origins in the Industrial Revolution, but environmental pollution can be traced to manufacturing in ancient times. Goods have been produced to some extent since the dawn of civilization. Pottery works and factories for the manufacture of glassware and bronze ware have been discovered in Greece and Rome. In the Middle Ages, large silk factories were operating in the Syrian cities of Antakya and Tyre. During the late medieval period, textile factories were established in several European countries. These were all fairly small operations, though, and had little impact on the environment beyond their immediate area.

During the Renaissance (fourteenth to seventeenth centuries), industrialization increased in many areas, primarily following advances in science and the development of new trading partners in Asia and the New World. Factories were created to produce such goods as paper, firearms, gunpowder, cast iron, glass, clothing, beer, and soap (Kaufman and Farr, 1995). These factories differed from those found today, though; generally they were large workshops where each laborer functioned independently. Industrial processes were largely carried out by means of hand labor and simple tools; mechanization or machinery was rare. Organized factories could be found, but home production was still the norm. The guilds were very strong at that time and resisted any attempts to increase the expansion of factories. Consequently, environmental impacts due to goods production were still minor and spread out over a large area.

1.3.1   The Industrial Revolution

This all changes with the onset of the Industrial Revolution, which began with the application of power-driven machinery to manufacturing. The Industrial Revolution brought many changes to the way people lived and worked. It led to the movement of people from rural to urban areas and a shift from home to factory production. It also was the impetus for the creation of a new working class. The Industrial Revolution is considered to have begun in Britain in the early 1700s and then to have spread rapidly throughout much of Europe and North America in the early nineteenth century. A form of Industrial Revolution is still under way or is just beginning in many less developed countries.

By the early eighteenth century, Britain had burned up much of its forests to provide heat for its inhabitants and for its limited industry. However, large deposits of coal were available as a fuel, and there was an abundant labor supply to mine the coal and iron. What was needed was a way to transform the energy in coal into a form that could be used in manufacturing. Machines were being used in manufacturing in England at that time, but on a limited basis only. Matthew Boulton built a factory in 1762 which employed more than 600 workers to run a variety of lathes and polishing and grinding machines. Josiah Wedgwood and others used waterwheels and windmills in Staffordshire to turn machines which mixed and ground materials for making chinaware (Rempel, 1995).

The first major use of mechanization in industry, though, came in the British textile industry. The industry was fraught with severe inefficiencies: it took 4 spinners to keep up with the demand of 1 cotton loom and 10 persons to prepare yarn for 1 woolen weaver. Weavers were often idle because of the lack of needed yarn. A way to spin yarn more quickly was required. In 1764, James Hargreaves invented the spinning jenny.

This was quickly followed by the water frame for spinning yam invented by Richard Arkwright in 1769, and the spinning mule by Samuel Crompton in 1779. The ready supply of yam created by these inventions led to the invention of the power loom by Edward Cartwright in 1785, which enabled women to do the weaving in place of men. At about the same time, a machine was patented that printed patterns on the surface of cloth by means of rollers. Prior to these developments, most spinning, weaving, and textile manufacturing was done in the home. However, the new machines were generally too large to operate in a home and were often waterwheel driven, so textile manufacturing had to move to factories. The result of the use of all these machines was a 50 percent to 90 percent drop in the cost of manufacturing textiles, reflecting the reduced labor requirement, and an explosive growth in the sale of textiles, both in England and abroad. Another revolution in the textile and garment industries occurred in 1846 when the American Elias Howe invented the sewing machine. The American Civil War soon created another impetus for growth in the industry-the need for uniforms. Clothing manufacturers were forced to develop standardized sizes for uniforms, and eventually other clothing, to meet the needs of mass production practices.

The textile industry may have been the one that ushered in the Industrial Revolution, but the invention that usually is most associated with it is the steam engine. Because waterpower had been the only way to run machines, factories had to be located next to a river or stream. Steam engines released company owners from this restriction, allowing them to locate factories near the raw materials supplies, manpower, and markets, rather than basing factory location on the water supply. The first piston engine, developed in 1690 by the French physicist Denis Papin for pumping water, was never practical. The first modem steam engine was built by an English engineer, Thomas Newcomen, in 1705 to pump seepage water from coal, tin, and copper mines. It was not very efficient, but it was used to pump water from mines. The breakthrough in steam engine design came in 1763 when James Watt, a Scottish engineer, invented the reciprocating steam engine, changing it from one that operated on atmospheric pressure to a true "steam engine." He also added a crank and flywheel to provide rotary motion (Rempel, 1995). The value of these engines was quickly recognized, and Watt produced hundreds of them over the next several years, freeing industry from the need for water power. The development of the steamship by Robert Fulton in 1807 and of steam locomotives in the 1830s, both of which were driven by steam engines, vastly expanded the markets for industrially produced goods and helped to speed the spread of the Industrial Revolution.

Other major events that sped the Industrial Revolution along were the development of ways to inexpensively produce electricity, which could be used to power machines in factories that did not have ready access to coal for steam production; the internal combustion engine; the automobile along with the assembly line techniques developed by Henry Ford in 1913 to mass produce autos; aviation; and rapid worldwide communications systems. **In** recent years, there has been a new revolution in manufacturing practices with the advent of sophisticated factory equipment, often run by computers. Automation has significantly and rapidly changed the size and the skills of the factory work force. These advances in manufacturing have greatly reduced manufacturing costs and produced major increases in consumerism.

Before 1860, approximately 36,000 patents for new inventions had been issued in the United States. Between 1860 and 1890, an additional 440,000 patents were issued. In 1899, Charles H. Duell, U.S. commissioner of patents, stated that "everything that can be invented has been invented." However, an additional 900,000 patents were issued in the ftrst quarter of the twentieth century. The total is currently in excess of 5,500,000. Obviously, Commissioner Duell was wrong and industrialization has continued to grow at an ever-increasing rate.

1.3.2   Impacts of Industrialization

The result of all this improvement in mechanization was a great increase in industrial productivity, lower costs for manufactured products, and usually an increase in the standard of living of the population. However, this did not come without cost. Factories dumped waste materials from manufacturing processes into the water, air, and land. Because industries are usually clustered together near or in cities, these discharges have a negative cumulative effect on a small area. The rapid growth in production also greatly increased the demand for energy, raw materials, and natural resources, often taxing our supply of them and causing environmental damage due to resource extraction processes. Typically, industries have been set up to use only virgin materials because of the expense and complexity of renovating recycled materials into usable quality for manufacturing new products. Therefore, there is often no market for the materials in a product after it has served its useful purpose and it is discarded into a landfill, creating more pollution. It has only been in about the last decade that this practice has begun to change.

The Industrial Revolution has also brought with it a change in the social structure of industrialized countries. Industrialization usually results in increased wealth for everyone, although it is not equally distributed, resulting in new class distinctions. Because of the increased wealth, populations tend to increase. The population rapidly shifts from a mainly rural one to an urbanized culture as people move to where the jobs are. The clustering of industries in a common area and the resulting urbanization creates severe stress on the environment. Areas that could previously assimilate the wastes from the rural community can no longer handle them and environmental degradation occurs. Some of these impacts are discussed in Chapter 3. In many cases, the environmental threats can be reduced by more efficient utilization of resources by industry and by better design of products so that they can be more easily recycled after use. The intent of this book is to show how pollution prevention can often be easily accomplished and how it will benefit industry as well as the environment.

1.4   WHAT IS POLLUTION PREVENTION?

Congress, the EPA, and environmental professionals came to the conclusion in the 1980s that a new industrial waste management philosophy was needed if the ever-expanding industrial pollution and resource depletion problems were to be solved. Indiscriminate use of virgin resources in manufacturing and subsequent end-of-pipe treatment of resulting wastes would not provide the resource sustainability and environmental quality

demanded by the public. As a result, a new paradigm was developed which emphasized minimizing the use of harmful or overexploited resources and eliminating or minimizing waste production at the source in the industry's production area. This philosophy became known by many names, including waste minimization, source reduction, waste reduction, green engineering, and sustainable engineering, but the name that is most often associated with it is *pollution prevention.* Pollution prevention, or P2 (said as *P-two,* not P-squared, because we do not want to square the amount of pollution!), is the term adopted by EPA and the term usually used in federal legislation.

1.4.1 Waste **Definition**

Before we can discuss how waste reduction or pollution prevention programs should be structured, *waste* must be defmed. Congress developed a legal definition, included in the Resource Conservation and Recovery Act, which is described in detail in Chapter 3, but there are many other defmitions that can be used more readily.

We usually tend to think of waste as a solid product left over at the end of a process or action, but waste is a much broader issue than that. It encompasses wastage of energy or water in producing or using a product. We must focus on the total picture when we are describing waste. For example, home beverage can recycling programs can be very beneficial in conserving natural resources and decreasing the amount of landfill space required, but driving several miles to deposit a few newspapers, empty cans, and glass or plastic bottles in collection bins can be very wasteful of gasoline. The resources consumed in doing this, together with the further resources needed to take the materials from the collection point to a reprocessing center, could exceed the resources saved by not throwing them away. It is wasteful to allow food, which has consumed resources and energy in its production, to be damaged or spoiled. Extreme measures to reduce packaging may have the effect of reducing the use of paper, metals, glass, and plastics at the expense of the food they would protect, despite the value of the wasted food being many times greater than the value of the now-avoided packaging (World Resource Foundation, 1996). Thus we must be careful in how we define waste.

Industrial waste is usually described as materials coming from a manufacturing process that are not directly used within the corporation and that are marked for disposal or release to the environment (Graedel and Allenby, 1995). They may be a waste to that process or that company, but they may still have value to someone else. For example, the spent pickle liquor from a steel mill is considered a significant waste problem by the steel industry, but it has great potential as a neutralizing agent and coagulant in other applications. The problem is that the cost of marketing and transporting it to the potential user often makes its use uneconomical. Thus the same industrial process by-product could be categorized as a waste or a usable commodity, depending on its quality and the ready accessibility of a market for it. A waste may not necessarily have to be a waste. There is a better defmition of a waste:

A waste is a resource out of place.

It is the responsibility of pollution prevention personnel to find the right place to turn the waste into a resource.

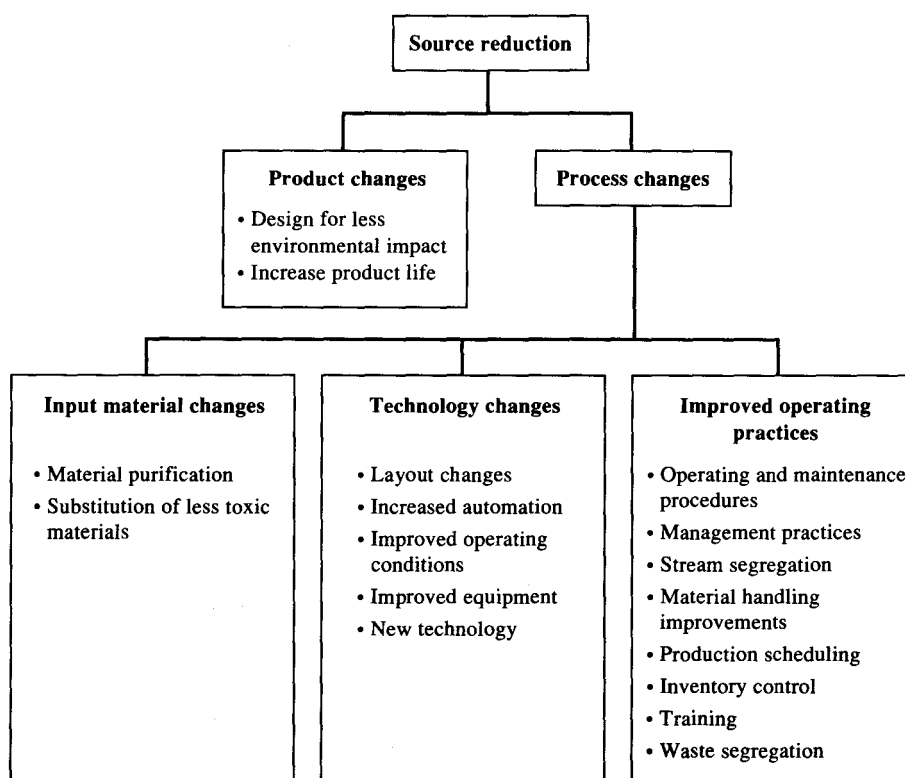## 1.4.2 Pollution Prevention Definition

Pollution prevention is a term used to describe production technologies and strategies that result in eliminating or reducing waste streams. The EPA defines pollution prevention as

> the use of materials, processes, or practices that reduce or eliminate the creation of pollutants or wastes at the source. It includes practices that reduce the use of hazardous materials, energy, water or other resources and practices that protect natural resources through conservation or more efficient use.

Thus pollution prevention includes both the modification of industrial processes to minimize the production of wastes and the implementation of sustainability concepts to conserve valuable resources.

Pollution prevention activities range from product changes to process changes to changes in methods of operation. This wide variety of activities is depicted in Figure 1.4.

The main premise underlying pollution prevention is that it makes far more sense for a generator not to produce waste than to develop extensive treatment schemes to ensure that the waste poses no threat to the quality of the environment (Freeman, 1995).

FIGURE 1.4
Typical source reduction methods. (Adapted from U.S. EPA, 1992)

1.4.3   Other Terms

We can avoid confusion by defining a few more terms that are commonly used to describe pollution prevention before we move on. *Source reduction* is an activity that reduces or eliminates the waste at the step where the pollution is created. *Waste minimization* and source reduction are often used interchangeably. *Emission reduction* is an activity that reduces or eliminates pollutants within the industry boundary limits so that they are not emitted into the environment. *Waste reduction* is any activity that reduces the amount of waste that is generated at any step of manufacture, use, or disposal. Thus, changes to an industrial process to increase efficiency of process chemicals utilization is deemed source reduction, while treatment of the residual chemicals leaving the process to either destroy them or recycle them back to the process is emission reduction. Waste reduction encompasses both of these. *Recycling* refers to the recovery and direct reuse of a material from a waste stream. For example, chromium can be recovered from the drag-out water from a plating bath rinse system by reverse osmosis or ion exchange and recycled back to the plating bath for reuse. *Reclamation* generally indicates that the recovered chemical is used in some other application. An example is the recovery of spent pickle liquor from a steel mill operation and its use as a neutralizing agent in another industry.

1.4.4   Sustainability

A final definition is that of *sustainability* or *sustainable waste management.* Another synonymous term that is enjoying current favor is *integrated waste management.* These are difficult terms to define and have different meanings to different people. Discussion of how sustainability should be defined was initiated by the Bruntland Commission, a group assigned to create a "global agenda for change" by the General Assembly of the United Nations in 1984. They defined sustainable very broadly:

> Humanity has the ability to make development sustainable-to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs. (World Commission on Environment and Development, 1987)

> Professor Robert K. Ham of the University of Wisconsin, a leading authority on solid waste management, states that "sustainable" means an action or process can continue indefinitely. No resources are used to extinction or faster than they are naturally replenished. "Sustainable waste management" implies that there would be no degradation of land, water, or air by wastes; however, this is not feasible and regulatory authorities generally allow some degradation to levels deemed to be acceptable. Ham finds the term "integrated waste management" to be more practical in that it requires use of multiple waste management techniques to minimize resource, environmental, and economic impacts. It includes waste reduction, recycling, treatment, and environmentally safe disposal (Thurgood, 1996).

N. C. Vasuki, chief executive officer of the Delaware Solid Waste Authority, says that a society has attained its sustainable development goal when the material and economic aspirations of its members are satisfied through optimum materials management

and minimum use of natural resources. Essential prerequisites for attaining such a goal include the following (Thurgood,   1996):

- A free and democratic system to develop consensus on materials use policies.
- A relatively free market system which adjusts to supply and demand of materials.
- Timely use of appropriate technology to minimize environmental degradation.
- Recognition   that a risk-free society is not feasible.
- Elimination of hidden subsidies and equitable allocation of costs.
- A regulatory framework for establishing a rule of law and an adjudication system for equitably enforcing laws.

Finally, Dr. Peter White, principal scientist at Procter & Gamble, states that an integrated waste management system should manage all of the waste in an environmentally and economically sustainable way. He defines *environmental sustainability* as reducing overall environmental burdens by optimizing both consumption of resources and generation of emissions. *Economic sustainability* means that the overall costs are acceptable to all sectors of the community that are served-householders,   businesses, institutions, and government. Integrated waste management considers both of these to achieve the most acceptable result based on overall environmental burdens and costs. It involves the use of a range of different waste minimization schemes and treatment options (White, 1996).

The topic of sustainability is a vital one to any discussion on pollution prevention. It is discussed in more detail in Chapter 14.

1.5   THE POLLUTION PREVENTION HIERARCHY

Integrated waste management provides the flexibility to use an almost limitless variety of waste minimization, waste treatment, and waste disposal techniques. Until recently, only the last two were seriously considered. This changed with passage of the Pollution Prevention Act (PPA) of 1990 (see Chapter 4 for more details). The preamble to the PPA says:

> The Congress hereby declares it to be the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible; pollution that cannot be prevented should be recycled in an environmentally   safe manner, whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally   safe manner whenever feasible; and disposal or release into the environment   should be employed only as a last resort and should be conducted in an environmentally   safe manner.

Thus Congress made pollution prevention a national policy rather than just a desired goal, and it established a hierarchy for determining how pollution should be managed. It established source reduction as the preferred method to be used for waste management,   if it is feasible and cost effective. Congress realized that all pollution could not be eliminated through source reduction alone, and it set recycling (and presumably other methods of waste reuse such as reclamation) as the preferred alternative
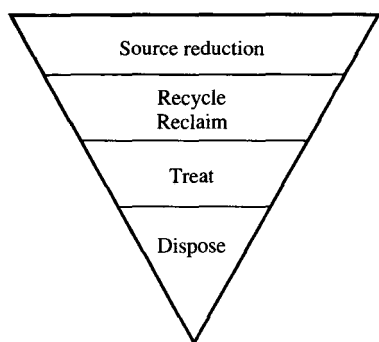
FIGURE 1.5
The pollution prevention hierarchy.

for management of residuals that remain after all viable source reduction measures are taken. Anything that remains after these steps should be treated to render it less hazardous and more compatible with the environment. Disposal into secure chemical landfills or direct release into the environment is allowed only as a last resort. These options were depicted in Figure 1.2.

In almost all cases, total pollution elimination through source reduction or recycling will not be possible. There will always be some residuals that cannot be prevented or reclaimed. Recovery systems are not 100 percent efficient, and residual streams may not be pure enough to recycle directly or to recover economically. The remaining pollution requiring treatment after source reduction and recycling should be greatly reduced in volume, however, thus making treatment easier and much less expensive. Again, it is unlikely that treatment will detoxify all pollution. Some will always need to be disposed of, either to a secure chemical landfill or directly to the environment at levels that the environment can safely assimilate. This amount should be much reduced from the amount of the original waste, though. Thus the pollution prevention hierarchy can be depicted as an inverted triangle, where the area of the band denoting the management option is indicative of the amount of pollution involved (see Figure 1.5). The objective of pollution prevention is to make the pointed base as small as possible.

1.6   RECYCLING VS. **POLLUTION   PREVENTION**

A close examination of the EPA defmition of pollution prevention indicates that it refers only to elimination of pollution at its source. Recycling or reprocessing of a recovered material into a form that can be used in another process is not deemed pollution prevention by the EPA. This is a much narrower definition than that used by many states, which include recycling and reuse in their definition of pollution prevention, because all three options lead to a reduction in the amount of material wasted to the environment or needing treatment before discharge.

In this book we use the broader defmition of pollution prevention that includes recycling and reuse of residuals from industrial processes. Most of the book is devoted to source reduction, recycling, and reuse, but treatment and final waste disposal are discussed as necessary to complete the picture of integrated or sustainable waste manage-

ment. The reader desiring more knowledge on industrial waste treatment can find it elsewhere (Conway, 1980; Eckenfelder and Dasgupta, 1989; Nemerow and Dasgupta, 1991; Sell, 1992).

L7 ENVIRONMENTAL ETHICS

Most pollution prevention activities are initially begun because of regulatory pressure, an understanding that there could be cost savings associated with minimizing waste generation, or a desire to improve a corporate image. In recent years, however, some companies have moved beyond these impetuses to espouse pollution prevention on a more moral basis. They base their pollution management decisions on environmental ethics.

Environmental ethics is a systematic account of the moral relationships between human beings and their natural environment. It assumes that moral norms can and do govern human behavior toward the natural world (Des Jardins, 1997). Environmental ethics is concerned with humanity's relationship to the environment, its understanding of and responsibilities to nature, and its obligation to leave some of nature's resources to posterity. Pollution, population control, resource use, food production and distribution, energy production and consumption, the preservation of the wilderness and of species diversity all fall under the purview of environmental ethics (Pojman, 1994).

The inspiration for the recently developed study of environmental ethics was the first Earth Day in 1970, when environmentalists started urging philosophers who were involved with environmental groups to do something about environmental ethics. Discussions on environmental ethics go back much further than this, however, and include the writings of Henry David Thoreau, John Pinchot, and John Muir. Many books have been written recently discussing environmental ethics. Among the better ones for developing an insight into this rapidly developing field are those by Callicott and Da Rocha (1996), Des Jardins (1997), Gunn and Vesilind (1986), Hayward (1994), and Pojman (1994). The book *Management for a Small Planet,* by Stead and Stead (1996), should be required reading for anyone interested in the need for corporations to develop an environmental ethic for their corporate practices.

Rather than attempt to condense the philosophy into a few paragraphs, the reader is directed to the references just mentioned. We only briefly discuss the impact of these philosophies on corporate management.

There are several philosophies used to describe environmental ethics. One of the early ones, defined by Gifford Pinchot, is *conservationism.* Its basis is the view that wilderness is a resource that must be utilized and protected at the same time. The value system that is expressed in this philosophy puts people's needs above all others. Wilderness, as such, receives no moral standing beyond needing to be available for human consumption in a sustained manner. Conservationists work to protect natural and wilderness areas from nonessential forms of permanent destruction, ensuring the future existence of the areas for human utilization. The Sierra Club is an example of an organization that espouses this philosophy. Its mission statement includes the line "to practice and promote the responsible use of the earth's ecosystems and resources."

Another philosophy, which dates back to the writings of Henry David Thoreau and John Muir, is that of *preservationism.* This philosophy promotes the ethic that

nature is meant to be enjoyed and experienced by humans and that it is our duty to protect the wilderness for our future enjoyment. This philosophy again places the value of nature on human utilization of it, but it is directed at benign uses of nature (enjoyment), rather than on sustainable extraction of resources.

A third environmental ethics philosophy, which has developed only over the past decade or so, is often referred to as *deep ecology,* a term coined by Arne Naess. Deep ecology extends the base of morality to include all life on Earth, including plants and animals. According to this philosophy, decisions should be made from a viewpoint that incorporates other positions in addition to human ones. In some respects this is not really a "new" ethic; as it is similar to the philosophy long espoused by many Native Americans and by many other cultures around the world. The most well known, and most notorious, organization espousing deep ecology is the group Earth First! Its slogan is "No compromise in defense of mother earth," and its belief, often expressed violently, is that Earth must be actively defended from development for its own sake and for the health of its ecosystems.

Recently, a new philosophy, termed *social ecology,* has begun to develop. Social ecology places a strong value on human existence while still recognizing the uniqueness of nature. It identifies human interactions as the main problem to be solved. The ultimate goal is to create an environment where humans interact with one another and the environment in a responsible manner (Knauer, 1997).

All of these philosophies have a common element-there is a responsibility for all people to minimize their impact on the environment as much as they can. This includes organizations and businesses. Since the Industrial Revolution, societies all over the world have based their hopes on the concept of unlimited economic wealth. The desire for economic growth has been raised to almost the same status as religion (Stead and Stead, 1996). As eloquently stated by Campbell and Moyers (1988), you can tell which institution a society considers most important by the relative height of its buildings. In medieval times, the churches were the tallest buildings. After the Renaissance, the tallest buildings were the seats of government. Today, the tallest buildings are the centers of economic activity. This philosophy of unlimited economic growth must now be tempered by a need to maintain sustainability. This necessitates a rethinking by industry of acceptable methods of doing business. In other words, industry must develop an underlying set of environmental ethics upon which corporate decisions are made.

Corporate ethics involves the moral issues and decisions confronting corporations and the individuals working in those corporations, including moral conduct, character, and ideals. Corporate environmental ethics concerns the way corporations conduct business in relation to their impact on the environment. Values are the key ingredients people use to judge right and wrong. Thus a person's ethical system is the sum total of the values he or she holds dear. Corporations have ethical systems that are primarily composed of the dominant values of the key strategic decision makers in the firm. This means that ethical considerations are an inherent part of corporate strategic decision-making processes. Effectively incorporating Earth into strategic decision-

making processes means extending the firm's ethical reasoning to include the planet (Stead and Stead, 1996).

Sustainability   should be the core value for a corporation's   ethical system; it allows for positive economic success and environmental   responsibility.   It is based on an understanding   that economic   success and ecosystem   survival are both worthy and necessary goals for individuals and organizations. Acceptance   of this tenet would allow environmentalists   and industrialists   to cooperate to achieve common goals of adequate industrial growth within the constraints of resource preservation.

One way of achieving this cooperative style of industrialism is for businesses to use what is referred to as *stakeholder management.* Stakeholders are persons or groups that can affect or are affected by the achievements   of the business's objectives. Stakeholders include customers, shareholders, suppliers, competitors, activists, and advocacy groups, all of whom have an interest in the practices of the corporation. Stakeholder management refers to serving the varied, often conflicting, needs of these multiple stakeholders (Stead and Stead, 1996). It requires giving weight to the ethical, social, and political dimensions   of a situation along with the economic   dimensions, bringing ethical considerations   to the forefront of strategic decision making. It is based on the theory that organizations   that serve the needs of the greater society are more likely to prosper than are self-serving organizations.

Consumers   are becoming   more demanding   and are insisting on high-quality goods that save time and energy and preserve the environment. They are searching out manufacturers   that they perceive as socially and environmentally   responsible. About one in seven Americans is actively involved in "green organizations"   (Bhat, 1996). These people are concerned   about the impact that products have on the environment. They are more likely to buy products in recyclable or biodegradable packages, and they are willing to pay for this. We now have large numbers of "green consumers" buying "green products" and then recycling the wastes. Green products are those that are of high quality, durable, made with nontoxic materials, produced   and delivered using energy-efficient processes, packaged in small amounts of recyclable material, not tested on animals, and/or not derived from threatened species. As environmental   standards being developed by the International   Organization   for Standardization   (under ISO 14000, to be described more fully in later chapters) become widely adopted, it will become easier for the public to decide what are and are not environmentally   sound products. There are now several investment groups specializing in "ethical stock funds," investing only in companies that practice environmentally   conscious manufacturing.

In 1990, the members of the Chemical Manufacturers' Association (CMA) agreed to a set of guidelines designed to improve the way chemical manufacturers man-age the environmental   aspects of their businesses. The following nine guidelines are contained within the Responsible Care program:

1. To safely develop, produce, transport, use, and dispose of chemicals.
2. To make health, safety, and the environment priority considerations in planning for both current and new products.

CHAPTER
2

PROPERTIES
AND
FATES
OF
ENVIRONMENTAL
CONTAMINANTS

Essentially all industrial processes yield by-products that become waste materials. When a product reaches the end of its useful life, it is often considered a waste material and is disposed of to a landfill or incinerator. Even when wastes are recycled or reprocessed into other goods, there are usually residual materials that must still be disposed of, and these become waste. All of these wastes can contribute to the contamination of our environment.

Pollution prevention and waste minimization techniques may be successful in reducing the amount of contaminants that enter the environment. However, for these techniques to be useful and to be applied in an effective way, they must be sound from economical, environmental, and public health standpoints. No pollution prevention activity will be implemented by industry if it prices the product out of competition with similar products or if the activity makes only a minimal impact on environmental quality or public health safety. Thus one of the main objectives of this book is to assist the engineer or business manager in deciding whether a particular waste minimization strategy will be beneficial to the company involved.

To effectively evaluate the usefulness of a proposed product design or production line change, the environmental impacts of the changes must be known. This means that the decision maker must have some basic understanding of the materials involved and their environmental and public health impacts. He or she must also understand the fate of these materials in the environment, since these fates will often dictate the long-term risks and costs associated with disposal of a particular material. Disposal of a more toxic material will not always lead to greater long-term costs to the industry because that material may be easily degradable and short-lived in the environment. Moreover, the contaminant, although very toxic, may be essentially immobile at the disposal point in the environment, minimizing any potential risk. In addition to evaluating the economic advantages of making process or process chemical changes, anyone contemplating such changes should investigate the properties of the existing by-products and any new by-products anticipated from the changes and determine their environmental implications.

Many of these environmental impact assessments will need to be made by a qualified engineer or scientist, but the plant engineer or business manager should have enough understanding of the by-product properties and environmental fates to be able to make an informed judgment as to the best decision for the plant. This decision maker does not have to be an environmental engineer or chemist. The impacts and fates in the environment of the contaminants commonly encountered in industrial wastes and some of their pertinent properties are discussed in this chapter. With an understanding of these concepts, the person contemplating a waste minimization initiative can make a more informed decision.

This chapter discusses common classes of industrial contaminants, including solvents, plasticizers, hydrocarbons, dioxins and furans, and plating metals. It is not intended to be an exhaustive discussion of these contaminants, but rather a brief introduction to the nomenclature used in naming these compounds, their properties and toxic effects, and their environmental fates. The discussion assumes the reader has had only an introductory course in chemistry. Readers interested in a more detailed description of environmental contaminants are referred to the book by Watts (1998).

2.1   ORGANIC CHEMICALS

Organic compounds are those that contain carbon and usually hydrogen. In addition, they may contain oxygen, nitrogen, sulfur, phosphorus, halogens, metals, or other elements. They run the gamut from simple (e.g., methane, CH_4) to highly complex (e.g., fulvic acids). A general knowledge of the nomenclature of organic compounds is critical to an understanding of environmental regulations and waste minimization assessments.

2.1.1   Nomenclature of Organic Compounds

Because of the many hundreds of thousands of different organic compounds available or potentially available, it is necessary to carefully name them to avoid confusion as to what compound is being described. Some compounds have common names associated with them, but in general it is essential that a commonly accepted nomenclature system

TABLE 2.2
Names of the more common normal saturated organic acids

Common name	IUPAC name	Formula
Formic	Methanoic	HCOOH
Acetic	Ethanoic	CH]COOH
Propionic	Propanoic	C_2H_8COOH
Butyric	Butanoic	C_3H_7COOH
Valeric	Pentanoic	$C_4H9COOH$
Caproic	Hexanoic	CsH1,COOH
Enanthic	Heptanoic	$C_6H_{13}COOH$
Caprylic	Octanoic	$C_7H_{15}COOH$
Perlagoric	Nonanoic	$C_9HI7COOH$
Capric	Decanoic	C9H'9COOH
Palmitic	Hexadecanoic	$C,sH_3,COOH$
Stearic	Octadecanoic	$C17H_{35}COOH$

Unsaturated organic acids are also commonly found in nature and are used as process chemicals. For example, they are used in the production of plastics such as Plexiglas and in a variety of oils such as linseed oil. The common unsaturated organic acids are listed in Table 2.3.

Many saturated and unsaturated monocarboxylic acids occur in nature as constituents of fats, oils, and waxes. Thus they are often referred to as *fatty acids.* Many have very objectionable odors, such as butyric acid, which gives rancid butter its noxious odor.

Esters are compounds formed by the reaction of alcohols and organic acids. The general formula of an ester is R-COO--R', where R and R' refer to organic groupings. They are named based on the alkyl nomenclature and the unprotonated salt of the carboxylic acid involved in their formation. An exception is when the alkyl group contains only two carbons; it is then named acetate rather than ethanate. The name of the alkyl group is placed first, followed by the name of the salt of the carboxylic acid, ending in -ate. For example, the compound

$$H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - O - CH_2 - CH_3$$
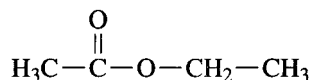
Ethyl acetate
(IUPAC name: Acetic acid ethyl ester)

is composed of the salt of acetic acid and an ethane group from ethanol. It is named ethyl acetate. Esters are used widely in industry. Many have pleasing aromas and are used in perfumes and flavoring extracts. Others are used as solvents.

TABLE 2.3
Common unsaturated organic acids

| Name	Formula
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic acid	$CH_3(CH_2CH=CH)_3CH_2(CH_2)_6COOH$

Ethers are formed by combining two alcohols; during the reaction a molecule of water is removed. Ethers have the general formula R—O—R'. They are generally named by combining the names of the two alcohols involved in the synthesis reaction.

$$CH_3-CH_2-O-CH_2-CH_3$$
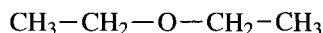
Diethyl ether

Ethers are widely used in industry as solvents. Many are highly flammable, and some may become explosive if exposed to air for a prolonged period. Diethyl ether has been used widely as an anesthetic.

Aldehydes are the oxidation products of primary alcohols (R—OH), and *ketones* are the oxidation products of secondary alcohols (R—(C(OH)H)—R'); they have two alkyl groups attached to the carbonyl group (—CO—). The aldehydes contain a double-bonded oxygen and a hydrogen on the terminal carbon. They are named by adding -al to the basic alkane name. Ketone names end in -one.
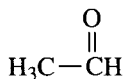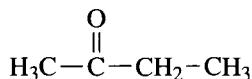
Acetaldehyde
(IUPAC name: Ethanal)
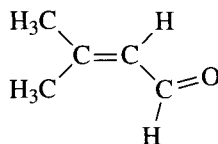
Senecialdehyde
(IUPAC name: 3-Methyl-2-butenal)
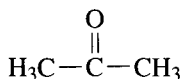
Acetone
(IUPAC name: 2-Propanone)

Methyl ethyl ketone
(IUPAC name: 2-Butanone)

Aldehydes and ketones are usually referred to by their common names. Table 2.4 lists the aldehydes and ketones common in industrial use.

Acetaldehyde and formaldehyde are two commonly used chemicals in organic synthesis reactions. Ketones are commonly used as solvents in industry and as a precursor in the synthesis of many organic chemicals.

TABLE 2.4
Common aldehydes and ketones

Common name	IUPAC name	Formula
Aldehydes		
Fonnaldehyde	Methanal	HCHO
Acetaldehyde	Ethanal	CH_3CHO
Propionaldehyde	Propanal	C_2H_8CHO
Butyraldehyde	Butanal	$C)H_7CHO$
Acrolein	2-Propenal	$CH_2=CHCHO$
Ketones		
Acetone	Propanone	$CH_3COCH]$
Methyl ethyl ketone (MEK)	Butanone	$CH_3COC_2H_8$
Methyl isopropyl ketone	3-Methyl-2-butanone	$CH_3COC_3H_7$
Methyl isobutyl ketone (MIBK)	4-Methyl-2-pentanone	$CH_3COCH_2CH(CH_3h$

A number of *cyclic aliphatic compounds* are found in petroleum. These are usually five- or six-ring saturated aliphatic compounds, although cyclic alkenes are also known. The most common cyclic aliphatic is cyclohexane.
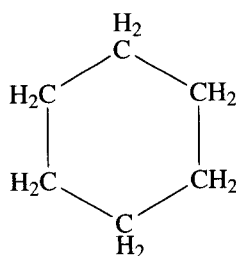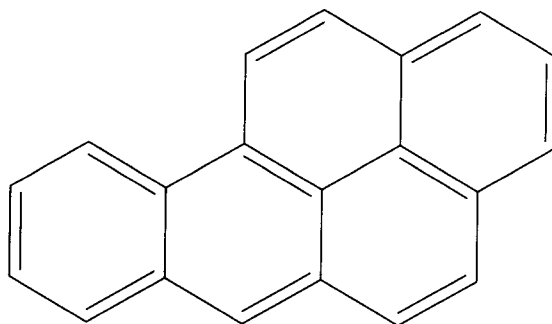

Cyclohexane

Cyclic alcohols and ketones are also known, including the ketone cyclohexanone.
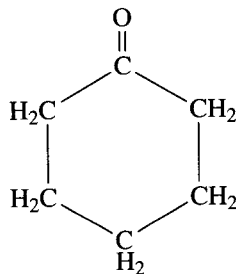

Cyclohexanone

Benzo[*a*]pyrene

Detailed descriptions of PAHs and their environmental significance can be found else-where (Chakrabarty, 1982; Chaudry, 1994; Rochkind-Dubinsky, Sayler, and Blackburn, 1987; Watts, 1998). The procedure for naming substituted PAHs is complicated and won't be described here. The reader is referred to Cahn (1979), IUPAC (1961), and Watts (1998).

Many chlorinated aromatic compounds have important industrial uses. Chlorinated benzenes (e.g., chIoro benzene, hexachlorobenzene) are widely used as industrial solvents and as insecticides. *Polychlorinated biphenyls* (PCBs) have the structure
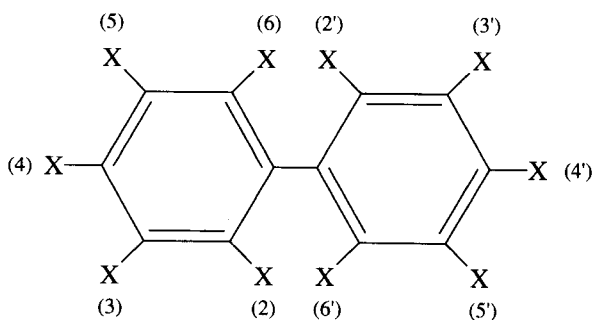
where parentheses denote the carbon number and X can be either a chlorine or a hydro-gen. PCBs are heat-stable oils used extensively as transformer cooling oils and hydraulic fluids and as solvents and plasticizers.

There are 10 sites on the biphenyl molecule where chlorine can be substituted for hydrogen atoms. This results in 209 possible PCBs (called congeners), depending on the number and arrangement of chlorines on the molecule. PCBs are formally named using the same nomenclature as previously cited. For example,
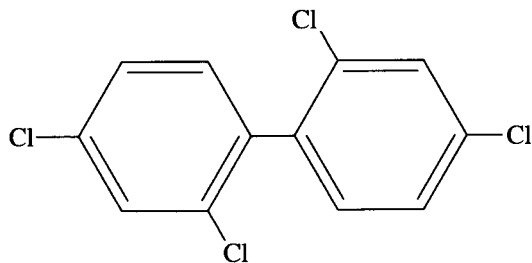
2,2' ,4,4' -Tetrachlorobiphenyl

In the United States, PCBs were marketed by Monsanto under the trademark Aroclor, followed by a four-digit number, for example, Aroclor 1221. The number denotes the number of carbons and the degree of chlorination. The fIrst two digits refer to the 12 carbons contained in the biphenyl. The last two digits represent the average weight percentage of chlorine in the PCB mixture. Aroclor 1221 is a 12-carbon biphenyl mixture containing 21 percent chlorine, by weight. Production of PCBs has been banned in the United States since 1977, but much of it is still in use and it continues to be a signifIcant environmental and public health problem.

The last groups of organic compounds we will discuss are the *polychlorinated dibenzodioxins* (PCDDs) and the *dibenzofurans* (PCDFs). These are not compounds that are produced for any useful purpose, but rather are unwanted by-products formed during the manufacture of other organics or during combustion of chlorinated organic materials such as plastics. Chlorinated dioxins are derivatives of dibenzo-p-dioxin. Between one and eight chlorine atoms may be substituted on the dioxin molecule, resulting in 75 possible congeners. An example of a PCDD is a compound commonly called TCDD:
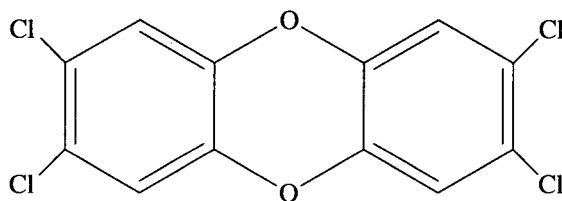
2,3,7,8- Tetrachlorodibenzo-p-dioxin   (TCDD)

TCDD is a major health risk because it is highly persistent in the environment, bioaccumulates in animals, and is extremely toxic. Polychlorinated dibenzofurans are similar in structure to dioxins, but with only one oxygen between the benzene rings. A typical furan compound is
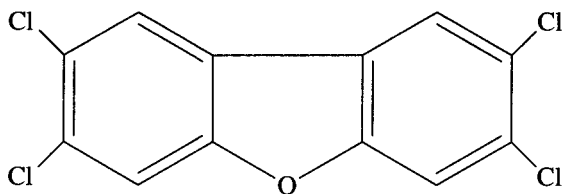
2,3,7,8-Tetrachlorodibenzofuran

PCDFs form in a similar fashion to PCDDs and pose similar environmental and public health problems.
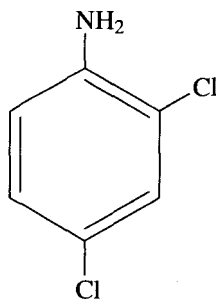
Example 2.3. Draw the structure of the following compounds:
(a) 2,4-Dichloroaniline.
(b) 2-Bromo-3-chlorobenzoic acid

Solution.
(a) The base compound, aniline, is a benzene with an amino group ($-NH_2$) at the I position. Chlorines are substituted for hydrogens at the 2 and 4 positions. Therefore, the structure is

(b) The base compound is benzoic acid, which is a benzene with a carboxyl group (- COOH) at the 1 position. A chlorine is substituted at the 3 position and a bromine is substituted at the 2 position. Therefore, the structure is
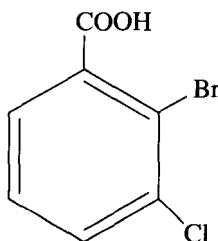
2.2   METALS AND INORGANIC NONMETALS

The division between metals and inorganic nonmetals is not well defined. In general, those elements that easily lose electrons to form positive ions are considered to be metals. Metals usually conduct electricity readily. Elements that hold electrons firmly and tend to gain electrons to form negative ions are called nonmetals (Sawyer, McCarty, and Parkin, 1994). The periodic table of the elements seen in Appendix A is divided into seven horizontal rows (periods) and 16 vertical columns (families). The heavy line divides metals from nonmetals.

Heavy metals are defined as those with atomic numbers greater than that of iron and with densities greater than 5.0 g/cm^3. Many heavy metals (e.g., lead, cadmium, chromium, mercury) are of great environmental concern because of their toxicity.

The most significant source of anthropogenic metals in the environment is metal finishing operations, either from rinsing metals after plating or from disposal of spent metal plating baths. Often these wastewaters are discharged into receiving streams near

the industry or to municipal wastewater treatment plants, where some passes through
to the receiving stream without being removed. The plating bath sludges or the sludges
from the municipal treatment plant are often disposed of in landfills, where the metals
can leach into the underlying groundwater. Waste metals in discarded products can also
eventually solubilize and enter groundwater or surface waters. Metals in wastes under-
going incineration, such as tin cans and other metallic refuse, may volatilize under the
high temperatures present and become an air pollutant. The nonvolatilized metals will
accumulate in the fly ash or bottom ash and can threaten groundwaters after landfilling.

     Small quantities of many metals are essential nutrients for humans and other
animals, but too much of them can be toxic. Metal toxicity is often associated with the
species of metal present. Forms that are essentially insoluble generally pass through the
human body and are excreted without doing any damage. More soluble forms, though,
can be retained in tissue or the blood stream and may cause severe toxicity. Because of
chemical or biochemical transformations that can occur in the environment or in the
body, the metal species present may not be the one that was discharged into the envi-
ronment as a waste material. For example, under anaerobic conditions in sediments or
in the human gut, metallic mercury can be combined with methyl groups to form
methylmercury or dimethylmercury. Both are much more soluble than the parent mer-
cury and can cause severe biological damage. Thus knowledge of all known species of
a particular metal contaminant is important because the metal may be transformed into
much more hazardous compounds than what an industry is discharging.

     A major reason for concern about inorganic contaminants in general, and heavy
metals in particular, is that they often bioaccumulate in nature. Concentrations in
organisms increase as one goes up the food chain. These compounds are more soluble
in tissues than they are in water or in the tissue of the lower order organism that has
been consumed. Thus concentrations found in tissue can be orders of magnitude
greater than found in the water at the initial industrial discharge point. What may
appear to be innocuous amounts in an industrial waste effluent entering a receiving
water may be concentrated to toxic levels in fish or later in humans that consume
that fish. For example, oysters and mussels can contain mercury or cadmium at con-
centrations hundreds of thousands times greater than that of the water in which they are
growing.

     In this section, we examine only a few inorganic contaminants of significant
industrial usage. Those chosen for discussion are discussed in other parts of this book.
More detailed descriptions can be found elsewhere (Meyers, 1977; Sax, 1987, 1992)
for these and other inorganics.

2.2.1   Arsenic

Arsenic compounds are extremety toxic. Anyone who remembers the old movie
Arsenic and Old Lace is aware of its lethal nature. Less than 0.1 g of arsenic is usually
lethal. **It** is also a known carcinogen. Copper chromium arsenate (CCA) was formerly
widely used as a wood preservative for such things as wood decks and outdoor furni-
ture; its use has now been largely curtailed because of its toxicity. Although the indus-
trial use of arsenic has decreased over time, arsenic is still widely used in agriculture

as a herbicide and as an animal disinfectant. Arsenic and its compounds are commonly used in industry as process chemicals.

Arsenic is not a true metal, but rather is classified as a semimetal or metalloid; its properties lie between those of a metal and those of nonmetals. Arsenic has five electrons in its outer shell. It can share three electrons with another atom, making it a 3+ ion (arsenite), or it can lose all five electrons, making it a 5+ ion (arsenate); it can also exist in an elemental form in the a state, but only under very low oxidation-reduction conditions not generally found in nature. Under reducing conditions (anaerobic), arsenic may exist in the 3- state (arsine), accepting three electrons to fill its outer electron shell. Under aerobic conditions, arsenate (AsO_4^{3-}) $(As(V))$ is the most common form; under low oxidation-reduction potential conditions $(E_h < 100 \, mV)$ the most common arsenic species is arsenite $(AsOl-)$ $(As(III»$. (Note: the Roman numeral refers to the oxidation or valence state of the element.) Under very strong reducing conditions, highly toxic arsine gas (AsH_3) may be formed. As(III) is considered to be more toxic than As(V); unfortunately, As(V) is often converted to As(III) in the human body.

The average inorganic arsenic content of drinking water is about 2.5 *JLg/L*. The maximum allowable concentration for arsenic in drinking water is 0.05 mg/L.

2.2.2 Cadmium

Cadmium is a metal that usually occurs in nature together with zinc, and most of the cadmium in use in industry is produced as a by-product of zinc smelting. Cadmium is widely used in metal plating because it is very resistant to corrosion. It is also commonly used as a stabilizer in polyvinyl chloride (PVC) plastics. Cadmium compounds have been used for hundreds of years as pigments in paints, and more recently in plastics. They have also been used in television screens. Cadmium has also found widespread use as an electrode in rechargeable "ni-cad" (nickel-cadmium) batteries, but these are being phased out because of concern over their significant environmental impacts. When municipal solid wastes are incinerated, the cadmium in the batteries is volatilized and is emitted from the exhaust stack as an air pollutant. Because of the great toxicity of cadmium, its use has declined over recent years.

Cadmium is almost always found in the 2+ valence state. Cadmium compounds with simple anions such as chloride are salts rather than molecules. Cadmium is highly toxic. Only about I g is a lethal dose. Cadmium is not quickly eliminated from the human system and can easily bioaccumulate to toxic levels. Its half-life in humans is estimated to be 20-30 years.

Due to its similarity to zinc, an essential nutrient for plants, plants absorb cadmium from irrigation waters and from soils where cadmium may have accumulated from atmospheric deposition or from land spreading of wastes containing cadmium. Eating crops contaminated with cadmium can lead to serious health problems. Strict regulations govern the amount of cadmium that can contact crops used for human consumption. Most serious episodes of cadmium contamination, though, have been associated with smelting operations.

Because of its great toxicity, the drinking water standard for cadmium has been set at 5 *JLg/L*.

2.2.3 Chromium

Chromium is a transition metal exhibiting valence states from $2-$ to $6+$, although the $3+$ and $6+$ species are generally the only ones of interest. It is commonly present as Cr(VI) in the chromate $(CrOi\text{-})$ and dichromate $(Cr2Ol\text{-})$ forms, and as Cr(III) in the chromic (Cr3+) state. Cr(VI) compounds are generally soluble in water, whereas Cr(III) compounds are insoluble.

Chromium is used primarily in metal plating because of its resistance to acid attack and as pigments, but it is also used in leather tanning, as a catalyst in chemical processes, and in the manufacture of electronic equipment. All chromium in the United States comes from foreign sources, primarily from South Africa.

Chromic and chromate salts are irritating to exposed tissues. Some chromium compounds are known carcinogens. Because of their toxicity, the total chromium concentration is limited to 0.1 mg/L in drinking water.

2.2.4 Lead

Lead is widely used in industry because of its unique properties. It has a low melting point (327°C), high density, malleability so that it can easily be shaped into pipes, and high acid resistance. Its primary use is in automobile batteries (about 65 percent of all lead used), but it is also used in electroplating, pigments, plastics, glass, and electronics equipment. Because of its toxicity and ability to bioaccumulate, the use of lead in paints for residential purposes has been banned, as has its addition to automobile gasoline. Lead has been commonly used for water distribution pipes since Roman times, but new lead pipes are no longer installed; many are still in use, however, and probably will be for a long time because of their durability. It is still used in construction for roofing and flashing, and in many types of electrical solder.

In pure form, lead does not usually cause environmental or health problems. It is only when it dissolves yielding ionic forms that it becomes toxic. Lead ions usually exist in the 2+ state. It can also exist in the tetravalent form, particularly when complexed with organic radicals. Leaded gasolines used in the past contained lead in the form oftetraethlylead $(Pb(C_2H_S)4)$, added to prevent premature ignition, or "knocking." Automobile emissions of this lead resulted in serious environmental degradation and many cases of lead poisoning, particularly in children. Although it has a low boiling point, its vapor point is quite high (1740°C) and its vapor pressure is low, so volatilization of elemental lead is not usually a major problem.

At high levels, lead is a general metabolic poison. At lower concentrations, it can interfere with the production of hemoglobin, leading to anemia. It can also cause kidney dysfunction, high blood pressure, and permanent brain damage. Lead poisoning is of particular concern with young children who are prone to eat paint chips or soil around buildings, which may contain residues of lead paint or lead from automobile exhaust. This practice is called *pica*. Chronic exposure to lead in this way in young children can lead to serious and potentially permanent neurological damage.

Fortunately, a major recycling infrastructure has been developed for lead-containing materials, particularly lead batteries. Consequently, most lead-bearing materials are now recycled, and the amount entering the environment is much reduced from what it was in the past. The amount of lead recycled in 1988 was approximately 79 percent of the amount of lead refmed that year.

2.2.5 Mercury

Mercury is unusual among metals in that it is a liquid at room temperature. It can exist in valence states of 0, 1+, and 2+. It can exist in both organic and inorganic forms. Its ability to expand uniformly with changes in temperature makes it ideal for use in thermometers. In the elemental form, its ability to conduct electricity is used in fluorescent light bulbs and mercury lamps used for exterior lighting. It is also widely used in miniature batteries, as an industrial catalyst in the production of chlorine and chlorinated compounds, in the pharmaceutical industry, and in fungicides and insecticides.

Mercury is highly volatile and its vapor is very toxic. Because of this, there has recently been a movement to replace mercury vapor lamps with somewhat less damaging sodium vapor lamps. These newer lamps pose less of a toxicity hazard and are more efficient.

The common ion of mercury is the 2+ species, $Hg2+$, known as the mercuric ion. Mercuric sulfide (HgS) is highly insoluble in water. Thus the presence of sulfide in water often makes the mercury immobile. Mercuric nitrate ($Hg(N0_3h)$, on the other hand, is water soluble. At one time it was used to treat the fur used in the manufacture of felt for hats. The workers exposed to the felt often developed nervous disorders, depression, and insanity. This is the derivation of the term "Mad Hatter" in *Alice in Wonderland.*

Mercury salts, such as mercuric chloride ($HgCl_Z$), can become methylated in anaerobic waters or sediments by anaerobic bacteria. The result is the formation of the highly toxic volatile liquids methylmercury (CH_3HgX), where X is an anion, usually a halide, and dimethylmercury ($Hg(CH_3h$). These compounds are much more toxic than the inorganic mercury salts. They can quickly evaporate into the atmosphere above the liquid, becoming an air pollutant; they can also be rapidly taken up by fish and other organisms in water and be bioaccumulated in fatty tissue, where they become harmful to that organism or to others that consume it. During the 1960s it was discovered that large fish such as tuna and swordfish could have mercury concentrations in their tissues that were one million times higher than the concentrations in the waters through which they swam. Residents of the Japanese fishing village of Minimata became exposed to serious methylmercury poisoning through the fish they consumed from Minimata Bay. A chemical plant using mercury as a catalyst in polyvinyl chloride production discharged mercury-laden wastewaters into the bay. The mercury bioaccumulated in the fish to levels as high as 100 ppm, far in excess of the recommended limit of 0.5 ppm mercury in fish for human consumption. The result was mercury poisoning of thousands of people and the deaths of hundreds of them.

Mercury has also been widely used in the production of chlorine and chlorinated compounds and sodium hydroxide. In this process, metallic sodium is produced by reduction of NaCI in solution in an electrolysis cell using mercury as the cathode:

$$Na^+(aq) + Hg + e^- \rightarrow Na \quad \text{(as a Na} - \text{Hg amalgam)}$$
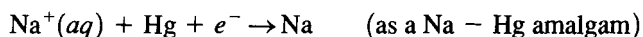
The freed chlorine from the sodium chloride is recovered. The metallic sodium that is produced is in the form of an amalgam with mercury. The amalgam is then separated from the salt solution and reacted with water in a separate reactor to produce high-purity sodium hydroxide that is free of any salts. The overall reaction is

$$2\text{NaCl}(aq) + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH}(aq) + \text{Cl}_2(g) + \text{H}_2(g)$$
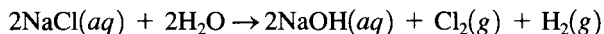
The mercury is recovered and reused, but some escapes into the air and into the plants' cooling water. The amounts of mercury lost to the environment in the past were enormous. In recent years, this process is being phased out and replaced by a membrane process that does not require the use of mercury. The NaCl solution and the chloride-free solution are separated by a membrane through which the Na^+, but not the Cl^-, can pass.
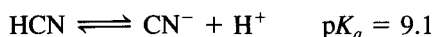
Because of its severe toxicity, the maximum allowable concentration of mercury in drinking water is 2 μg/L.

2.2.6   Cyanides

Cyanide is not an element but rather an inorganic nonmetallic anion with the structure

$$\text{C} \equiv \text{N}^-$$

It is the conjugate base of the weak acid hydrogen cyanide (HCN):

$$\text{HCN} \rightleftharpoons \text{CN}^- + \text{H}^+ \qquad pK_a = 9.1$$

Under neutral or acidic conditions, the higWy toxic HCN gas is formed. In high concentrations, this gas can be lethal. Cyanide binds with metal-containing enzymes (cytochromes) that participate in respiration. Asphyxia can result from exposure to hydrogen cyanide. Cyanide solutions should never be mixed with acids because of this potential for a life-threatening situation, but it has happened accidentally on numerous occasions.

Cyanide salts are commonly used in metal plating baths. The cyanide in the metal-cyanide salt helps the metal ions to be plated to reach hard to get at places in pieces being plated. Considerable effort has been expended in recent years to find ways to eliminate the need for cyanide in plating baths, but much more research is needed. Cyanides are also used as industrial intermediates and in the recovery of gold and silver during ore refining.

The maximum allowable concentration of cyanides in drinking water is 0.2 mg/L.

2.3   CONTAMINANT TRANSPORT AND TRANSFORMATION IN THE ENVIRONMENT

Because of the potential hazard that exposure to hazardous compounds poses to humans and the environment, the levels of toxic and carcinogenic substances in the environment have become important criteria for evaluating environmental quality. The amount of a material which enters the environment, though, is not always indicative of the amount that will be found there. The concentration of a contaminant at any point in the environment depends on the quantity added and the processes that influence its fate. This can include both *transport* and *transformation* mechanisms.

Transport processes tend to move materials from one point to another and may involve intermedia exchanges between atmospheric, aquatic, and soil environments, as

well as movement within each of these media. Transport may be due to advective, dispersive, or diffusional processes.

Associated with transport processes are partitioning processes, which dictate **bow** much of the material will be in the gas, liquid, and solid phases. Partitioning is dependent on the compound's solubility, density, polarity, ionic state, and vapor pressure. Another fonn of partitioning is bioaccumulation,   in which compounds are taken up by living organisms and concentrated in their tissues.

Transformation processes within each media chemically alter the contaminants to new compounds that may have lower, equal, or greater toxicity. Transfonnations may be due to chemical, photochemical, or biological processes. The rates at which chemicals are transfonned are critical to an understanding of the seriousness of a particular pollution incident. For example, a small spill of sodium acetate may have minimal environmental impact because it is rapidly biodegraded by bacteria in soil and water, whereas a small spill of creosote may have much greater implications because of its greater persistence in the environment.

Many books have been dedicated to the topic of contaminant fate and transport in the environment (Clark, 1997; Hemond, 1994; Knox, 1993; LaGrega, Buckingham, and Evans, 1994; Schnoor, 1997; Thibodeaux, 1996). In the following sections, we will only superficially describe these processes so that the reader will better understand why avoiding introduction of these materials into the environment through pollution prevention techniques may be desirable. In addition, the reader will develop a better understanding of the process of establishing priorities for waste reduction.

Before beginning this discussion, though, it is essential to describe how concentrations of materials in the environment are expressed.

2.3.1   Contaminant Concentrations

Except when a major spill occurs, toxic materials in the environment are usually found in very low, although possibly still harmful, concentrations. Concentrations of materials can be expressed in several ways, depending on whether they are present in air, water, or soil. In most cases, chemical concentrations   in aqueous solutions are expressed in tenns of mass per unit volume, usually as mg/L (one-thousandth of a gram per liter). When concentrations   are very dilute, as in groundwaters, they may be expressed as ILg/L (one-millionth of a gram per liter). In some cases, aqueous concentrations are expressed as parts per million (ppm) or parts per billion (ppb), a mass/mass designation, and considered equivalent to mg/L or ILg/L. Technically, this is incorrect because the unit basis is not equivalent. However, if the solvent is water, which has a density of 1.00 g/cm^3 at 4°C, a 1.0 mg/L solution does essentially equal 1.0 ppm.

$$1.0 \text{ ppm} = \frac{1 \text{ mg contaminant}}{10^6 \text{ mg media}}$$

$$1.0 \text{ mg/L} = \frac{1.0 \text{ mg contaminant}}{10^3 \text{ mL solvent}}$$

Assuming the solvent is water, with a density of 1.00 g/cm^3 (or 1×10^3 mg/mL),

$$1.0 \text{ mg/L} = \frac{1.0 \text{ mg contaminant}}{(10^3 \text{ mL solvent})(10^3 \text{ mg/mL})} = \frac{1.0 \text{ mg contaminant}}{10^6 \text{ mg solvent}} = 1.0 \text{ ppm}$$

Therefore, for practical purposes,

$$\frac{\text{mg}}{\text{L}} = \frac{\text{mg}}{\text{kg}} = \text{ppm}$$

At other temperatures, the density of water varies from 1.00 g/cm^3 and this relationship does not hold. Therefore, it is usually safer to use mg/L units.

Contaminant concentrations in soils or sludges are usually expressed on a mass/mass basis. The most common expression is mg contaminant/kg soil, which is equivalent to ppm.

Air contaminant concentrations are expressed either on a mass/volume (μg contaminant/m^3 air) or a volume/volume (ppm) basis, where

$$\text{ppm} = \frac{1 \text{ part contaminant by volume}}{10^6 \text{ part air by volume}}$$

2.3.2 **Transport** Processes

Prediction of the fate of toxic pollutants in the environment requires knowledge of which processes act on the pollutants. Figure 2.1 illustrates the transport and transformation processes which are potentially important. Transport processes will be discussed first. They can be subdivided into loading processes, advective processes, dispersive processes, and diffusive processes.

LOADING PROCESSES. Loading processes are mechanisms by which contaminants are introduced into the environment. Contaminants can reach the environment through emissions into air or water or application to land. Once the contaminant reaches the environment, it is acted on by many other processes that tend to cause it to move within that medium or to move to another medium. For example, particulates emitted into the air from a smoke stack will move from the stack due to wind, thermal density gradients, and so on. Gravity will act on them, possibly carrying them to the ground or to water, converting them from an air contaminant to a water pollutant or soil contaminant. The same can be said for contaminants added to soil. They may volatilize into the atmosphere, becoming an air pollutant; they may be washed by overland stormwater flow into a water body, creating a water pollution problem; or they may seep into the groundwater, creating a pollution problem there.

Industrial contaminants can enter the environment from a wide variety of sources. They may come directly from industry in the form of air emissions from smoke stacks or process reactors exposed to the atmosphere, or from process wastewaters discharged into receiving streams with or without prior treatment. In other cases, wastewaters may be directed to a municipal treatment plant (often termed a pub-
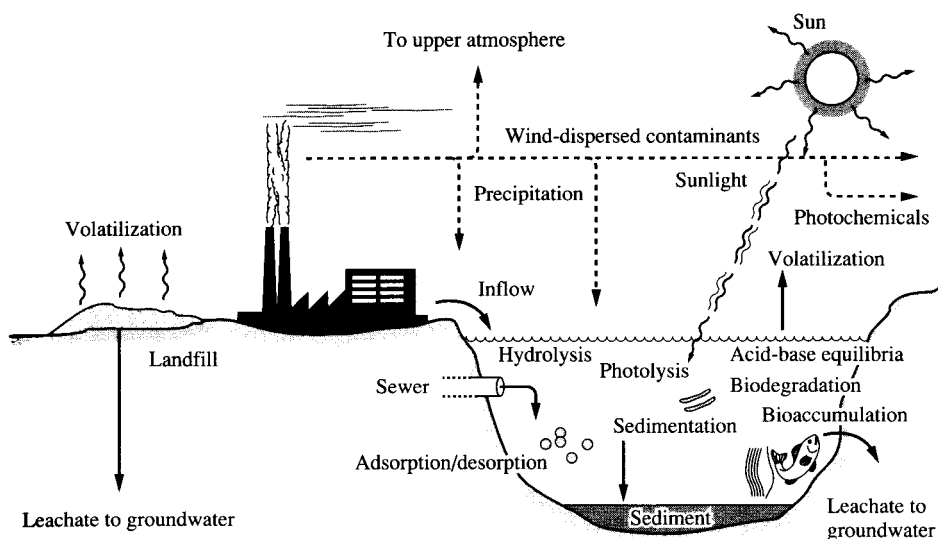
FIGURE 2.1
Fate of industrial contaminants in the environment.

lidy owned treatment works, or POTW), but the POTW effluent may still contain some of the contaminants. Solid wastes from the industry may be disposed of in a landfill, creating possible land or groundwater pollution, or may be incinerated, creating a potential air pollution problem; the resulting fly ash and bottom ash often contain heavy metals and must still be properly landfilled. These can all be referred to as *point sources.* Another significant source of contaminants released to the environment from many industrial sources, particularly chemical and petrochemical industries, is what is termed *fugitive emissions.* They can be described as unintentional emissions from leaking process equipment such as valves and pumps. These can be in the form of gases or liquids. (Fugitive emissions are described in more detail later.)

Other sources of pollution due to a specific industry may not be obvious. Transportation of the process ingredients to the factory and of the finished products from the factory require the use of fuels and energy, the production and use of which also create pollution. The same can be said for the process chemicals and raw materials themselves. Use of the product by the consumer may also involve creation of polluting materials, as may disposal of the product after it fulfills its useful life. The design and composition of these products may dictate their eventual environmental impacts.

Thus there are many sources of waste loads on the environment associated with a particular industrial process. It is the responsibility of industry and its pollution prevention experts to evaluate all potential environmental inputs caused by its products, from the raw materials processing stage through production and use (and possible reuse) of the product to final disposal, in order to minimize the total life-cycle environmental impacts.

The path that the contaminant will take can sometimes be predicted by analyzing wind patterns or groundwater gradients. In a surface stream, the contaminant will be transported with the stream.

ADVECTIVE PROCESSES. Advection is the movement of a contaminant away from the source due to the physical movement of the medium in which it is contained. Contaminants in the air are moved from the source by winds; those in water by currents, and those in groundwater by pore water movement. These factors tend to move the contaminant away from the source and prevent the buildup of high concentrations at that point. If the emission is a pulse release, the concentration at the source will reach a peak quickly, and then the mass of contaminant will be transported away from the source, leaving no contaminant behind. Assuming no dispersion occurs, the mass of contaminant will move with the carrying medium (wind, groundwater, etc.) and the contaminant concentration will remain constant. However, if the contaminant emission is continuous, new contaminant will continually replace the material moving away from the source, and the concentration all along the transport path will be constant. The main consequence of advective processes is the transport of contaminants from the contamination source to other areas.

DISPERSIVE PROCESSES. Pure advection never occurs. There is always some mixing of contaminants in a unit of air or water with surrounding uncontaminated air or water, resulting in a reduction of contaminant concentration in the original unit of medium. This spreading of a contaminant as it moves downwind, downstream, or downgradient is termed dispersion. In the atmosphere, this dispersion is usually due primarily to atmospheric turbulence, which causes units of air to mix with surrounding units of air. It may also be caused by thermal or density differences between the air in the contaminant plume and the surrounding air. Similar effects can be seen in surface or groundwaters. The most significant consequences of dispersive processes are the spreading of the contaminant over a greater area and the dilution (reduction) of the contaminant concentration in the plume (see Figure 2.2).

Computer models are available for predicting the impact of dispersive processes on a contaminant plume, but discussion of these is beyond the scope of this book. The reader is referred to Clark (1997), Schnoor (1997), and Thibodeaux (1996) for more information.

DIFFUSIONAL PROCESSES. Dispersion processes are concerned with the movement and mixing of the air or water carrier of the contaminants. However, the individual contaminant molecules or ions will also move in response to concentration gradients in the air or water. They will tend to move from a point of higher concentration to one of lower concentration. This movement is termed *diffusion*. Molecular diffusion can be described using Fick's law:

$$f = D \frac{dC}{dx}$$

where f =   mass flux of contaminant (g/cm$^2 \cdot$ sec)

$\quad D$ =   contaminant diffusion coefficient in the particular medium (cm^2/sec)

$\quad dC/dx$ =   contaminant concentration gradient (g/cm$^3 \cdot$ cm)
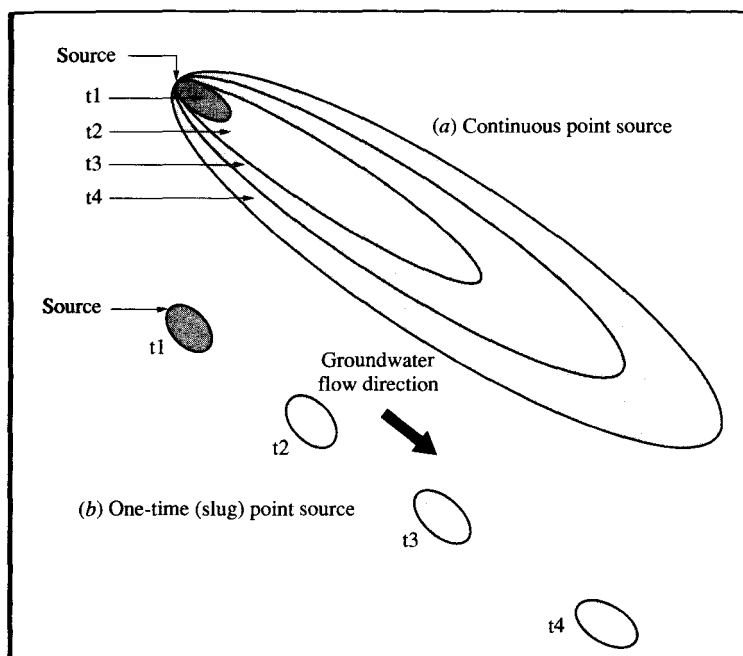
ftGURE 2.2

Plume migration affected by dispersion and source type. (Adapted from LaGrega, Buckingham, and Evans, 1994)

Diffusive effects can also be modeled, but again discussion of this is beyond the scope **of** this book. The effects of molecular diffusion are again to dilute the contaminant over a greater area and to reduce its concentration within the plume.

To assess the impact of a contaminant release into the environment and the potential effects on the general public, it is essential that valid predictions of actual exposure concentrations be made. This requires that the combined effects of advection, dispersion, and diffusion of the contaminants in the plume be determined. The analysis is made more complicated by the fact that the form and properties of the contaminant may change during transport. For example, a particulate air contaminant may settle to earth and be removed from the airstream. Gaseous contaminants may become dissolved in water droplets in the air and be removed by precipitation as rain. In both cases, they may undergo chemical reaction in the atmosphere, changing to a new compound with new diffusive properties. Similar actions may occur with contaminants in surface or groundwaters. The effects of partitioning and transformation processes on contaminants are described in the following sections.

2.3.3   Partitioning Processes

Compounds in the environment are rarely found in their pure form. Rather, they dissolve and diffuse through media, trying to achieve a minimum concentration difference with the surrounding material. Many factors govern the rate of dispersion of the compound, as described above. Other factors that govern dispersion are based on the

tendency of a material to want to be associated with one phase or another. This divi-
sion between two phases is termed *partitioning.* Partitioning is dependent on the prop-
erties of the compound and media it is in contact with. There are many properties that
can affect partitioning,   but we limit this discussion to solubility, acid-base effects,
adsorptive effects, and volatilization   effects. The impacts of these on the transport
processes discussed earlier are described.

ACID-BASE IONIZATION. Many acids and bases are used in industry, as are the salts
of these acids and bases. These run the gamut from very strong acids and bases, such
as sulfuric acid and sodium hydroxide, to very weak ones, such as carbonic acid and
sodium sulfide. They may be in the form of gases, liquids, or solids. These materials
may be very corrosive and may cause severe personal injuries and environmental dam-
age. As will be seen, the degree of ionization of these materials may playa significant
role in their transport and eventual fates.

The classical definition of an *acid* is a compound that yields a hydrogen ion (H+)
upon addition to water. A *base* yields a hydroxyl ion (OH-) upon addition to water.
These definitions   are fairly simplistic and not totally accurate, but they suffice for our
purposes. In the case of a strong acid, the bond between the hydrogen atom and the
anionic group is weak so that essentially all of the hydrogen atoms leave the molecules
when the acid is placed in water. Ionization is essentially   100 percent complete. The
same holds true for strong bases, where all of the base ionizes, liberating hydroxyl ions.
Weak acids and bases hold on to their H+ and OH- groups better, and they only
partially ionize.

For a monoprotic   acid (one that contains only one ionizable hydrogen), such as
acetic acid, Arrhenius's theory of ionization states that the dissociation ratio can be
described as

$$HAc \rightleftharpoons H^+ + Ac^-$$

$$\frac{[H^+][Ac^-]}{[HAc]} = K_a = 1.75 \times 10^{-5} \qquad \text{at } 25°C$$

where Ac^- is used to denote the acetate ion (CH_3COO^-), $[H^+]$ is the concentration of
dissociated hydrogen ions in moles, $[Ac^-]$ is the moles of dissociated acetate ions, and
$[HAc]$ is the amount of undissociated acetic acid at equilibrium. The larger the value
of K_a, the *dissociation constant,* the greater is the ionization and the stronger is the
acid. Diprotic acids act in a similar fashion but have two dissociation constants, one for
each ionizing hydrogen atom.

Water acts as a weak monoprotic acid. Its dissociation can be depicted as

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\frac{[H^+][OH^-]}{[H_2O]} = K_a$$
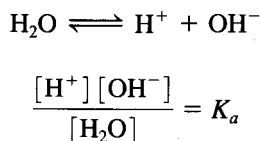
The dissociation of water is very small, so the term $[H_2O]$ changes almost infinites-
mally with repect to the ions. Consequently, it is usually considered a constant and the
expression is rewritten as

TABLE 2.6
Factors affecting solubility of organic compounds

As molecular size increases, solubiliIy decreases

As molecule polarity increases, solubility increases

As the number of double or triple bonds increases, solubility decreases

The order of decreasing solubility is Aliphatic> Aromatic> Cycloaliphatic

As branching increases, solubility decreases

As halogenation increases, solubility decreases

As temperature increases, solubility increases

Polar substituents such as carboxyl, amine, alcohol, and nitrite increase the solubility of the base compound

Acid/base salts are more soluble than the undissociated species

TABLE 2.7
Water solubility of selected normal aliphatics of the same class

Compound	Molecular weight	Water solubility, mg/L
Butane	58.12	61.0
Pentane	72.15	39.6
Hexane	86.1 8	10.9
Heptane	100.20	2.0
Octane	114.23	1.46
Nonane	128.26	0.122
Decane	142.29	0.021
Dodecane	170.34	0.005

ADSORPTIVE EFFECTS. Sorptive properties of a material are very important in describing the fate of the material in the environment. *Sorption* can be defined as the transfer of a material from one phase to another. Sorption can be divided into two categories: absorption and adsorption. *Absorption* involves the movement of one material into another, for example the dissolution of oxygen into water. *Adsorption* involves the condensation and attachment of one material onto the surface of another material, for example, the accumulation of a toxicant on the surface of an activated carbon particle. Here we concentrate on adsorptive properties.

Sorption is an equilibrium process in which compounds partition between the liquid (or in some cases gaseous) phase and a solid surface, based on their affinity for the two phases. It is an equilibrium process, so some of the material will be found in each phase. The stronger the affinity for the solid, the less will remain in solution. Sorption occurs when the net sorbent-solute attraction overcomes the solute-solvent attraction. (Note that the solute is the contaminant being sorbed, the sorbent is the solid surface doing the sorbing, and the solvent is the water.)

There are three general types of adsorption: physical, chemical, and electrostatic. Physical adsorption is due to the weak forces of attraction between molecules, or van der Waals' forces. This type of adsorption is fairly weak and is easily reversible if the contaminant concentration in the liquid phase decreases. It is usually the dominant mechanism for sorption of organics to solid surfaces. Chemical adsorption involves much stronger forces, resulting from bonding interactions between the organic compound and constituents on the solid surface. These bonds are relatively irreversible. Electrostatic adsorption is caused by electrical attraction between the adsorbate and the surface. It is of particular importance for ionic materials such as metals and their salts. Materials of opposite charge are attracted to one another. The greater the charge on the ion, the greater the attraction. For example, AP^+ will be attracted to a negatively charged surface much more strongly than will be Na^+. For ions of equal charge, smaller ions will be bound more tightly than larger ones because of their higher charge-to-mass ratio.

Partitioning of a material between two phases contributes, to a large degree, to the ultimate fate of the material. A contaminant in aqueous solution that is discharged into a river will be partitioned between the water phase and any solid material present (suspended solids, bottom sediments, fish, etc.), and its future movement will be dictated by movement of the solid rather than that of the water. The same holds true for contaminants discharged onto land, where the contaminant will partition between the groundwater and the soil. The movement of a material that has a strong tendency to sorb to solids may be significantly impeded by its attachment to the solid surface. In addition, adsorptive forces may seriously alter its rate of volatilization or transformation in the environment. Generally, sorbed materials are less available for volatilization, biodegradation, or photochemical attack than are dissolved species. Sorption effects can also be used to remove a toxic material from water. Many organics have a stronger affinity for the surfaces of activated carbon than they do for the water phase that they are in. By bringing the water into contact with activated carbon, the toxic organic will transfer from the water phase onto the surface of the activated carpon, leaving a relatively contaminant-free water.

The tendency for a material to sorb to a surface is dependent on the characteristics of the solid surface, the hydrophobicity of the solid and the sorbent, and the charge on the solid and the sorbent. Since adsorption is a surface phenomenon, the rate and extent of adsorption are related to the surface area of the solid involved. Smaller particles, such as clays, will have a greater tendency to sorb organics than sand particles because of clay's greater specific surface area (particle surface area/particle volume). Activated carbon is particularly suited for adsorption because of its enormous specific surface area, ranging from about 600 to 1200 m^2/g (see Table 2.8). The more hydrophobic (nonpolar) the sorbate is, the less likely it will be to remain in the polar aqueous phase. Therefore, unsubstituted alkanes will have a greater tendency to be attracted to a hydrophobic solid surface than will their alcohol analogues. The hydrophobicity of the sorbent is also important. The higher the organic content of a soil, for example, the greater is the tendency for adsorption of aqueous phase organics to occur. Finally, as described previously, charged ions, such as metals, may be removed by sorptive processes if the solid surface contains oppositely charged locations.

TABLE 2.8
Properties of selected adsorbents

Material	Particle diameter, mm	Particle density, g/cm³	Specific surface area, m²/g
Watco 517 (12 X 30)	1.2	0.42	1050
Darco	1.05	0.67	600--650
Calgon Filtrasorb 300 (8 X 30)	1.5-1.7	1.3-1.4	950-1050
Westvaco Nuchar W-L (8 X 30)	1.5-1.7	1.4	1000
Calgon RB (powdered activated carbon)	0.008	1.4	1100-1300

A number of empirical mathematical expressions have been developed to describe sorption equilibrium concentrations. The resulting plots, called *isotherms*, show the relationship between the amount of a compound that will sorb onto a surface relative to the aqueous concentration (or gaseous concentration for gas-solid sorption) at equilibrium. Several sorption models are in common use, including the *Langmuir isotherm* (assumes the surface is homogeneous and the adsorbed layer is only one molecule thick) and the *Freundlich isotherm* (assumes a heterogeneous surface with different types of adsorption sites). Each has its own governing assumptions and each produces a differently shaped plot. The appropriate one to use is usually decided through analysis of experimental data using each model, selecting the one that provides the best fit. The equations for the two models are:

Langmuir:
$$C_s = \frac{x}{m} = \frac{abC_e}{1 + bC_e}$$

Freundlich:
$$C_s = \frac{x}{m} = K_F \cdot C_e^{1/n}$$

where
C_s = amount of contaminant sorbed on the solid per unit of solid (g sorbate/g sorbent)
C_e = concentration of contaminant remaining in solution at equilibrium (g/cm³)
x = mass of contaminant adsorbed (g)
m = mass of solid sorbent (g)
a, n = empirical coefficients
b = saturation coefficient (m³/g)
K_F = Freundlich isotherm constant (mg/g)

It should be stressed that these models are all equilibrium models, and the values of C_s and C_e are the concentrations achieved only after equilibrium is reached. This may be a slow process, and equilibrium may never be reached in a natural system.