing agent, typically potassium dichromate in sulfuric acid. The oxidizing agent performs the same function in the COD test of bacteria in the BOD test. The advantage of the COD test is that it produces results in a matter of hours, rather than days. The disadvantage of the test is that the oxidizing agent may oxidize materials that are not oxidized by bacteria, resulting in a slightly different assessment of the level of pollution of the water sample.

A third measure of oxygen demand is the **total organic carbon** (TOC) test. In this test, solids in a sample of water are collected and then burned at temperatures of about 1,000°C. The volume of CO_2 produced is measured, and from this value, the total mass of organic carbon in the sample can be determined. The TOC test can be completed in minutes.

Results obtained by these three tests are usually quite similar, but may differ since each measures a slightly different component of polluted water.

EXPLORE Exploration Activities

1. Why are oxygen-demanding wastes pollutants?

2. What does the term *BOD* mean?

3. How does the COD test differ from the BOD test?

4. At what BOD level is water considered to be polluted?

BACKGROUND

Pathogens

Pathogens are disease-causing organisms. They may be viruses, bacteria, protozoa, parasitic worms, or other microorganisms. The most important source of pathogens in water is wastes from infected humans and other animals. A person infected with cholera, for example, expels cholera bacteria in her or his feces and urine. Those bacteria may then enter a public water supply and be passed on to other humans.

At one time, waterborne pathogens were a major health problem throughout the world. The desire to prevent diseases such as typhoid fever, dysentery, polio, and infectious hepatitis was, in fact, the primary reason for early campaigns to introduce pollution control systems in public water supplies. The use of chlorination in water treatment plants today destroys virtually all pathogenic organisms. Thus, waterborne pathogens are seldom a problem in the more developed nations of the world.

The majority of humans alive today do not have access to purified water.

That is not the case in many less developed areas, however. The majority of humans alive today do not have access to purified water, as is the case in industrialized nations. As a result, diseases such as cholera, typhoid fever, salmonellosis, shigellosis, hepatitis A, amoebic dysentery, gastroenteritis, and giardiasis still cause millions of deaths worldwide each year.

A simple test used to estimate pathogens in water involves a count of the number of **coliform bacteria** present in a water sample. Coliform bacteria are harmless microorganisms that live in the human digestive tract. Each person excretes millions or billions of coliform bacteria every day. A person infected with a pathogen will excrete both coliform bacteria and pathogens.

To estimate the concentration of pathogens in water, a count is made of the number of coliform bacteria present in a sample of water. The number of bacteria present indicates the amount of fecal matter discharged into the water. Since the bacteria die quickly in water, the count indicates how long it has been since the fecal matter entered the water. Then, from the concentration of coliform bacteria in the water sample, a rough estimate of the concentration of pathogens can be made.

Coliform bacteria may originate in sources other than the human intestinal tract.

A distinction is made between **total coliform count** and **fecal coliform count.** Coliform bacteria may originate in sources other than the human intestinal tract. For example, some coliform bacteria feed on decaying vegetable matter. The number of coliform bacteria that originate exclusively from the human digestive system—the fecal coliform count—provides a more accurate assessment of the probable number of pathogens present in a water sample. Fecal coliforms can be distinguished from nonfecal coliforms because of the way they ferment a certain form of sugar, lactose, at the temperature of 44.5°C.

The U.S. Environmental Protection Agency has established an upper limit of 2.2 coliform bacteria per 100 mL of drinking water. Higher concentrations (200 coliform bacteria per 100 mL) are permitted for aquatic activities, such as fishing, boating, and swimming.

EXPLORE Exploration Activities

1. Why are waterborne pathogens a major health problem in less developed regions of the world?

2. Why are coliform bacteria used to measure the level of pathogens in water?