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Long-Term Problems of Land Contaminated by Nonradioactive Hazardous Chemicals: Sources, Impacts, and Countermeasures

C. F. Baes III
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ENVIRONMENTAL SCIENCES DIVISION

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C. F. Baes III
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Environmental Sciences Division
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This report examines the environmental behavior and fate of nonradioactive hazardous chemicals, methods for assessing environmental impacts, and alternatives for achieving land decontamination and cleanup. Nonradioactive hazardous chemicals can be reactive, corrosive, or toxic. Reactive chemicals may be explosive, flammable, or capable of undergoing spontaneous change upon exposure to air, water, or a mixture of other chemicals. Toxic chemicals have a high probability of being carcinogenic, mutagenic, teratogenic, or lethal to humans and wildlife. The major pathways of entry into the environment are accidents in handling and storage, industrial accidents, illegal or accidental dumping, leaching from buried toxic wastes, land-treatment of waste waters, herbicide and pesticide use, and use of industrial products. (continued)

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The factors that affect the persistence and fate of hazardous chemicals in soil or sediment are chemical structure and chemical properties, particularly water solubility and volatility; soil or sediment properties, particularly percent organic matter; climate; soil microorganisms; and form of application. Soil organic matter is the most important soil property affecting availability of organic chemicals for plant uptake. Polar and water soluble organic chemicals have the greatest likelihood of being bioaccumulated by plants. Bioaccumulation of an organic chemical in animals is related to its tendency to dissolve in body fat. This property is commonly measured by the n-octanol:water partition coefficient (K_{OW}).

Three types of simple models are currently in use for assessing ecotoxicological hazard of hazardous chemicals. The benchmark approach uses a chemical for which considerable environmental data exists to represent a general class of chemicals. It is of limited use because toxicity, persistence, solubility, and bioaccumulation data are highly variable and chemicals can ararely be placed into discrete groups. Quantitative Structure Activity Relationship (QSAR) models are based on correlation between empirical measures of toxicity or bioaccumulation and simply measured or calculated physicochemical parameters. High uncertainty associated with octanol-water partitioning or water solubility data and orders of magnitude variability about predictions based on regression equations are shortcomings to QSAR models. Screening models use a minimum set of several simple chemical properties to assess whether chemicals are of concern. Chemicals that have log K_{OW} greater than 3.5, persistence half-time greater then 14 d, and log Henry's Law constant, H_C, less than -2.86 are of significant environmental concern.

Cleanup of hazardous contaminants on land may involve dispersal, removal and storage, stabilization, or treatment. Both dispersal and removal/storage alleviate acute, local, immediate threats, but additional remedial action may eventually be necessary. Stabilization and treatment are more permanent solutions. Stabilization involves methods to isolate the contaminant or limit its dispersal. Treatment involves biological, chemical, and physical approaches to detoxify or destroy the hazardous chemicals.

Costs of cleanup will depend upon the composition and quantity of contamination and the geographic location, extent, and accessibility of the contaminated area. Costs include personnel, equipment and fuel, maintenance and repair, land rental or purchase, depreciation/amortization, materials, administration/overhead, tools, utilities, insurance, and economic loss of the land. Cleanup by dispersal or removal and storage is cheaper than cleanup by chemical and physical treatment processes.

PREFACE

This report is the second product of a project entitled "Residual Ecological Problems of Contaminated Land Areas." The project was supported by the Federal Emergency Management Agency (FEMA) under contract FEMA EMW-84-E-1737 with the Department of Energy (DOE 40-1457-84).

The work is intended as a state-of-the-art assessment of research in the subject area. Under no circumstances is this work intended as an original analysis of the subject area, but a review and synthesis of existing materials. The first report generated under this project title, "The Long-Term Problems of Contaminated Land: Sources, Impacts and Countermeasures" (ORNL-6146), primarily addressed land contamination with radionuclides. The scope of the present work includes ecological problems of land areas contaminated with hazardous chemicals, exclusive of radionuclides.

The authors express their appreciation to Rita Oran and Cheryl Phillips of the Environmental Sciences Division of Oak Ridge National Laboratory for their help in assembling this document. Also, we wish to recognize Nancy Merrick for her invaluable assistance in obtaining reference materials.

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EXECUTIVE SUMMARY

The annual production of nonradioactive hazardous wastes in the United States exceeds 67 million metric tons. Hazardous chemicals are toxic, reactive, or corrosive. Toxic means carcinogenic, mutagenic, teratogenic, or lethal. Reactive means explosive, flammable, or capable of spontaneous reaction. Corrosive means strongly acidic or basic.

Sources of contamination include transportation accidents or spills, waste treatment and industrial discharges, industrial accidents, runoff from agricultural lands, leaking dump sites, and illegal dumping. This report reviews sources, impacts, and countermeasures for hazardous chemical contamination of land and water, with particular attention to pesticides, polynuclear aromatics, halogenated hydrocarbons, acid esters, and toxic metals. The following are examined in detail:

* Hexachlorobenzene is an industrial waste that is highly toxic to humans, produces pathological conditions in animals, is volatile, and accumulates in sediments and animal fat.
* Polychlorinated biphenyls, which are industrial chemicals widely used for heat transfer fluids and dielectric fluids, have low acute toxicity, but they contain highly toxic impurities and are environmentally persistent.
* Polychlorinated dioxins and furans are toxic impurities in the production of chlorophenols and herbicides, highly chlorinated, persistent in soil, nonpolar, and devoid of biologically labile functional groups.

* Chlorinated hydrocarbon pesticides are ubiquitous in the environment because of their widespread use in the past. They are extremely persistent and bioaccumulate through food chains.
* Polybrominated biphenyls are fire retardants, extremely persistent in soils and sediment, water insoluble, and lipophilic. They do not bioaccumulate to the same extent as PCBs in animal fat, but appear to have a great affinity for avian fat.
* Polycyclic aromatic hydrocarbons, which are generated by combustion, are very environmentally stable and show carcinogenic and mutagenic properties. Although poorly taken up by plant roots, they readily penetrate into plants and dissolve into plant oils from surface applications.
* Phthalic acid esters, which are insoluble, lipophilic, colorless liquids commonly used in plastics, are of low acute toxicity, but they appear to be teratogenic and mutagenic and reduce reproduction rates in aquatic insects and fish.
* Arsenic, which is found near smelters or on agricultural lands treated with lead arsenate insecticides, is extremely toxic to plants and animals in the trivalent arsenite forms and may be carcinogenic.
* Cadmium, which is found near lead and copper mines, refineries, and smelters, is toxic to all body systems and functions of mammals, accumulates in the liver and kidney, and has been associated with arterial hypertension, renal tubular dysfunction and softening of the bones ("itai-itai" disease), teratogenic effects, and cancer.

* Chromium, which is used in steel alloys and in cement, is essential for sugar and fat metabolism. Chromium is irritating, corrosive, very toxic to plants and animals in the hexavalent forms, and is carcinogenic.
* Copper, which is found around mines, refineries, and smelters, is essential to plants and animals, but severely toxic to plants and moderately toxic to sheep in high concentrations.
* Mercury, which has many medical, agricultural, and industrial uses, can accumulate in the liver; in the brain, where it interferes with mental functions and coordination; in the intestinal lining; and in the kidneys, where it damages the tubules that readsorb salts and sugars from urine.
* Manganese, which is used in fertilizers, steel alloys, and manufacturing, is essential for plants and animals. It can cause pneumonia, nasal congestion, nose bleeds, and severe psychiatric and neurologic disorders in exposed humans, and it can produce toxicity in plants under low soil pH conditions.
* Nickel, which is used in the production of steel alloys, is severely toxic to plants and is irritating or toxic and carcinogenic to animals.
* Lead, which is used in paint, fungicides, and gasoline, is immobile in soils and the food chain. In animals it accumulates in bone, teeth, and nerve tissue by replacing calcium. Lead poisoning gives rise to blood disorders, anemia, nervous disorders, kidney and heart problems, brain damage, and blindness.

* Selenium, which is a by-product of refining copper, lead, nickel, gold, and silver ores, is essential to some plants and all vertebrates. Selenium toxicity resembles that of arsenic, and it adversely affects the kidneys, liver, and spleen.
* Zinc, which is used in die-cast alloys and galvanized iron and steel, is essential in both plants and animals. It is relatively nontoxic to animals, especially mammals, but can produce chills, high fever, depression, nausea, vomiting, head and muscle aches, intestinal disorders, vomiting, diarrhea, and bowel disorders.

The potential risk of toxic substances is a function of concentration, environmental persistence, or environmental half-time ($T_{1/2}$), inherent toxicity, and food-chain bioaccumulation potential. Persistence is dependent on chemical structure and properties including water solubility, affinity for lipids, molecular charge, and volatility. Soil and sediment properties (e.g., pH, percent organic matter, and clay content), temperature, and moisture also affect persistence. Temperature and moisture affect the rate of biological degradation, which involves dehalogenation, oxidation, reduction, hydrolysis, and ring cleavage. Positively charged organics are usually very persistent because of their adsorption to the negative surface charges of clays and organic matter. Organics with net negative charge are not strongly adsorbed by soil and are readily leached to groundwater.

Organics most likely to be accumulated by plants are polar and water soluble. Nonpolar molecules tend to sorb onto the root surface without passing into the plant. However, organics can move directly from the surface soil to aboveground plant parts through volatilization.

Bioaccumulation of organics in animals is a function of dietary, behavioral, and physiological factors, but it is related to a chemical's tendency to dissolve in body fat. This lipophilic property is measured by the n-octanol:water partitioning coefficient, K_{ow}. Bioaccumulation factors for organics in fat are negatively correlated with water solubility and positively correlated with K_{ow}. Because of their diet, predators are at greatest risk of bioaccumulating lipophilic organics. However, grazing herbivores may bioaccumulate toxic organics through ingestion of soil. Also, small animal species tolerate less of a toxic compound than larger species.

Computer models are used to assess the environmental impact of hazardous chemicals because of the cost of conducting site-specific field investigations and toxicological studies. Data needs for these models include measurements of photodegradation, oxidation, hydrolysis, biodegradation, sorption to soil and sediment, volatility, bioaccumulation, and elimination from biota. Since these data are usually unavailable, three approaches, based on minimum data requirements, are taken. These three modeling approaches are the (1) "benchmark," (2) quantitative structure-activity relationship (QSAR), and (3) sreening-level approaches.

In benchmark models, chemicals for which environmental behavior and fate data already exist are used to assess a class of chemicals, and comparison with the benchmark is done to predict the environmental fate on the basis of the reference chemical. This approach is limited because chemicals can rarely be placed in discrete groups and chemical properties are often as highly variable within as among groups.

QSAR models are based on correlation between empirical measurements of biological activity and measured physicochemical parameters, particularly water solubility and K_{ow}. However, these two parameters are difficult to precisely measure and are associated with order-of-magnitude variability. These two shortcomings have been addressed through the use of molecular connectivity indices, which are calculated from the number and types of atoms and chemical bonds in a molecule. Since they are calculated, the uncertainties associated with empirical measurements are eliminated. Furthermore, connectivity indices are highly correlated with soil sorption for nonionic organics and with bioaccumulation of organics in fish.

Screening-level models classify chemicals as either nonhazardous or potentially hazardous and do not require precise or accurate data. The danger in their use is in wrongly classifying a chemical as not bioaccumulating or toxic. Nevertheless, the following predictions are made with a screening-level model based on $T_{1/2}$, K_{ow}, and Henry's law constant (H_c):

* <u>Chemicals that persist and bioaccumulate in animal fat</u>

$$\log K_{ow} > 3.5,$$

$$T_{1/2} > 14 \text{ d, and}$$

$$\log H_c < -2.86.$$

* <u>Chemicals that are mobile in soil and taken up by plants</u>

$$\log K_{ow} < 3.5 \text{ and}$$

$$\log H_c < -2.86.$$

* <u>Chemicals of low ecotoxicological concern</u>

$$\log K_{ow} > 7 \text{ and}$$

$$T_{1/2} < 0.1 \text{ d or}$$

$$\log H_c > 2.$$

These predictions do not apply to organometallic, highly ionized, gaseous, polymeric, and/or covalently reacting chemicals.

Cleanup of contaminated land and waters may include dispersal, removal and storage, stabilization and containment, or treatment. Dispersal may alleviate a local contamination, but exacerbate a regional or global problem. Removal and storage shifts the problem from one geographic location to another and from an immediate time frame to a future time frame. In situ stabilization or containment is a more permanent solution and involves engineering methods to alter local hydrology or isolate and control contaminant dispersal by wind and water. Treatment involves biological, chemical, or physical detoxification or destruction of the chemical. Surface waters are more amenable to treatment than groundwaters because they are more accessible and their flow rate and direction are known. Cleanup of groundwater contamination is complex and uncertain because the hydrogeologic environment is not easily observed and varies both spatially and temporally.

Dispersal of soluble substances with water and neutralizing agents is inexpensive and easily implemented. Acids are most often neutralized with sodium hydroxide (NaOH), lime (CaO), periclase (MgO), and magnesite ($MgCO_3$). Bases are most often neutralized with hydrochloric acid (HCl) and sulfuric acid (H_2SO_4).

For contaminants not amenable to dispersal, the most common form of handling is storage in landfills. Landfills utilize the absorptive capacity of soil to isolate waste and provide storage to prevent direct contact with humans and the environment. In terrestrial environments,

collection of the contaminant is by sweeping, scraping, grubbing, or bulldozing. In aquatic environments, collection is by pumping; dredging; containment and skimming; precipitation, coagulation, or ion-exchange on gels; and filtration.

In situ stabilization of contaminated land may be the only practical alternative when the area involved is large and when alternative methods of cleanup or decontamination are too costly. Stabilization prevents transport to subsurface areas and groundwater through control of wind and water, which are the primary mechanisms of contaminant dispersal. Control may include surface water runoff and infiltration control through the use of drainage canals, culverts, dikes, subsurface drains, impermeable barriers, capping or surface sealing, and stabilization with vegetation or fine-grained soil cover.

In situ biological degradation of organics and fixation of toxic metals occur naturally, but they can be optimized by aerating the soil (through plowing or disking and adding crushed lime or wood chips to provide additional porosity), by maintaining moisture levels between 63 and 79% (by adding mulch, straw, or manure), and by adding fertilizer. Soil pH should be neutral-to-alkaline so that toxic metals do not inhibit microbial activity.

Physical and chemical treatments of contaminated land detoxify, deactivate, or destroy the contaminant via photolysis, oxidation, reduction, dechlorination, and hydrolysis. These processes are impractical in the field and require construction of special facilities at high initial cost. However, costs may be recovered if treatment by-products can be recycled or sold. Briefly, treatment processes are described below:

* Photolysis breaks chemical bonds by light energy. Effectiveness is dependent on the compound structure, light wavelength and energy, and the medium in which the reaction occurs.
* Wet oxidation occurs in aerated solution under high temperatures and pressures, often with a catalyst such as the Cu^{2+} ion. Ozonation destroys carbon-carbon bonds and aromatic rings. 2,3,7,8-TCDD dioxin can be destroyed with an efficiency of 97%. Molten salt oxidation occurs below the surface of sodium carbonate (Na_2CO_3) or sodium sulfate (Na_2SO_4) at temperatures between 800 and 1000°C. This process destroys DDT, Malathion, chlordane, and mustard gas with efficiencies as high as 99.9%. Microwave plasma oxidation breaks carbon-carbon bonds, with destruction efficiencies of greater than 99% for Malathion, PCBs, phenylmercuric acetate, and Kepone. In all oxidation treatments, primary end products are carbon dioxide and water.
* Reduction via metal powders degrades PCBs, chlordane, Kepone, atrazine, and N-nitrosodimethylamine. Under acidic conditions, formaldehyde reduces chromium VI to chromium III.
* Dechlorination reduces the toxicity of chlorinated hydrocarbons by replacement of chlorine atoms with hydrogen atoms at high temperatures and pressures. Molten sodium metal and polyethylene glycol in oxygen dechlorinates PCBs, DDT, Kepone, and pentachlorophenol.

* Alkaline hydrolysis has been used to degrade Malathion, parathion, methyl parathion, DDVP, and carbaryl.
* Incineration utilizes combustion to compact, detoxify, and destroy noxious organic materials. The products of incineration are carbon dioxide; water vapor; and ash and sulfur-, nitrogen-, and halogen-containing products, which may require secondary treatment via afterburners, scrubbers, filters, handling, and storage.

ABSTRACT

BAES, C. F., III, C. T. Garten, Jr., and V. R. Tolbert. 1987. Long-term problems of land contaminated by nonradioactive hazardous chemicals: sources, impacts, and countermeasures. ORNL-6239. Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee. 200 pp.

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in body fat. This property is commonly measured by the n-octanol:water partition coefficient (K_{ow}).

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1. INTRODUCTION AND SCOPE

This report deals with the potential long-term ecological problems of land and water contaminated by nonradioactive hazardous chemicals. A previous report (Baes et al. 1986) examined various problems and countermeasures associated with alternatives for land use following contamination by radioactive materials. That report identified several needs with respect to information on the long-term ecological problems of nonradioactive hazardous chemicals. This report elaborates on the needs identified in the previous report and provides a compilation of additional information for assessment of transport and fate of nonradioactive hazardous chemicals. The report is written primarily for the nonspecialist; therefore, many simplifications and generalizations have been made.

There exists an immense potential problem with the contamination of lands and water supplies by nonradioactive hazardous chemicals. For example, in 1985, the annual production of nonradioactive hazardous wastes by manufacturing industries in the United States exceeded 67 million metric tons (Tucker and Carson 1985). This volume of production creates more than 280 kg of hazardous chemical waste per U.S. citizen. Sources of chemical releases to the environment include industry effluents, pesticide use, buried toxic wastes, and illegal or accidental dumping.

In this report, we will review several well-known incidents involving chemical contamination of the environment leading to poisoning of wildlife, livestock, and people, or restrictions on land as examples

of the ways that lands become contaminated. We will also examine the behavior and potential ecological impacts of residual hazardous wastes in the environment and present possible countermeasures and associated costs for the reclamation of contaminated resources. Finally, we will briefly examine models used to assess health risks from hazardous chemicals.

1.1 DEFINITION OF HAZARDOUS CHEMICALS

Hazardous wastes can be generally classified as toxic, reactive, corrosive, and/or radioactive chemicals (Tucker and Carson 1985). Toxic hazardous wastes are those chemicals that have a high probability of being carcinogenic, mutagenic, teratogenic, or lethal. High-level radioactive wastes are a classic example. Toxic hazardous wastes, by virtue of their physicochemical effects on biological systems, are a threat to humans and wildlife. Reactive hazardous wastes may be explosive or flammable or be capable of undergoing spontaneous chemical change upon exposure to air, water, or a mixture of other chemicals. Reactive wastes may also form toxic products if mixed with other chemical wastes. Corrosive wastes are strongly acid (pH < 2) or strongly basic (pH > 12).

Many of the hazardous wastes of current environmental concern are organic chemicals. Unterberg et al. (1981) have presented a classification scheme for the long-term environmental hazard of organic compounds that includes the following groups:

* pesticides,
* nitrosoamines,
* polynuclear aromatics,
* halogenated hydrocarbons,
* aromatic phenols,
* amines,
* nitroles,
* aromatics, and
* hydrocarbons (acids and esters).

Environmental hazard from these groups of chemicals arises from their known or suspected carcinogenic properties, their potential for bioaccumulation in food chains, or their persistence in soils and water. In this report, we will discuss the environmental fate that can be expected for various classes of organic and selected inorganic pollutants on the basis of their persistence in and interaction with soil and water.

1.2 SIGNIFICANCE OF PERSISTENCE

Although the persistence of a chemical in soil or water may be variable and difficult to quantify, some measure of environmental persistence is needed to assess potential environmental hazard. Environmental persistence can be defined in several ways. Environmental half-time ($T_{1/2}$), or the time required for 50% of an initial amount of chemical to disappear, is frequently used to characterize the persistence of substances in soil and water. Persistence may also be

defined as the $T_{95/100}$, or time required for 95% of an initial amount of chemical to disappear (this is equivalent to roughly four times $T_{1/2}$).

Disappearance rates of chemicals from soil and water will frequently depart from the assumptions implicit in the first-order calculation of $T_{1/2}$. For example, the rate of disappearance of organic contaminants from soil may proceed rapidly in the first few days following contamination because of application losses and volatilization, and then proceed more slowly weeks following contamination because of leaching and biodegradation of material in the subsoil (Fig. 1.1). Such a disappearance pattern is inadequately described by a single parameter. Despite this, $T_{1/2}$ is still a generally useful index to environmental persistence, particularly if it is calculated separately for the multiple components that contribute to disappearance from soil or water.

The scope of this review is limited to chemicals with an environmental persistence (as defined by the time to 95% disappearance) of greater than one year. Short-lived toxic chemicals may still pose hazards to wildlife or people if present in the environment at sufficiently high concentrations. However, the problems associated with resource use or cleanup and residual long-term ecological effects are more serious for environmentally persistent hazardous wastes than for chemicals that may be completely degraded over several weeks or months by biological or physicochemical processes.

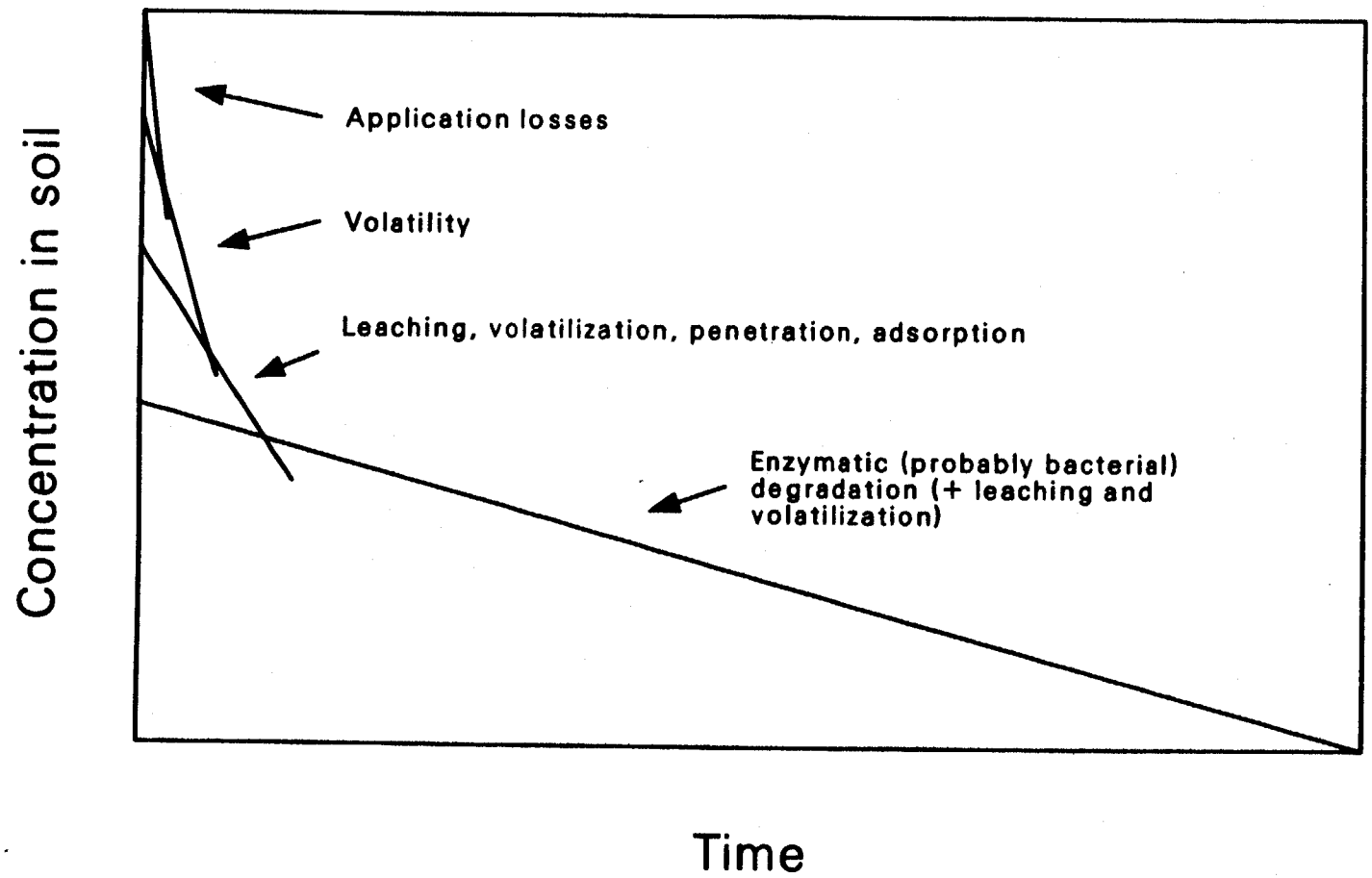

Figure 1.1. Disappearance of a chemical from soil due to application, volatilization, leaching, and biological degradation losses. Source: Edwards, C. A. 1966. "Insecticide residues in soil," Residue Rev. 13:83-132.

1.3 BACKGROUND ON ENTRY OF HAZARDOUS CHEMICALS INTO THE ENVIRONMENT

Hazardous wastes can be single chemicals or complex mixtures. Typically, in environmental studies, hazardous wastes are complex mixtures of chemicals, each with varying degrees of persistence and toxicity. The data required for hazard assessments are often highly variable for individual chemicals, and this fact makes it difficult to place chemicals into discrete groups, based on chemical structure or on physicochemical properties, for risk assessment purposes (Daniels et al. 1985). Production, release rates, volatility, solubility, soil sorption, bioconcentration potential, persistence, and ecotoxicity will all vary from chemical to chemical.

This situation complicates a generalized approach to the evaluation of long-term ecological problems associated with hazardous waste. There are some general observations about the behavior of chemical classes (mostly based on many years of experience with pesticides) that can be stated, but the lack of similarities among specific chemicals with respect to quantitative data limits these statements to qualitative generalities. Nonetheless, this qualitative information coupled with a few quantitative measurements can be sufficient for a preliminary assessment of ecotoxicologic hazard.

As will be evident from the examples that follow, circumstances surrounding the release of hazardous chemical wastes to the environment are as varied as the uses of the chemicals themselves. Nonetheless, there are several general categories of releases, as illustrated by the following examples:

1. Accidents in storage and handling: In the fall of 1973, a mixture of polybrominated biphenyls (PBBs), a fire retardant, was accidentally substituted for magnesium oxide in dairy feed in Michigan. The result was that thousands of animals had to be destroyed because of excessive residues in their body fat (Carter 1976). Michigan residents, mostly farm families, were exposed to PBBs in their diets during the several months that the contamination went unrecognized.
2. Industrial accidents: In July 1976, an accident at a chemical plant near Seveso, Italy, contaminated a large inhabited area with several chemicals including a highly toxic impurity 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD). The accident resulted in the deaths of thousands of small domestic animals, health problems in residents, and the evacuation of homes within the most highly contaminated areas (Bisanti et al. 1980).
3. Illegal or accidental disposal or dumping: More than 12 years ago, as many as 100 sites in the State of Missouri were contaminated with dioxin (TCDD) contained in waste oil that was sprayed on unpaved roads and in dirt arenas to control dust (Sun 1983). As a result of the spraying, some people became ill and hundreds of animals became sick and died.
4. Hazardous waste dumps and landfills: Landfills have long been a major disposal method for wastes from municipalities and industries. In some cases, such as Love Canal in New York, organic chemicals have been found in surface waters and sediments adjacent to former hazardous waste dumps (Elder et al. 1981) and in groundwater leachate plumes beneath landfills (Reinhard et al. 1984).

5. Land use of waste water and sludge: Land treatment of waste water and sludge to remove contaminants by filtration through soil is an emerging technology that performs with promise in removing biodegradable organics, suspended solids, nitrogen, phosphorus, pathogenic organisms, and trace organics. However, the accumulation in soil of persistent pollutants (e.g., heavy metals) as well as their long-term phytotoxicity and potential food-chain transfer remains to be evaluated through future research (Crites 1984).

6. Agricultural uses: In 1981, approximately 500,000 metric tons of pesticides were used in the United States and roughly half of the total amount used was herbicides (Hileman 1982). Under some circumstances, pesticide runoff into streams and rivers, infiltration into groundwaters, and disposal of unused chemicals or chemical containers can present a significant environmental problem. An example of this is the occurrence of aldicarb in potable groundwater from areas with high rates of aldicarb application, high rainfall, and strongly acid, sandy soils (Back et al. 1984).

7. Industrial products: Two examples of environmental contamination by commonly used industrial products are phthalic acid esters (PAEs) and polychlorinated biphenyls (PCBs). PAEs are lipophilic ("fat loving"), medium viscosity, colorless liquids used as plasticizers, as pesticide carriers, in insect repellants, and in dyes, cosmetics, and lubricants. The estimated production of PAEs in the United States during 1973 was 450,000 metric tons.

Phthalates, most notably di-2-ethylhexyl phthalate (DEHP), are now ubiquitous in the environment and are potential teratogens and mutagens (Mathur 1974). Toxic PCBs, which have a variety of commerical uses that include electrical insulating fluids, heat transfer fluids, protective coatings, plastics, and rubber are also widely distributed in the environment (Risebrough et al. 1968).

2. ENVIRONMENTAL BEHAVIOR OF NONRADIOACTIVE HAZARDOUS CHEMICALS

2.1 FACTORS AFFECTING PERSISTENCE

A considerable amount of general knowledge on the environmental behavior of organic hazardous wastes can be inferred from many years of experimental research on pesticides. The majority of pesticides are no more than organic chemicals with toxicologic properties toward pest organisms. Their widespread production and agricultural use creates the potential for environmental problems centered around fate of field applications as well as disposal of unused chemicals and chemical containers.

The various factors that affect the persistence and fate of pesticides and other organic chemicals in soil can be broadly classified and ranked in order of importance as follows (Lambert et al. 1965; Edwards 1966):

1. chemical structure and chemical properties (e.g., water solubility and volatility),
2. soil properties (e.g., percent organic matter),
3. climate,
4. soil microorganisms, and
5. form of application.

The importance of chemical structure and chemical properties, such as molecular charge and water solubility, will be discussed in Sections 2.2.1, 2.2.2, and 2.2.3. Soil properties, such as percent

moisture and soil temperature, are important secondary determinants of biological activity and microbial degradation of foreign compounds.

Placement in soil is considered a dominant factor affecting the persistence of volatile organic chemicals because soil overlying organic contaminants will retard losses by volatilization. Organic chemicals released onto the surface of the ground may exhibit a rapid disappearance from soil because of initial volatilization, followed by a more prolonged persistence time as the chemical penetrates into subsoil layers. Soil temperature and, therefore, climatic conditions will be important determinants of the rate of volatilization as well as the rate of biological activity resulting in degradation. Granular forms of pesticides typically persist longer in soil than liquid forms (Matsumura 1975).

Organic matter is an important absorbant for many foreign organic chemicals in soil. Un-ionized, nonpolar, and lipophilic compounds can be adsorbed to varying degrees by soil organic matter (Weber 1972). Herbicide phytotoxicity decreases and retention of foreign compounds in the soil increases with increasing soil organic matter (Upchurch 1966; Weber 1972; Edwards 1966). Approximately 10-15% of the soil organic matter is made up of decomposing plant and animal components and bacterial products, while 85-90% of the soil organic matter is composed of humic material (Weber and Weed 1974). Humic materials are large macromolecules of plant and microbial origin. They are chemically reactive materials with multiple adsorption sites, and they are rather strong reducing agents (Stevenson 1972).

2.2 EXPERIENCE WITH PESTICIDES

It is well recognized from experience with pesticides, that chemical structure is an extremely important determinant of water solubility, environmental stability, volatility, and soil adsorption of organic chemicals. Therefore, chemical structure has an important effect on all aspects of the environmental fate and behavior of hazardous organic chemicals. There are some general trends for the soil persistence of different categories of organic pesticides, loosely based on chemical structure, which are discussed in the following sections.

2.2.1 Pesticides with Long-Term Persistence

Organochlorine compounds (or chlorinated hydrocarbons in general) are among the most persistent of all chemicals in soil. The time required for 75-100% disappearance of chlorinated hydrocarbons from soil is typically measured in years or decades, depending upon the compound (Kearney et al. 1969; White 1979). Organochlorines are typically un-ionized, nonpolar compounds that are weakly adsorbed by soil organic matter, but poorly leached from soils because of their low water solubilities (White 1979).

Positively charged (cationic) organic chemicals can also be very persistent in soils because of their strong adsorption to soil clays. The bipyridyl herbicides, diquat and paraquat, are slightly soluble, positively charged compounds that are biologically inert after adsorption onto soil clay (White 1979). After adsorption, paraquat is more easily degraded upon exposure to sunlight.

Electrical charge on a compound is one of the most important properties influencing the adsorption and deactivation of organic chemicals in soil (Adams 1973). A chemical must be in an un-ionized form for significant rates of volatilization to occur. In the normal range of soil acidity (pH 5 to 7), organic chemicals with a net negative charge (anionic) will not be strongly adsorbed by soil because of a negative surface charge on clays and organic matter (Upchurch 1966). Anionic compounds are, therefore, usually more available for leaching to groundwater. Positively charged (cationic) compounds may be strongly adsorbed to both soil clay and organic matter (Stevenson 1972; Weber 1972), reducing both their availability for downward leaching and their biological activity.

2.2.2 Pesticides with Intermediate Persistence

Triazine and phenylurea compounds have soil persistence times that are typically measured in months [maximum persistence of approximately 18 months (White 1979)]. The triazine herbicides are weakly basic compounds whose persistence in soil is governed by pH-dependent adsorption reactions. Adsorption of basic organic compounds to clays and organic colloids is greatest in acid soils (Weber and Weed 1974). Such compounds may be easily leached from alkaline soils (Weber 1972). The phenylurea herbicides are nonionic compounds with varied water solubilities that are only weakly adsorbed to soil. As for many other herbicides, deactivation of triazines and phenylureas occurs by soil microorganisms.

Microbial degradation may involve a variety of different chemical reactions, including dehalogenation, oxidation, reduction, hydrolysis, and ring cleavage (Kilgore and Li 1976). Soil microorganisms are capable of degrading several chlorinated hydrocarbon pesticides by dehalogenation or oxidation. Phenoxyalkanoic acids are also degraded microbially by oxidation. Compounds with nitro substituents (e.g., pentachloronitrobenzene) may be microbially degraded to amines, and organophosphates may be microbially degraded by amide or ester hydrolysis. Soil microbes can also cleave aromatic rings (Kilgore and Li 1976).

Since the above reactions are biologically mediated, microbial degradation is slowest in cold, dry soil. Warm and moist soils, which favor microbial activity, usually favor the degradation of organic chemicals. Compound structure and inert carriers are important determinants of the degradation rate. Degradation rates for pure compounds are usually not the same as for commercial formulations (Stojanovic et al. 1972). Soil microorganisms can partially degrade organic chemicals that are analogues of normal substances in the soil, a process termed "co-metabolism." Among the naturally occurring organic substances, sugars, amino acids, most proteins, and some polysaccharides are degraded or metabolized by soil microorganisms in a few days, weeks, or months. However, degradation of other organic compounds like humic substances, lignins, anthraquonines, resins, waxes, and some polysaccharides may require several months or even years (Martin and Page 1978).

Excessive concentrations of hazardous organic chemicals in the soil can alter the composition of microbial populations and favor the survival of one group of microorganisms over another (Stojanovic et al. 1972). Metabolic adaptation, through the induction of specific enzymes needed to metabolize a foreign molecule, may cause an increase in the number of microorganisms in the soil capable of degrading a particular compound. This "enrichment" effect will result in a more rapid degradation of subsequent applications of the chemical to soil (Hiltbold 1974). Inoculation of soils with bacteria capable of degrading organic chemicals can be a potentially useful aid in decontaminating soil (Kearney et al. 1969). It has been reported that mixtures of pesticides are more biodegradable by microorganisms than single compounds if at least one of the compounds present is rapidly biodegraded (Stojanovic et al. 1972).

2.2.3 Pesticides with Short Persistence Times

Carbamate and organophosphate compounds and toluidine and phenoxyalkanoic acid compounds generally do not persist in soils longer than one year (White 1979). Carbamate and organophosphate insecticides, in particular, generally do not persist longer than three months in soil (Kearney et al. 1969). Toluidine herbicides are insoluble, dinitroaniline derivatives that are adsorbed by soil organic matter. Volatilization and microbial degradation are the principal pathways for the disappearance of toluidines from soil (White 1979). Phenoxyalkanoic acids, like the herbicide 2,4-D, are negatively charged compounds in soil and, like anionic compounds, are weakly adsorbed by soil

particulates. Because of their poor soil sorption, acidic herbicides are among the most easily leached of all organic pesticides from soil to groundwater (Pionke and Chesters 1973). Their high leachability from soil is offset by high plant uptake and rapid microbial degradation (White 1979).

2.3 UPTAKE BY PLANTS

Because of its affinity for foreign organic chemicals in the soil, organic matter is the most important single soil property affecting the uptake of nonpolar organic chemicals by plant roots (Nash 1974). Other factors, such as soil acidity or soil texture, become increasingly important determinants as the polarity of the organic compound increases or the percent of soil organic matter decreases. Plant roots are generally not very discriminating toward small organic molecules with a molecular weight less than 500 atomic mass units, except on the basis of polarity. Nonpolar molecules will tend to adsorb to the plant root surface rather than pass through the epidermis into the plant. For this reason, plants do not bioaccumulate very nonpolar organic compounds (such as chlorinated hydrocarbons) beyond levels found in soil (Matsumura 1975). Organic chemicals that have the greatest likelihood of being bioaccumulated by plants are polar and water soluble compounds (Nash 1974; Matsumura 1975). Therefore, although organic matter is the single most important soil property affecting availability for plant uptake, water solubility and polarity are the most important properties of a compound affecting its entry into the plant root.

An organic contaminant can accumulate in plant tissue by means other than root uptake and translocation to aboveground tissues. Volatilization can be an important pathway for the movement of organic chemical compounds directly from the surface soil to aboveground plant parts. Organic compounds with a vapor pressure greater than 1×10^5 mm Hg at 22°C are easily volatilized from soil (Weber and Weed 1974). Foliar absorption of volatile compounds is more important than uptake from soil via plant roots for some chlorinated hydrocarbons (Nash 1974). Surfacial contamination of plant foliage near the ground may also occur by wind or rainfall resuspension of soil particles bearing organic contaminants.

Foliar absorption is a second potential mechanism for the entry of organic contaminants into plant tissues. On foliage, polar, aqueous organic chemicals do not penetrate the waxy, hydrophobic layers of the leaf as easily as nonpolar, lipophilic compounds (Finlayson and MacCarthy 1973). Although semilipophilic and nonpolar compounds penetrate leaves more easily than polar ones (Matsumura 1975; Richardson 1977), environmental variables, such as temperature and humidity, have a measurable effect on the extent of foliar absorption. High temperatures and high humidity tend to increase organic chemical entry into leaves (Richardson 1977). The stage of plant growth is also important to organic chemical uptake via foliar absorption because the leaf cuticle thickens and hardens as the plant matures (Richardson 1977).

The plant itself is also important. Carrots and beets have a recognized affinity for strongly adsorbing insecticides on their root

surfaces (peels). Plants also tend to accumulate lipophilic organic contaminants in oily parts, such as seeds, more than plant parts that have a high water content. Crops with a high fat content may concentrate small amounts of organochlorine and organocarbamate insecticides to approximately one-tenth of the concentration found in soil (Finlayson and MacCarthy 1973; Matsumura 1975).

2.4 FOOD-CHAIN TRANSFER TO ANIMALS AND ANIMAL PRODUCTS

It is well known that predaceous animals are at the greatest risk of bioaccumulating lipophilic organic contaminants through food chains (Stickel 1973). For example, birds that eat other birds or fish tend to have higher residues of chlorinated hydrocarbons in their bodies than birds that eat seeds. Generally, animals that feed primarily on seeds accumulate only small amounts of residues, even in areas of heavy pesticide use (Stickel 1973).

Bioconcentration or bioaccumulation of foreign organic chemicals is compound specific and animal specific (Matsumura 1975). Bioaccumulation of a specific organic chemical is related to its chemical properties, specifically the tendency of the chemical to dissolve in body fat. The lipophilic property of an organic chemical is commonly measured by its partitioning behavior in a two-phase system of n-octanol and water. Kenaga (1980) has shown that bioaccumulation factors in animal fat for various organic chemicals are negatively correlated with water solubility and positively correlated with n-octanol:water partition coefficients (K_{ow}s). In some cases, animals concentrate foreign organic chemicals in direct proportion to dietary intake; therefore,

the concentration ratio (CR) is constant over varying levels of chemical in the diet. However, for other chemicals, such as some chlorinated hydrocarbons, bioaccumulation can vary in inverse proportion to the dietary concentration (Britton and Charles 1974).

Bioconcentration is animal specific because of physiological, behavioral, and dietary differences among species. Given a constant level in the diet, small animal species are at a greater immediate risk from toxic hazardous wastes than larger species because of their higher metabolic rate, and consequently, their greater relative daily food intake. A dairy cow, which typically weighs about 900 kg, eats only 1.5% of its body weight per day, while a small bird or a mouse weighing, 20 to 25 g, may eat 12 to 18% of its body weight per day (Kenaga 1972). The amount of a toxic substance that can be tolerated in the diet is less for smaller animals than for larger animals, given a constant level in the diet. Physiological differences due to gender can also be important to bioaccumulation and metabolism of foreign compounds. For example, male broiler poultry have higher bioaccumulation factors for organochlorine pesticides than female broilers because of a dilution effect from the higher fat content of the females (Kan 1978). Also, egg laying in birds and fish is a contaminant-voiding process and can result in lower bioaccumulation factors in females than in males (Kendall et al. 1978; Guiney et al. 1979).

Ingestion of contaminated soil is another potentially important route for the transfer of organic contaminants to animals. In particular, birds or other animals that feed on soil invertebrates may be affected by this route of exposure (Matsumura 1975). Considering

the low degree of plant uptake for many organic chemicals from soil, direct ingestion of soil by grazing herbivores may be the predominant dietary source of organic chemicals to livestock inhabiting areas contaminated by hazardous wastes. Under poor pasture conditions, soil intake by cattle can account for up to 14% of the dry-matter intake, but a range of 0.5 to 1.2 kg of soil per animal per day (4 to 8% of the dry-matter intake) is more likely (Zach and Mayoh 1984).

Bioaccumulation factors for the transfer of organic chemicals from diet to animal fat have been reviewed recently (Garten and Trabalka 1983). Among the pesticides, organochlorines exhibit the greatest degree of bioaccumulation, and organophosphates or carbamates are bioaccumulated the least in food chains. Bioaccumulation factors for the transfer of several important organic contaminants to milk, eggs, and animal fat will be reviewed in Section 2.6 of this report.

2.5 FOOD-CHAIN TRANSFER IN AQUATIC ENVIRONMENTS

Fish and shellfish are known for their capacity to accumulate organic compounds at thousands of times their concentration in the surrounding water. Toxic compounds may be introduced to the aquatic environment from industrial effluents, pesticide use/runoff, accidental releases or accidental discharge, or from leaking buried toxic wastes. The availability of organic contaminants for transfer along the aquatic food chain is dependent upon a number of both physical and biological factors. Physical factors that could influence the bioconcentration of organic contaminants are those that would affect the residence time of the contaminants in the aquatic systems or that affect the availability of contaminants for uptake.

The flushing rate or the rate of flow through the system will influence the dilution rate for contaminants in aquatic systems. Connor (1984) found that the concentration ratio of chlorinated or polynuclear aromatic hydrocarbons in fish to the sediments from their habitat increased with the hydraulic retention time of the basin.

Voice, Rice, and Weber (1983) and Isaacson and Frink (1984) found that both the sediment composition and organic matter content influence the binding affinity of chemicals such as chlorobenzene, naphthalene, and phenols to the sediment. Voice et al. (1983) found that partition coefficients increased as much as an order of magnitude for every order of magnitude decrease in solids concentration and that partitioning was dependent on octanol-water partition coefficients and on organic carbon content of the sediment.

Several authors have demonstrated that octanol-water partition coefficients may be used to predict the extent to which organic contaminants will be concentrated from water by fish and shellfish (Chiou et al. 1977; Veith et al. 1979b, 1980; Oliver and Niimi 1983; Mackay 1982). The partition coefficient is related to physical adsorption on solids, biomagnification, and lipophilic storage (Chiou et al. 1977). Chemicals that have low octanol-water partition coefficients may be accumulated in smaller quantities and, therefore, may have less of an ecosystem effect because of the low degree of food-chain bioconcentration.

Sorption of compounds to sediment particles may be extensive and not necessarily the sole result of hydrophobic interactions. The penetrability and accessibility of organic matter associated with

sediment exert a major influence on the sorption of compounds to sediment particles. Once compounds have sorbed to the sediment, desorption is slow and, depending upon the nature of the compound, its binding affinity, and the organic content of the sediment, up to 90% of a compound has been found to be irreversibly sorbed to the sediment (Isaacson and Frink 1984). The presence of other chemical compounds and the water quality parameters that may influence metabolic activity of aquatic organisms (e.g., temperature) may also influence the bioconcentration and biomagnification by aquatic biota.

2.6 COMPOUNDS THAT PRESENT SPECIAL ENVIRONMENTAL PROBLEMS

This portion of the report is devoted to a review of the food-chain transfer of several important and well-known hazardous organic chemicals. Background information on each compound is briefly examined along with available data on food-chain transfer and environmental mobility. The data selected for review are those that would be useful in predicting the transfer of chemicals through a generic food chain. The usefulness of such data will become evident in Section 4, which deals with models used to assess the potential food-chain impact of organic chemicals. Many of the compounds discussed below are of primary concern from the standpoint of potential persistence on contaminated lands and/or bioaccumulation through food chains.

Despite some serious limitations, soil persistence data are presented as half-times. These data should be interpreted with caution because environmental persistence can be highly variable depending upon soil conditions (as well as many other factors). Therefore, the

half-time in soil is a qualitative guideline to indicate if a chemical will persist for weeks, months, or years.

Concentrations of the various compounds reviewed in the forthcoming sections are most often given in parts per million (ppm) and parts per billion (ppb). One part per million is equivalent to 1 mg/kg or 1 µg/g in solids and 1 mg/L or 1 µg/mL in liquids. One part per billion is 1 µg/kg in solids and 1 µg/L in liquids.

The transfer from soil to plant is expressed as a plant/soil concentration ratio (CR value) and is calculated as:

$$CR = \frac{\text{concentration per unit mass plant tissue}}{\text{concentration per unit mass dry soil}} . \qquad (1)$$

Concentration factors are reported on either a fresh weight or dry weight basis.

Transfers of organics to animals are expressed as bioconcentration factors (BCF) and are usually based on long-term feeding studies where a compound is incorporated into the animal's diet. Therefore, BCF values are calculated as:

$$BCF = \frac{\text{concentration per unit mass tissue}}{\text{concentration per unit mass food}} . \qquad (2)$$

Bioconcentration factors have been found or calculated from data in the literature for cow or cattle fat, bird fat, whole milk, whole eggs, and fish.

2.6.1 Hexachlorobenzene (HCB)

Hexachlorobenzene (HCB) is a fungicide used on seed grains and occurs as an industrial waste product in the manufacture of chlorinated solvents and pesticides. HCB is globally distributed and is known to possess a high degree of toxicity in humans and to produce a wide variety of pathological conditions in animals (Courtney 1979). Courtney (1979) has recently reviewed the toxicology of HCB in animals as well as known incidents of HCB poisoning in humans. Outbreaks of HCB poisoning in humans occurred in Turkey in 1955-59 and in Saudia Arabia in 1967. These incidents involved accidental contamination of food or the misuse of HCB-treated seed wheat. In addition to local incidents of poisoning, HCB is present in the global environment. HCB levels in humans with no known history of exposure are approximately 6 ppm in fat and 0.15 ppm in milk (Courtney 1979). Concentrations of HCB in air and precipitation in rural areas or over the Great Lakes region are 0.1 to 0.3 ng/m^3 and 1 to 4 ng/L, respectively (Eisenreich et al. 1981).

"Hex" wastes from industry have found their way into many landfills. Technical HCB contains about 1% pentachloronitrobenzene (PCNB). PCNB, another fungicide, also contains HCB impurities, and so these two compounds can be found together in pesticide-treated soils or at industrial disposal sites. HCB is volatile and does not persist on surface soil (Table 2.1). Although HCB is metabolized by birds and mammals, it is lipophilic and exhibits a high potential for bioaccumulation in animal fat (Table 2.1). Milk is the major route of HCB elimination in cows (Fries and Marrow 1976). By comparison, PCNB, although more persistent in soil than HCB, exhibits a very low potential

Table 2.1. Chemical and food-chain properties for hexachlorobenzene (HCB)

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.006		1
Log K_{ow}	5.45		1
Food-chain properties			
Half-time in soil	14 d	Volatile; more persistent in subsurface soil	2
Plant/soil, CR	0.12-1.6	Lettuce; fresh weight; greenhouse study	3
Cow fat/diet, BCF	2.8-3.1	60-d feeding	4
Milk/diet, BCF	2.9-3.4	40-60-d feeding; milk fat value	4
Bird fat/diet, BCF	11-19	Poultry; steady state	5
Whole egg/diet, BCF	1.3-1.9	Poultry; steady state	5
Fish/water, BCF	3.7-4.3	Laboratory data	6
	4.3-5.7	Lab and field	7

Note: CR = concentration ratio. BCF = bioconcentration factor.

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for bioaccumulation in food chains (Table 2.2). When fed to chickens, PCNB is extensively metabolized (Simon et al. 1979). When potatoes are grown in PCNB-treated soil, most of the PCNB residues (including the metabolite pentachloroaniline) are found in the peel (Gorbach and Wagner 1967). From the standpoint of agricultural use of contaminated lands, HCB is a greater problem than PCNB.

Hexachlorobenzene is known to accumulate in bottom sediments of rivers, estuaries, and marine systems; and HCB exhibits biomagnification in food-chain transfers from fish to fish (Oliver and Niimi 1983) and fish to birds (Zitco, Hutzinger, and Choi 1972; Gilbertson and Reynolds 1972). The estimated half-life of HCB in fish could be in excess of seven months (Niimi and Cho 1981). Aquatic snails and mosquito fish have been found to bioconcentrate HCB 7000 to 3000 times, respectively, relative to water. Crayfish, largemouth black bass, sailfin mollies, daphnia, and algae have also been found to bioconcentrate HCB (Metcalf et al. 1973b; Laseter et al. 1976).

HCB is lipophilic and is accumulated from the blood into the hydrophobic lipid-rich cell membranes of the gut, kidneys, gills, liver, and brain of fish (Johnson et al. 1974; Laseter et al. 1976). There appears to be little metabolic alteration of HCB in fish and especially high retention by the digestive system (Laseter et al. 1976; Metcalf et al. 1973b). However, highly polar materials and conjugates, which are generally indicative of metabolic alteration of chemicals, have been found in mosquito fish (Metcalf et al. 1973b).

Table 2.2. Chemical and food-chain properties for pentachloronitrobenzene (PCNB)

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.44		1
Log K_{ow}	4.21		1
Food-chain properties			
Half-time in soil	> 60 d	Lab study; two soil types	2
Plant/soil, CR	0.4-3.0	Lettuce; fresh weight; greenhouse study	3
Cow fat/diet, BCF	< 0.002	16-week feeding study	4
Milk/diet, BCF	< 0.001	56-d feeding; whole milk basis	4
Bird fat/diet, BCF	0.003 - 0.02	Poultry; 35-week feeding study	5
Whole egg/diet, BCF	< 0.001	Poultry; 35-week feeding study	5
Fish/water, BCF	1.1	Steady state	6

Note: CR = concentration ratio. BCF = bioconcentration factor.

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2.6.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are industrial chemicals that are widely used for heat transfer fluids; protective coatings; solvents; and improving the resistance of plastics, paints, and rubber (Peakall 1972). One of the best known uses of PCBs is as dielectric fluids in transformers and capacitors used for electric power transmission. Many of the uses of PCBs have been discontinued, and although never intended for release into the environment, PCBs are globally distributed in air, water, and biota (Risebrough et al. 1968; Peakall 1972). Total PCB levels in air and precipitation from rural areas or over the Great Lakes region are 0.4 to 3 ng/m^3 and 10 to 100 ng/L, respectively (Eisenreich et al. 1981). Concentrations in fatty tissues of nonoccupationally exposed humans are approximately 1 ppm or 1000 times the average daily PCB intake (Miller 1983a). Sewage outfalls, industrial disposal into rivers, as well as leaching from dumps and landfills are the major likely sources of PCB entry into the environment (Hammond 1972).

Commercially produced PCBs are mixtures of different PCB isomers. PCBs manufactured in the United States, under the trade name Arochlor, are coded so that the last two digits give the weight percent of chlorine. Arochlor 1254, a well-studied mixture, contains 54% chlorine, but as many as 18 different isomers (Peakall 1972). PCB chlorine content usually averages between 40 and 60% (Hammond 1972).

In 1968, an incident of PCB poisoning occurred in Yusho, Japan, when more than 1000 people ate rice oil contaminated with approximately 2000 - 3000 ppm as a result of PCB leakage from a heat exchanger during manufacture (Hammond 1972; Peakall 1972; Miller 1983b). Approximately

1000 persons reported illness associated with PCB poisoning (Miller 1983b). Although the acute toxicity of PCBs is low compared to that of other widespread organochlorine pesticides, the toxicological properties of PCB mixtures are complicated by the presence of highly toxic impurities, such as chlorinated dibenzofurans, which may be responsible for symptoms first attributed to PCBs (Peakall 1972; Hammond 1972).

PCBs with low chlorine content are more rapidly metabolized, less persistent, and more toxic than more highly chlorinated PCBs (Peakall 1972). Iwata and Gunther (1976) found that lesser chlorinated biphenyls disappeared more rapidly from field soil treated with Arochlor 1254 and that lesser chlorinated biphenyls were translocated into carrots five to eight times more than the most highly chlorinated biphenyl studied. Feeding experiments with Arochlor 1242 show that it exhibits a lesser tendency for bioaccumulation than Arochlor 1254. Fries et al. (1977) reported a poultry fat/diet bioaccumulation factor of 2.9 to 4.5 and a whole egg/diet BCF of 0.35 to 0.72 in a nine-week feeding study of white leghorns. These bioaccumulation factors are less than those observed in long-term feeding studies with the more highly chlorinated Arochlor 1254 (Table 2.3).

Table 2.3 presents the chemical and food-chain properties of a well-studied PCB, Arochlor 1254. The chemical properties that make PCBs so useful for industrial applications, their chemical inertness, thermal stability, and low water solubility, contribute just as well to their environmental persistence. Although considered environmentally persistent, loss rates of PCBs in soil are variable; lesser chlorinated compounds degrade and volatilize faster than more-chlorinated

Table 2.3. Chemical and food-chain properties for the PCB Arochlor 1254

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.056		1
Log K_{ow}	6.47		2
Food-chain properties			
Half-time in soil	> 1 y	Rate depends on percent chlorination	3
Plant/soil, CR	0.02-0.06	Foliage; fresh weight	3
	0.03-0.5	Roots; fresh weight	
Cow fat/diet, BCF	2.0-4.9	60-d feeding study	4
Milk/diet, BCF	4.6-5.7	Milk fat; 60-d feeding study	4
Bird fat/diet, BCF	5-20	Poultry; 32-week feeding study	5
Whole egg/diet, BCF	0.2-1.2	Poultry; 32-week feeding study	5
Fish/water, BCF	5.0	Water only	6
	4.6-5.8	Lab and field	7

Note: CR = concentration ratio. BCF = bioconcentration factor.

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compounds. Like other chlorinated organic compounds, PCBs exhibit high bioaccumulation from the diet into animal and fish fat (Table 2.3). PCBs, in combination with other environmentally dispersed organochlorines like DDT + metabolites and dieldrin, have been identified as a likely cause of reduced reproductive success and rapid population declines in wild birds (Wiemeyer et al. 1975). Feeding experiments with poultry show a drastic reduction in hatchability of chicks at PCB levels of 10 to 20 ppm in the diet (Scott 1977).

Although the primary use of PCBs has been historically as an electrical insulating material, consequently, mainly in the terrestrial environment, the aquatic ecosystem has been contaminated by industrial discharge (Brown et al. 1985), aerial transport (Safe 1984), as well as sewage effluent discharge into surface waters (Brown et al. 1985). By far the major source of aquatic contamination is from industrial sources. For example, it was estimated that the General Electric Company (GE) capacitor-manufacturing facilities at Hudson Falls and Fort Edward, New York discharged PCBs to the Hudson River at a rate of 14 kg/d over an approximately 30-year period (Brown et al. 1985). Following the elimination of direct discharge of PCBs to the river, the riverbed, which had been the primary sink for PCBs, became the major source of PCB contamination in the river system. Concentrations of PCBs in sediments at 40 sites in the upper Hudson River near the GE plants exceed 50 ppm. With distance downstream and subsequent dilution with less contaminated sediment and partitioning into the water phase, there is an average contamination of approximately 10 ppm in tidal sediments of the Hudson River (Bopp et al. 1981).

The levels of PCBs in most fish species sampled between 1970 and 1974 exceeded the U.S. Food and Drug Administration (FDA) tolerance level, which at the time was 5.0 ppm. Levels of PCBs were higher in fish from the upper river in the vicinity of the plants than from those in the lower river. The PCB concentrations decreased from 145 ppm in 1977 to 10 ppm in 1981 for largemouth bass and 9.9 ppm in 1978 to 2.6 ppm in 1982 for striped bass. Only 10% of the fish sampled in 1983 were below the current FDA limit of 2.0 ppm. Both spatial and temporal trends in PCB concentrations in macroinvertebrates are generally consistent with results of the fish monitoring program (Brown et al. 1985).

The decreases in PCB concentrations in aquatic biota in the Hudson River with time is attributed primarily to declines in the less chlorinated PCB congeners. The more chlorinated forms are known generally to be more soluble in lipids, more resistant to degradation, and less volatile and are expected, therefore, to be more persistent in the environment (Brown et al. 1985). According to Jensen (1984), PCB concentrations in fish are reduced by increased fishing pressure, which removes more older fish from the population. The older fish, which have had a longer time to accumulate contaminants, have higher PCB body burdens than younger fish that are still putting metabolic constituents into growth rather than fat stores -- the primary sites for PCB storage. Initial increased fishing pressure would increase the PCB transfer from the larger lake trout to the human population; however, as high fishing pressure continued, younger fish with lower PCB levels would be the primary constituents of the catch. These younger, smaller

fish would have lower PCB levels and would transfer lower levels to the human population (Jensen 1984).

Octanol-water partition coefficients (K_{ow}s) are widely used in correlations concerning pollutant partitioning between water and sediment (Schwarzenbach and Westall 1981), in aqueous solubility relationships (Mackay et al. 1980), and in bioconcentration factor determinations (Mackay 1982; Veith and Kosian 1983). Some PCB congeners that have low solubilities in water or are insoluble and have high water partition coefficients have been shown to have higher bioconcentration factors in fish (Chiou et al. 1977). Knowing the K_{ow} values for PCB congeners, of which there are a total of 209 possible, is especially valuable because K_{ow}s allow predictions of equilibrium distribution of these compounds in the aquatic environment (Rapaport and Elsenrelch 1984).

Most highly chlorinated PCB compounds are metabolized slowly, if at all, by species of fish that have been studied [e.g., brook and rainbow trout (Hutzinger et al. 1972; Melancon and Leck 1976)], and the persistence of the compounds in fish is accounted for by their resistance to metabolism and their lipophilicity (Binder, Melancon, and Lech 1984). Hutzinger et al. (1972) found that the rate of metabolism of 2,5,2',5'-tetrachlorobiphenyl (TCB) in rainbow trout was as low as 0.1% of the accumulated amount. The whole-body half-life of TCB was found to be approximately 1.75 y for female and 1.43 y for male rainbow trout prior to spawning. During spawning, there was approximately a threefold increase in the elimination rate with the compound being transferred to the gametes (Guiney et al. 1979). While this process

has the beneficial effect of reducing the body burden for mature fish, there is the potential for deleterious effects on the offspring. Fry were found by Guiney et al. (1979) to eliminate PCBs more rapidly and to have a shorter whole-body half-life than any other stage, probably as the result of low body fat content.

2.6.3 Polychlorinated Dioxins and Furans

Polychlorinated dibenzo-p-dioxins, such as 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), and polychlorinated dibenzofurans are toxic impurities that are formed during the production of commercial chlorophenols and herbicides (Helling et al. 1973). Chlorinated phenols have been in use since the 1930s as bactericidal and fungicidal agents; as wood, paper, and leather perservatives; and as sanitizing agents. TCDD is a trace contaminant of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), which was one constituent of chemical defoliants widely used in Vietnam from 1962 to 1971 (Young et al. 1983). TCDD has also been found in the environment adjacent to abandoned chemical dump sites, such as the Love Canal area in Niagara Falls, New York (Smith et al. 1983).

Chlorodioxins are highly toxic. The level of toxicity varies in test animals because of differences in species' sensitivity, but like PCBs, dioxin toxicity decreases with increasing chlorination (Helling et al. 1973). Therefore, more highly chlorinated dioxins, like octachlorodibenzo-p-dioxin, are less toxic than TCDD, which has an LD_{50} as low as 0.6 to 2 ppb in guinea pigs. Polychlorinated dibenzo-p-dioxins and structurally similar polychlorinated dibenzofurans

tend to increase in toxicity when chlorine atoms occupy lateral positions on the dioxin or furan molecule (Josephson 1983).

Considering the widespread use of herbicides and chlorinated phenols, there are a variety of routes by which trace levels of chlorodioxins can enter food chains to humans. However, two well-known recent incidents involved TCDD contamination of terrestrial landscapes. During the early 1970s, horse arenas and unpaved roads in Missouri were sprayed with used oil containing TCDD to control dust. Horses died and people became ill as a result of contact with the contaminated soil (Harris 1981). Investigations have revealed that there are numerous dioxin-contaminated sites in Missouri and other states (Josephson 1983; Harris 1981). Several communities were contaminated with dioxin through the practice of spraying waste oil (at least 18,500 gal. statewide) to control dust. The community of Times Beach was disincorporated and abandoned in 1983 by residents who participated in a $33-million Federal government purchase of contaminated properties.

A second incident of TCDD contamination involved an accidental explosion at a chemical plant near Seveso, Italy, in 1976. A large inhabited area of more than 1000 ha was contaminated by a chemical cloud containing trichlorophenol (TCP) and the impurity TCDD. Thousands of small animals died within a few weeks after the incident, and mortality of farm animals (mostly poultry) occurred within the most highly contaminated area [average 2.25 ppb TCDD soil (Fanelli et al. 1980)]. Autopsies of dead rabbits and poultry revealed pathological symptoms such as hepatic lesions (Fanelli et al. 1980). Residents were evacuated from the most highly contaminated areas.

The chemical and food-chain properties of TCDD are presented in Table 2.4. TCDD is persistent in soil because it is an insoluble, nonpolar, chlorinated molecule, devoid of biologically labile functional groups (Helling et al. 1973). TCDD is protected from photolysis by soil (Plimmer 1978) and it is not readily leached (Helling et al. 1973). Current estimates of TCDD half-life in soil are as long as ten years (Sun 1983). Despite its environmental persistence, plant uptake of TCDD via roots from contaminated soil is negligible (Helling et al. 1973). However, feeding experiments with guinea pigs and rats have shown that TCDD bound to soil is bioavailable and potentially hazardous if TCDD contaminated soil is ingested (McConnell et al. 1984). Nash and Beall (1980) concluded that TCDD is about 75% as volatile as the insecticide DDT and that volatilization of TCDD from soil may be significant. Vaporization and resuspension of soil dust in the air are potential transport mechanisms for TCDD from waste disposal sites. Concentrations of TCDD on particulate matter in air at a waste disposal facility near Jacksonville, Arkansas, are comparable to average concentrations in soil, i.e., approximately 1 ppb (Josephson 1983).

Although TCDD has a relatively short persistence time on grass (Nash and Beall 1980), bioaccumulation by cattle grazing on contaminated lands can be expected to occur through either the ingestion of contaminated forage or soil. The bioaccumulation factor for TCDD from diet to beef fat has been reported as 3.5 (Kenaga 1980). Fat bioaccumulation factors for TCDD from long-term feeding studies with rats are variable, ranging from 24.5 at low doses to 3.7 at higher doses (Newton and Snyder 1978). Bioaccumulation factors for milk fat are

Table 2.4. Chemical and food-chain properties of the dioxin 2,3,7,8-TCDD

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.0002		1
Log K_{ow}	6.15		1
Food-chain properties			
Half-time in soil	> 1 y	Lab conditions; persistent under field conditions	2,3
Plant/soil, CR	< 0.02	Oat and soybean tops	4
Cow fat/diet, BCF	3.5	28-d feeding study	5
Milk/diet, BCF	0.1-0.2	Whole milk; 77-d feeding study	6
Fish/water, BCF	4.0-4.5	Calculated	7,8

Note: CR = concentration ratio. BCF = bioconcentration factor.

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approximately ten times higher than BCF values for whole milk (Jensen and Hummel 1982). The half-time for elimination of various dioxins from cow's milk is approximately 40 to 50 days (Jensen and Hummel 1982; Firestone et al. 1971).

In aquatic environments, tetrachlorodiphenyl ether (tetra-CDE) a possible precursor of 2,4,8-trichlorodibenzofuran (tri-CDF) and trichlorodiphenyl ether (tri-CDE) have been identified in extracts of organisms and in samples of suspended particulate material in Narragansett Bay, Rhode Island. The CDEs were also detected in the waste water of a chemical manufacturing plant located on the Pawtucket River (Lake et al. 1981). Concentrations were found in extracts of mussels, clams, sediment, and the hepatopancreas of lobsters caged in both the upper and lower portions of the bay as well as in a turtle sample (Keuhl et al. 1979). The compound was determined to be from PCB mixtures because of the dominance of the penta-CDF isomers. The Rhode Island study identified photochemical conversion of a tetra-CDE to a tri-CDF as a potential source of CDFs in the aquatic environment. Lake et al. (1981) determined that downstream transport from contaminated sediment is a source of contamination for aquatic biota.

Both polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have been found in turtles (Rappe et al. 1981), carp, largemouth bass, and striped bass in the Hudson River (O'Keefe et al. 1984). Levels of PCDD and PCDFs in striped bass from the Hudson River were significantly higher than in striped bass from Rhode Island coastal waters and the Chesapeake Bay. O'Keefe et al. (1984) concluded that there was a constant exposure source of PCDD and PCDFs for fish in

the Hudson River based on comparison of fish samples from 1981 and 1983 that showed no decrease in concentration between sampling periods. The source of PCDD and PCDFs in both sediment and fish in the Hudson River was thought to be a chemical such as trichlorophenol, possibly produced in the lower Hudson River area, where 2,3,7,8-TCDD is the only PCDD isomer that can be readily detected. Because of their strong adsorption to sediment/soil particles and persistence in the environment, PCDD and PCDFs have the potential for continued long-term contamination and bioaccumulation in the aquatic ecosystem.

2.6.4 Chlorinated Hydrocarbon Pesticides

Because of their widespread production and agricultural use, as well as their chemical stability and persistence, chlorinated hydrocarbon pesticides are ubiquitous in the environment. Ecological problems associated with the use of compounds such as DDT are well known because of attention given to this insecticide by environmentalists and the press. The legacy of widespread DDT use is still with us. Concentrations of chlorinated pesticides in air, from rural areas or from areas near the Great Lakes, range from 0.01 to 4 ng/m^3, and concentrations in precipitation range from 1 to 35 ng/L (Eisenreich et al. 1981). Chlorinated hydrocarbon pesticides and their residues are also found in surface waters and groundwaters. The probability of detecting chlordane, dieldrin, and p,p'-DDT in surface waters from New Jersey is 0.56, 0.39, and 0.17, respectively (Page 1981). Chlorinated hydrocarbon pesticides in combination with other organochlorines, like PCBs, have been identified as environmental

pollutants responsible for the reduced reproductive performance and population decline of certain raptors (e.g., Wiemeyer et al. 1975). Indications are that DDT residues are declining in marine predators, such as seals and brown pelicans, since the U.S. Environmental Protection Agency's ban on DDT use in the early 1970s (Addison et al. 1984).

Because of government bans or restrictions on use, there is only a remote possibility for further widespread environmental contamination by chlorinated hydrocarbon pesticides beyond present-day levels in the United States, although their use in foreign countries poses a threat through atmospheric dispersion. However, several of the more persistent organochlorine insecticides will remain for some time as part of our organic chemical background in the environment. Therefore, this review would be incomplete without the presentation of chemical, environmental persistence, and food-chain bioaccumulation data for p,p'-DDT (Table 2.5), dieldrin (Table 2.6), and endrin (Table 2.7). These three exemplary organochlorine insecticides are all characterized by low water solubility, long persistence times in soil, and high bioaccumulation in animal fat.

Most chlorinated hydrocarbons are persistent in and bioaccumulate in organisms in the aquatic environment. The most notorious of these compounds is DDT, which is ubiquitous in the environment and is available for uptake by aquatic biota through both water and food (Rhead and Perkins 1984). These authors found that the amount of DDT taken up from food and water was additive. The observed concentration factor for DDT taken up from contaminated water was a maximum of 131,000 while concentration from food was considerably lower (a maximum of 115). As

Table 2.5. Chemical and food-chain properties for the organochlorine p,p'-DDT

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.002		1
Log K_{ow}	5.76		1
Food-chain properties			
Half-time in soil	10.5 y	Field studies; avg. of 5 soils	2
Plant/soil, CR	0.05	Grass; dry weight	3
	7.1	Roots; dry weight	
Cow fat/diet, BCF	3.9-6.2	112-d feeding study	4
Milk/diet, BCF	0.02-0.08	Whole milk; steady state	5
Bird fat/diet, BCF	8-19	Poultry; steady state	6
Whole egg/diet, BCF	0.8-1.6	Poultry; steady state	6
Fish/water, BCF	4.5	Water exposure only	7

Note: CR = concentration ratio. BCF = bioconcentration factor.

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Table 2.6. Chemical and food-chain properties for the organochlorine dieldrin

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.074		1
Log K_{ow}	5.16		1
Food-chain properties			
Half-time in soil	3-4 y avg. of 5 sites	Field studies;	2
Plant/soil, CR	0.07	Grass; dry weight	3
13	Roots; dry weight		
Cow fat/diet, BCF	1.3-1.8	41-d feeding study	4
Milk/diet, BCF	0.36-0.41	Whole milk; steady	5
	state		
Bird fat/diet, BCF	12-17	Poultry; steady	6
	state		
Whole egg/diet, BCF	0.7-1.7	Poultry; steady	6
	state		
Fish/water, BCF	4.8	Water exposure only	7

Note: CR = concentration ratio. BCF = bioconcentration factor.

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Table 2.7. Chemical and food-chain properties for the organochlorine endrin

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.074		1
Log K_{ow}	5.38		1
Food-chain properties			
Half-time in soil	12 y one soil type	Field study;	2
Plant/soil, CR	0.014 field study	Wheat plants;	3
Cow fat/diet, BCF	0.4-0.8 study	12-week feeding	4
Milk/diet, BCF	0.06-0.08 steady state	Whole milk;	5
Bird fat/diet, BCF	7-10 state	Poultry; steady	6
Whole egg/diet, BCF	0.6 state	Poultry; steady	6
Fish/water, BCF	3.2	Water exposure only	7

Note: CR = concentration ratio. BCF = bioconcentration factor.

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with other compounds, the rate of release from fish was found to be inversely correlated to the lipophilicity of the compound (Ellgehausen et al. 1980).

Aldrin is converted in the environment to dieldrin, which is readily accumulated in aquatic biota such as mosquito fish, snails, and algae. The BCF for aldrin is 3,140 for fish and 44,600 for snails; dieldrin has a BCF of 5,960 for fish and 11,100 for snails (Metcalf et al. 1973b).

Kepone, an organochlorine hydrocarbon pesticide patented in 1951, is a persistent compound that may remain in aquatic sediment from one to ten decades. Studies in the James River in Virginia (Huggett and Bender 1980) showed that Kepone is associated with the organic portion of the sediment and that, depending upon the wave and tidal action and burrowing activities of benthic organisms, contaminated sediments may be either buried by uncontaminated mineral matter or resuspended and made available for uptake.

The maximum acceptable concentrations for dissolved Kepone were predicted to be 0.14 ppb in the freshwater zone of the James River and 0.026 ppb in the lower estuary [maximum acceptable concentrations are based on both the accumulation levels in and relative toxicity of Kepone to various finfish and shellfish species in each zone (Huggett and Bender 1980)]. Studies of fish (Huggett and Bender 1980) and blue crabs (Roberts and Leggett 1980) showed that the highest Kepone concentrations occurred in males. These studies showed that a significant portion of the Kepone taken up by females is transferred to the egg mass rather than concentrated in the flesh.

Birds in the Hopewell area of the James River were found to concentrate Kepone. Mallards were found to contain 0.14 to 0.5 ppm (wet weight) Kepone, whereas great blue herons contained 2400-36,000 ppm (Huggett and Bender 1980). Studies by Shaar et al. (1981) showed that Kepone resists microbial degradation, accumulates and resists metabolism in fish, and moves through the food chain. Kepone accumulation by bluegills, however, was about half that of DDT.

Bioconcentration of these and other organochlorine compounds, such as DDD and DDE, in the aquatic environment results from their high lipid solubility and water insolubility (Rhead and Perkins 1984) as well as their resistance to degradation by the mixed-function oxidase (MFO) enzymes (Metcalf et al. 1973b). Because of the tendency of organochlorine compounds such as aldrin to be biotransformed by aquatic organisms into other potentially more toxic/more resistant compounds, efforts to determine the presence of parent compounds in tissues should include analysis for degradation products and metabolites that may be more toxic than the parent compound (Lech and Bend 1980).

2.6.5 Polybrominated Biphenyls (PBBs)

At a Michigan chemical company in 1973, there was a mixup in handling of the fire retardant "Firemaster," a complex mixture of polybrominated biphenyls, and "Nutrimaster," a nontoxic magnesium oxide feed additive, that resulted in the incorporation of 500 to 1000 pounds of PBBs into livestock feed. PBB contamination in the feed as high as 13,500 ppm resulted, and approximately 30,000 cattle and thousands of other farm animals were contaminated by the feed and were destroyed

(Carter 1976; Kay 1977). Tons of contaminated eggs, milk, butter, cheese, and livestock feed were also destroyed. Michigan residents were exposed to diary products and eggs contaminated with PBBs during that time in 1973-74 when the contamination went unrecognized. Approximately 8000 Michigan residents, mostly farm families, were most heavily exposed. Kay (1977) has reviewed the circumstances and subsequent studies associated with the Michigan PBB incident.

PBBs, like PCBs, are water insoluble, lipophilic compounds. Available data (Table 2.8) indicate that PBBs in the diet do not accumulate as much as PCBs in beef fat or milk fat, but PBBs do exhibit the potential for bioaccumulation in eggs and poultry fat. PBBs are also more sensitive to photodegradation by ultraviolet light than PCBs (Kay 1977). Despite this, Jacobs et al. (1976) reported that PBBs were extremely persistent in soil because of their resistance to degradation (minimal breakdown was observed over a period of 24 weeks for all but one isomer). As expected on the basis of water solubility, there is negligible plant uptake of PBBs from contaminated soil, with the possible exception of surface contamination adsorbed to roots (Chou et al. 1978; Jacobs et al. 1976).

Studies in Sweden (Andersson and Blomkvist 1981) found PBBs in fish tissue; however, the source of pollution was unknown. Muscle and liver of pike were found to contain 0.15 ppm and 22 ppm of PBB, respectively. Zitko (1977) found that brominated biphenyls with six or fewer bromine atoms only were accumulated from water by juvenile Atlantic salmon. However, when brominated compounds were mixed with food, salmon accumulated additional compounds. Zitco (1977) found that PBBs were

Table 2.8. Chemical and food-chain properties for the PBB Firemaster BP6

Property	Value	Conditions	Reference
Chemical properties			
Solubility, ppm	0.011		1
Food-chain Properties			
Half-time in soil	> 6 mos.	Laboratory study	2
Plant/soil, CR	< 0.001	Foliage; fresh weight;	3
	< 0.006	Roots; fresh weight	
Cow fat/diet, BCF	0.08-0.2	15-d feeding study; 4x in sheep	4
Milk/diet, BCF	0.043	Milk fat; 60-d feeding study	5
Bird fat/diet, BCF	1.5-4	Poultry; 63-d feeding study	6
Whole egg/diet, BCF	1.0	Whole egg; 63-d feeding study	6
Fish/water, BCF	1.7		7

Note: CR = concentration ratio. BCF = bioconcentration factor.

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accumulated from water, but the accumulation was much less than for PCBs. When exposed to food containing PBBs and PCBs, the uptake of PBBs was greater than or equal to the uptake of the PCB Arochlor 1254.

Those PBB compounds with up to four bromine atoms that most closely resemble the corresponding chlorobiphenyls are accumulated to a lesser extent by salmon than the more substituted bromobiphenyls that correspond to PCBs such as Arochlor 1254 (Zitko 1977). Fish fed highly brominated compounds containing pentabromobiphenyls and hexabromobiphenyls metabolized the compounds to monobromobiphenyls to pentabromobiphenyls, which may have toxicological consequences in fish.

2.6.6 Polycyclic Aromatic Hydrocarbons (PAHs)

There are currently very few data on the behavior of PAHs in the terrestrial environment, and so most of the information in this section is based on a recent review of this topic by Edwards (1983). PAHs are aromatic hydrocarbons consisting of three or more fused benzene rings. Benzo(a)pyrene (BaP) is one of the best known and most studied PAHs, although there are a number of other carcinogenic (or mutagenic) PAHs of environmental significance, including: phenanthrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(e)pyrene, and coronene. PAHs may be formed during incomplete combustion of organic compounds even though the combusted material may not contain PAHs, per se. Electric power generation by fossil fuel plants, in addition to forest and agricultural fires, are the most significant contributors to the total global PAH inventory. Concentrations of total PAHs in air and precipitation from rural areas are 10-30 ng/m^3 and 50-300 ng/L, respectively (Eisenreich

et al. 1981). Effluents from various industrial processes, such as coal gasification, can result in locally elevated concentrations of PAHs in soil.

Typical concentrations of BaP in soils throughout the world range from 0.1 to 1.0 ppm, although concentrations near known sources can exceed 1.3 ppm (Edwards 1983). At field sites known to be contaminated with PAHs, compounds such as anthracene and pyrene are not present in surface soil layers due to volatilization, while less volatile PAHs, like benzo(a)anthracene and BaP, exhibit more uniform concentration profiles with depth (Marquenie et al. 1985). Soil microorganisms can metabolize some PAHs, but there is virtually no information on the persistence of PAHs in soils under field conditions. Lu et al. (1977) reported that BaP was very resistant to degradation in air-dried soil (17.4% moisture) incubated for four weeks at 27°C under laboratory conditions. PAHs are degraded by photolysis, but some of the degradation products are carcinogenic. There is considerable need for information on the interactions of PAHs with soil constitutents and the ramifications that such interactions might have for long-term persistence of PAHs in the environment.

There is little evidence for significant plant uptake of PAHs from contaminated soils. Despite the fact that atmospheric deposition by PAH-bearing particulates is a major contribution to existing concentrations in plants, PAHs cannot be easily removed from vegetation by washing with water. PAHs, which penetrate into plant parts and become dissolved in plant oils, may exhibit long (> 100 days) persistence half-times (Gunther et al. 1967). Edwards (1983) points

out that concentrations of PAHs in plants are usually less than those in the soil in which the plants are grown (concentration ratios range from 0.001 to 0.18 for total PAHs). Soil-to-plant concentration ratios for BaP range from 0.0001 to 0.33. PAH concentrations in plants are generally higher in aboveground parts than in belowground parts. PAHs incorporated by root uptake may be translocated and extensively metabolized within the plant (Edwards 1983; Edwards 1985 personal communication).

There is almost no information on the food-chain transfer of PAHs beyond the point of uptake via plant roots. The little information that is available indicates some potential for the accumulation of PAHs in animals. This is consistent with the high octanol-water partition coefficient of 6.2 for BaP. However, because PAHs bind covalently to cellular macromolecules, like DNA and protein, indices of their bioaccumulation in animal fat may not be a representative measure of their potential toxicity in food chains. Field measurements show that concentrations of benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and BaP in tissues of earthworms can equal the concentrations prevailing in the PAH-contaminated sediments to which worms are exposed (Marquenie et al. 1985). Although rapidly metabolized, some PAHs are biologically transformed by mixed function oxidases to epoxides, which upon hydration become carcinogenic precursors (Jacob and Grimmer 1983). Therefore, it is the PAH metabolites that result in long-term toxicological hazard to animals.

In the aquatic environment, PAHs partition between dissolved and particle-bound forms. Both forms may be incorporated into the sediment

by direct sorption to bedded sediments in the case of dissolved forms or by sedimentation (settling) in the case of the particle-bound forms. The particulate-bound form, which is less amenable to breakdown and is nonvolatilizable, is more persistent in the aquatic environment (Herbes et al. 1980). Because of the differences in the persistence of individual PAH compounds, the relative contribution to PAH mixtures will vary with the distance from their source and the time since initial contamination.

Aquatic organisms may bioaccumulate PAHs from both dissolved and particulate forms and may metabolize the compounds as they are passed along the food chain. Benthic fish can accumulate PAHs via uptake from water; via the food chain; via interstitial water into which a small proportion of the compounds, either bound to or associated with sediment, are slowly and continuously released (Varanasi and Gmur 1980); or via exposure to and ingestion of sediment particles (Conner 1984; Breck 1985).

Southworth et al. (1978a) showed that PAHs were rapidly taken up by the zooplankton Daphnia pulex and concentrated to several orders of magnitude above ambient aqueous concentrations. Bioaccumulation of benzo(a)acridine, a four ring hydrocarbon, was 352-fold (Southworth 1978b). Benzo(a)pyrene, a five ring hydrocarbon, would be expected to be about 13,000-fold for D. pulex (Southworth 1978a). This bioaccumulation is similar in magnitude to that of DDT concentrated by D. magna (Crosby and Tucker 1971).

The mixed-function oxidase (MFO) enzyme system in vertebrates and invertebrates initiates the metabolism of various lipophilic organic

compounds making them more available for excretion. This MFO system transforms PAH compounds to intermediate compounds some of which are highly toxic, mutagenic, or carcinogenic to the host (Neff 1979). The problem of bioaccumulation of high levels of PAHs is intensified in the presence of mixed-function oxidase inhibitors or for organisms, such as snails, which are deficient in microsomal oxidase (Lu et al. 1977).

The higher molecular weight polycyclic compounds, which also have higher K_{ow}s (e.g., greater than 3.5), have a far greater likelihood of accumulating in aquatic biota than the lower weight compounds, such as isoquinoline, which have low K_{ow}s and low concentration factors. The higher molecular weight compounds also exhibit longer elimination half-times.

2.6.7 Phthalate Esters (PAEs)

Phthalic acid esters (PAEs) are water insoluble, lipophilic, colorless liquids, with high boiling points (> 200°C), that are commonly used as plasticizers to promote the durability and flexibility of plastic products. Because of their leakage from plastic products, and their occurrence as natural products in plants, PAEs are widely found in the environment (Mathur 1974). Mathur (1974), in a review of the literature on PAEs in the environment, concluded that PAEs are more likely to be pollutants than natural products. Waste dumps and municipal landfills are a likely source of PAE contamination to the environment because many plastics are eventually disposed of by land burial. PAEs are ubiquitous in the environment. Concentrations of two of the more

commonly used PAEs, di (2-ethylhexyl) phthalate (DEHP) and di-n-butyl-phthalate (DBP), in rural air and precipitation are 0.5 to 5 ng/m^3 and 4 to 10 ng/L, respectively (Eisenreich et al. 1981). Analysis for PAEs in environmental samples is difficult because many analytical grade solvents, as well as water, used in laboratory work may be contaminated with trace amounts of PAEs (Mathur 1974).

Laboratory studies have demonstrated that PAEs are of low acute toxicity to animals, and chronic toxicity studies give no indication that PAEs are carcinogens (Peakall 1975). However, indications are that PAEs are teratogenic and mutagenic at low concentrations representative of those levels that could potentially be encountered in the terrestrial environment (Mathur 1974). Reproduction in waterfleas and fish is reduced by DEHP exposures in the part per billion and part per million range, respectively (Mathur 1974).

One of the reasons that phthalates are used in plastics is their resistance to biodegradation (Mathur 1974). The disappearance of PAEs from soil has been largely attributed to microbial activity. The half-life of DBP in nonsterile soil is probably less than one week (Shea et al. 1982). This is comparable to the rapid anaerobic degradation of lower molecular weight phthalate esters, like DBP, in municipal sewage sludge (Shelton et al. 1984). However, some PAEs, like DEHP and di-n-octyl phthalate, are more resistant to attack and biodegradation by microorganisms (Mathur 1974; Shelton et al. 1984). Therefore, these latter two compounds must be considered potentially persistent in the environment.

There is very little plant uptake of DBP from soil. Plant:soil CR values are approximately 0.001 for young corn shoots growing on sandy

soil (Shea et al. 1982). Because of their lipophilic nature, indications are that PAEs can accumulate in animals at lower trophic levels (Mathur 1974). However, due to rapid metabolism in mammals, PAE levels are not expected to increase with trophic level in the food chain (Peakall 1975).

Phthalate esters are found in the Great Lakes where concentrations in selected tissues of fish in Lake Superior range from 18-20 ppm. Levels in settleable solids are as high as 75 ppm (dry weight). This is probably a minimum level because the compounds also occur as polar conjugates and metabolites that may not be extractable using normal analytical techniques (Mayer and Sanders 1973).

Acute and chronic toxicities of PAEs to freshwater aquatic life occur at concentrations as low as 940 and 3 ppm, respectively, and could occur at lower concentrations among species that are more sensitive than those species tested (bluegill, fathead minnow, and Daphnia). Acute toxicity to saltwater aquatic life occurs at concentrations as low as 3 ppm and possibly lower for more sensitive species (USEPA 1980). Chronic toxicity of PAEs to one species of saltwater algae occurred at concentrations as low as 3.4 ppb (USEPA 1980).

Di-2-ethylhexyl phthalate (DEHP), the most widely used plasticizer in polyvinyl chloride plastics, is known to be toxic and to reduce reproduction by as much as 60% in Daphnia (Mayer and Sanders 1973; Sanders et al. 1973). Although DEHP is accumulated in fish, the water BCFs of 34-137 for fathead minnow measured in a 56-d study by Mayer (1976) was only about 1% of that observed for DDT by Metcalf et al. (1973a). The average half-life of DEHP in the fathead minnow was

12.2 days as the result of degradation and elimination. Metcalf et al. (1973a) found that at the end of 48 h the BCF at 10 ppm exposure was 365 in mosquito larvae and 47 in the guppy; at 0.1 ppm the BCF varied over a 48-h period from 8.5 to 265 in the guppy and from 120 to 858 in the snail. At a water concentration of 1.9-2.5 ppb - a level that most closely approximates concentrations in the Great Lakes as a result of municipal and industrial discharges (Glass et al. 1977) - fathead minnows reached steady state concentrations of 62 ppb after 28 days (BCF = 28).

The biodegradation rate for DEHP was found to be slow in algae, Daphnia, mosquito larvae, snails, and clams, but rapid in fish. Metcalf et al. (1973a) found metabolites of DEHP in algae, snails, and fish, but not in mosquito larvae in their laboratory microcosm. DEHP is extremely insoluble in water (Thomas and Thomas 1984) and partitions strongly into the lipids of plants and animals and is concentrated through aquatic food chains (Metcalf et al. 1973a). The slow degradation rates in the aquatic environment, the teratogenic properties, the potential for food-chain bioconcentration, and the ubiquitous use and distribution of PAEs make these compounds of long-term concern in the aquatic environment.

2.6.8 Toxic Metals

Of the 101 elements in the periodic table, all but 22 are considered to be metals. Metals are those elements that generally have luster, conduct heat and electricity, are usually malleable, and form positive ions. The nonmetals, are typically either gases or liquids at

room temperature, whereas the metals, with the exception of mercury, are solids at room temperature.

Many elements are essential nutrients for both plants and animals at low or trace concentrations. For plants, these include Ca, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Se, V, and Zn (Bowen 1979; Shacklette et al. 1978). For animals the same list applies, but also includes As, Cr, and Sn (Bowen 1979).

Metals that have toxic effects in plants and animals are often referred to as "trace" or "heavy" metals. However, these two terms cannot be precisely defined. The term "trace metal" originated in chemical laboratories to designate those metals commonly found in such low concentrations that they could not be quantitatively determined by the analytical methods of the day; hence "trace" metals (Shacklette et al. 1979). "Heavy metals" is also an imprecise term generally referring to metals of atomic number 22 (titanium) or greater. In this review we will use the term "toxic metals," which may include metals commonly referred to as trace or heavy metals.

From the standpoint of long-term land contamination, the toxic metals of greatest concern include As, Cd, Cr (VI), Cu, Hg, Mn, Ni, Pb, and Zn. Also of importance is the nonmetal selenium. These hazardous chemicals are significantly different from radionuclides and organics in one important respect. They do not decay away, nor do they degrade in the environment. Although their availability for food-chain transfer may be altered by changes in chemical form (i.e., valence changes) or through complexing by other organic compounds, they will persist in the environment until physically removed. Most of these metals have been

previously identified as essential in animals and plants. However, at sufficient concentrations all of the above can be toxic to both plants and animals.

Table 2.9 gives the toxicity levels and food-chain properties of the toxic metals discussed in the following sections. Relative water solubility is presented in terms of the soil/water distribution coefficient, K_d, which is given by:

$$K_d = \frac{\text{Concentration per milliliter of water}}{\text{Concentration per gram (dry wt.) of soil}} \cdot \qquad (3)$$

The concentration ratios for plants are as defined in Eq. (1). The bioconcentration factors for beef, pork, and chicken, are given for the meat (rather than fat). BCFs for eggs are for the egg's contents excluding the shell.

2.6.8.1 Arsenic

Arsenic compounds are extremely toxic to plants and animals. The trivalent forms (arsenites) are far more toxic than pentavalent forms [arsenates (Gough et al. 1979)]. In addition to its toxicity, arsenic may be a carcinogen (Bowen 1979). Arsenic can be found in (naturally) high concentrations in some soils in England, New Zealand, and Switzerland (Bowen 1979), but typically high concentrations in soils and sediments are associated with smelting or lead arsenate insecticide applications. Steevens et al. (1972) report that lead arsenate applications to orchards in the United States have rendered some soils phytotoxic. Kipling (1977) reported that some cows have died after

Table 2.9. Chemical and food-chain properties for 10 toxic metals.

Property	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn
Solubility										
K_d, mL/g[a]	200	6.5	850	35	10	65	150	900	300	40
Concentration ratio, bioconcentration factor										
Vegetation, CR[a]	0.04	0.6	0.008	0.4	0.9	0.3	0.06	0.05	0.03	1.5
Beef, BCF[b]	0.02	0.006	0.06	0.1	2.5	0.004	0.06	0.003	0.15	1.0
Pork, BCF[c]		0.01		0.08		0.01			1.1	0.5
Chicken, BCF[c]		0.06		0.04	0.002	0.004			0.6	0.5
Eggs, BCF[c]		0.01		0.05		0.007			1.0	0.3
Fish, BCF[d]	1.2		0.6	2.3	3.9	2.0	2.0	2.5		3.0
Toxicity[e]										
Plant, ppm	0.02	0.2	0.5	0.5		1.0	0.5	3.0	1.0	60
Man, mg/d	5.0	3.0	200	250	0.4			1.0	5.0	150
Lethality[e]										
Man, g/d	0.1	1.5	3.0		0.15			10		
Comments[f]	car. ter.	car.	car.				car.			

[a]Baes et al. (1984).
[b]Derived from values published in Baes et al. (1984) using the methodology of Ng et al. (1982).
[c] Ng et al. (1982).
[d]Foley et al. (1978) for As; Hildebrand et al. (1980) for Hg; Thompson et al. (1972) for Cr, Cu, Mn, Ni, Pb, and Zn.
[e]Values represent the lower value of a range given by Bowen (1979). Plant toxicities are based on solution concentrations, not soil concentrations.
[f]Car. = carcinogenic; Ter. = teratogenic.

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grazing potato fields that had been sprayed with arsenate insecticides. Typically arsenates applied to soil as insecticides remain near the soil surface (Hess and Blanchar 1977). Plant uptake of arsenic is very low (Table 2.9); therefore toxicity from consumption of foods of plant origin is unlikely. However, high concentrations of arsenic have been reported in seafood (Underwood 1971).

Gough et al. (1979) report that arsenic toxicity depends on the concentration of soluble, not total, arsenic in soil. Average total soil concentrations of arsenic are 6 ppm (Bowen 1979), whereas 100 ppm is considered to be highly contaminated (Hess and Blanchar 1977). Soils from apple orchards that were unproductive from excessive arsenate insecticide spraying had 3.4 to 9.5 ppm readily soluble arsenic in the top 15 cm (National Research Council 1977a).

Consumption of water contaminated by arsenic is considered the most common natural cause of arsenic poisoning in man (Gough et al. 1979). Concentrations of arsenic in excess of 50 ppm in drinking water constitute grounds for rejection (U.S. Public Health Service 1962). However, continued use of drinking water with concentrations of 0.4 to 10 ppm has been associated with illness and death (Wyllie 1937), and 0.8-ppm concentrations have been associated with skin lesions (Borgano and Grieber 1971).

2.6.8.2 Cadmium

Cadmium is a relatively rare element found in fairly uniform, low-level concentrations in the earth's crust. Concentrations in rocks average 0.05 to 0.3 ppm, and soil concentrations average 0.35 to 0.5 ppm

(Vinogradov 1959; Bowen 1979; Gough et al. 1979). However, cadmium is found in much higher concentrations in sulfide deposits that also contain copper, lead, and zinc. As a consequence, environmental cadmium contamination often occurs near lead and copper mines, refineries, and smelters. Cadmium is also used in electroplating, batteries, electrical equipment, manufacturing of polyvinyl chloride plastics and fertilizers, and in automobile engines and tires. It has been estimated that incineration of scrap steel, electrical equipment and automobile parts is responsible for over half of the estimated 2.1×10^6 kg of cadmium released to the environment in the United States every year (McCaull 1971).

Cadmium's toxicological properties have been recognized since the 1920s when it was used pharmaceutically in the treatment of syphilis and malaria (Prodan 1932). It is apparently toxic to all body systems and functions of mammals (Tipton 1960). This toxicity is likely associated with cadmium's ability to replace zinc, and other essential elements in several sulfur-containing organic radicals. Mammmals have no homeostatic mechanism for elimination of cadmium from the body, so it tends to accumulate in the liver and kidneys without regard for the amount already stored. Bowen (1979) reports that 200 to 9000 ppm cadmium in water is toxic to plants, and 3 to 330 mg/d is toxic to man (1.5 to 9 g/d is lethal). Excess body burdens of cadmium have been associated with arterial hypertension (Perry and Schroeder 1955), renal tubular dysfunction and softening of the bones ["itai-itai" disease (Fulkerson et al. 1973)], teratogenic effects (Carpenter 1967) and cancer (Parizek 1957).

Most reports of acute cadmium toxicity have been in connection with occupational exposures, but accidental exposures of the general public to cadmium-contaminated food and water have occurred. The most famous instance of cadmium poisoning from general contamination of the environment occurred in the Jintsu River Basin in Japan. As early as 1935 inhabitants of the area reported symptoms of severe pain in the groin, back, and joints; the tendency of bones to soften and break; muscular weakness; and loss of appetite (Fulkerson et al. 1973). However, it wasn't until 1961 that the "Itai-itai" (ouch-ouch) disease was linked to cadmium from nearby operations of the Mitsui Mining Company, which operated zinc, lead, and cadmium mining and smelting operations. Apparently large-scale contaminations of the Jintsu River occurred beginning in 1924 from several accidental releases of sludges from the mining, refining, and smelting facilities. Cadmium contamination of the river led, in turn, to contamination of local wells and soils used for production of rice and soybeans.

2.6.8.3 Chromium (VI)

Chromium in trace quantities is an essential element for sugar and fat metabolism and for the action of insulin (Mertz 1969). Chromium deficiency in animals produces symptoms similar to those for diabetes. Deficiencies of chromium have also been associated with heart disease and high blood cholesterol levels. Chromium is found in rocks in the trivalent form at concentrations of 4 to 90 ppm and in soils at concentrations of 70 to 200 ppm (Vinogradov 1959; Bowen 1979). The metal and trivalent forms of chromium are stable and relatively nontoxic; whereas, the hexavalent forms are irritating, corrosive, and

perhaps as much as 100 times more toxic than the trivalent forms (Waldbott 1978; Gough et al. 1979).

Chromium (VI) is very toxic to plants. Soil concentrations greater than 5 to 20 ppm have been associated with toxicity to tobacco, corn, tomatoes, oats, kale, and potatoes (Gough et al. 1979). It is also fairly toxic to animals. Bowen (1979) reports that 200 mg/d is toxic to humans, and 3 g/d is lethal. Chromate concentrations between 10 and 100 ppm have damaged lung cells of rats and at 10,000 ppm have stopped ciliary action and killed lung cells (Mass and Lane 1976).

Chromium is a known carcinogen (Sullivan 1969; Laskins et al. 1969). Occupational exposures (inhalation of dusts) in the chrome plating industry are often associated with perforation of the nasal septum, atrophy of the lining of the lungs, conjestion, bronchial inflammation, and ulcers and polyps in the respiratory tract that are often precursors of lung cancer (Waldbott 1978).

2.6.8.4 Copper

In trace quantities copper is an essential element in both plants and animals. Over 30 copper metalloenzymes are known (Bowen 1979). Many of these enzymes function in electron transport during photosynthesis and respiration, as dioxygen reducers, as oxygen carriers, and as catalysts in the oxidation of iron in mammalian blood (Bowen 1979).

High concentrations of copper in rock and soil are found naturally, and there are many reports of copper toxicity to plants in areas of copper deposits (Gough et al. 1979). Plant species show different levels of resistance to copper, and this fact is often used as a

geobotanical method of prospecting for copper. Using satellite imagery, areas in Norway have been identified where soil concentrations are as high as 7400 ppm and copper toxicity to vegetation occurs (Bolviken et al. 1977). Copper is also found in high environmental concentrations around mines, refineries, and smelters (National Research Council 1977b).

Copper toxicity to plants is severe. Agricultural usage of copper is approximately 70,000,000 kg/y (Bowen 1979). A mixture of copper sulfate and lime (Bordeaux) is widely used as a fungicide in vinyards. Because copper is highly toxic to plant roots, but is negligibly translocated to aboveground plant parts, it is also widely used to clear sewer lines and septic tanks of encroaching plant roots. Copper toxicity has been observed in crops grown on fields previously sprayed with Bordeaux (a mixture of copper sulfate, lime, and water) and 400 ppm total copper in the topsoil (Westgate 1952). Bowen (1979) reports 0.5 to 8 ppm in solution is toxic to plants.

Copper is the most common toxic metal found in aquatic organisms (Gough et al. 1979). Its toxic concentration is inversely related to water hardness, principally calcium content. Copper (sulfate) has long been used as an algicide for municipal drinking water reservoirs. One part per million of copper in the top 0.5 m of water is sufficient to control algae (Mackenthun and Ingram 1967).

Bowen (1979) reports that 250 mg/d of copper is toxic to man, but Hill (1977) states that copper toxicosis in humans and most higher animals is a rare problem. Sheep appear to have a high sensitivity to excess copper. Ingestion of as little as 1.5 g/d is fatal to sheep

(Case 1974). Most incidents of copper poisoning of livestock are associated with excessive consumption of copper-containing salts, use of copper-containing drenches, and contamination of feeds with copper. Excessive levels of copper can build up in the liver and central nervous system, and the metabolic inability of the body to excrete copper is the fundamental cause of Wilson's disease (Scheinberg 1969).

2.6.8.5 Mercury

Mercury is widely distributed in nature. It is commonly found in rocks at levels of 0.06 to 0.3 ppm and in soils at levels of 0.01 to 0.06 ppm (Vinogradov 1959; Waldbott 1978; Bowen 1979). Some volcanic rocks containing large quantities of cinnabar (HgS) contain from 1 to 30 ppm mercury (Jonasson and Boyle 1971). Coal contains anywhere from 0.09 to 33 ppm, and it is estimated that 2.7 million kg are released from coal combustion throughout the world each year (Joensuu 1971).

Mercury has many medical, agricultural, and industrial uses. As early as 1500 A.D. mercury was used in the treatment of syphilis. Today some organic mercury compounds are used as diuretics and topical antibiotics. Mercury amalgams are extensively used as fillings for teeth. In agriculture, mercury compounds have been widely used as fungicides. Inorganic mercury seed dressings were developed in 1914 in Germany and quickly came into widespread use throughout the world under the trade names Ceresan, Argosan, and Upsulun (Novick 1969). After World War II liquid alkylmercury compounds were introduced for the treatment of wheat and barley seeds. Methylmercury seed dressings marketed under the name of Panogen were extensively used in Sweden. Methylmercury is one of the most toxic mercury compounds, and in 1968

Swedish health officials warned against consumption more than once a week of fish from fresh and coastal waters. In industry mercury compounds are employed in prevention of mildew in paint and paper products. Other applications include its use in electrolytic production of chlorine and caustic soda. Mercury is used as a catalyst in the manufacture of many plastics, including vinyl chloride, and it is also widely used in scientific instruments, thermometers, barometers, switches, gauges, and in mercury lamps.

Mercury compounds include both inorganic and organic forms. The latter forms contain a carbon atom covalently bonded to the mercury atom. Inorganic mercury salts are fairly insoluble in water and, thus, are poorly taken up from soil by plants. However, metal mercury is very volatile and can contaminate food directly from the air (its vapor pressure approximately doubles with every 10°C increase). Furthermore, metal mercury aerosols and mercury fungicide compounds are easily absorbed by plants and translocated to other plant parts. Thus, mercury-treated leaves of apple trees and potato plants can lead to contamination of the respective fruits and tubers (Novick 1969). The important organic forms of mercury are aryl mercury (e.g., phenyl mercury), alkyl mercury (e.g., methyl mercury) and alkoxyalkyl mercury (e.g., methoxyethyl mercury). These organic forms are many times more toxic to aquatic and terrestrial animals than the inorganic forms. More importantly, inorganic forms of mercury can be transformed into organic forms through the action of bacteria under anaerobic conditions (e.g., in sewage sludges and lake sediments).

Inorganic mercury compounds accumulate in the liver, intestinal lining, and kidneys. In the kidneys, mercury damages the tubules that are important in readsorption of salts and sugars from the urine (hence its diuretic properties). Mercury metal rapidly diffuses through the alveolar membrane and reaches the brain where it interferes with mental functions and coordination, causing characteristic tremors. The aryl mercury salts when introduced into animals break down into inorganic mercury compounds and behave in the body accordingly. The alkyl mercury compounds, however, do not readily break down and become fairly uniformly distributed throughout the body (Grant 1969). Methyl mercury readily penetrates the brain membranes and affects the areas associated with coordination and visual perception. Severe poisoning can lead to disintegration of brain cells.

There are several instances of widespread mercury poisonings from environmental sources. In the early 1960s several instances of methyl mercury poisoning occurred in Iraq, Guatemala, and Pakistan (Bakir et al. 1973). These incidents were all related to the use of mercury fungicides in treating wheat seeds which were consumed rather than planted. Between 1953 and 1960 a total of 123 people living in villages near Minamata Bay in Japan had symptoms of tiredness, irritability, headaches, numbness of the limbs, difficulty in swallowing, and vision problems. The disease became known as "Minamata disease." Eventually 46 people died. The cause was methyl mercury released from a plastics manufacturing plant into the Minamata Bay. The local fishermen took their daily catch of fish from the bay home to their families. Fish from the bay had up to 100 ppm mercury with an average of 50 ppm

(Lofroth and Duffy 1969). A similar incident was reported in 1965 in Niigata on the Japanese island of Hon Shu. In 1972 the most catastrophic epidemic of methyl mercury poisoning occurred in Iraq (Bakir et al. 1973). In this incident 6530 people were admitted to hospitals and 459 died. The cause was the use in homemade bread of seed wheat, which had been imported from Mexico and had been treated with a methyl mercury fungicide.

2.6.8.6 Manganese

Manganese is a widely distributed element found in concentrations of 400 to 1500 ppm in rock and 850 to 1000 ppm in soil (Vinogradov 1959; Bowen 1979). It is an essential element for both plants and animals. Manganese enzymes function in photosynthesis in plants, and manganese-activated enzymes in animals are important in cartilage and bone formation (Bowen 1979). Manganese deficiency in animals is associated with retardation of growth, abnormal bone formation, and disturbances in the reproductive and central nervous systems (Waldbott 1978).

Manganese is used in fertilizers, steel alloys, manufacturing of dry cell batteries and glass, welding, and as an additive in gas and oil. Releases to the environment occur in the vicinity of steel manufacturing plants and near manganese mines. Occupational exposures to manganese dusts and fumes have resulted in pneumonia, nasal congestion and nose bleeds, severe psychiatric disorders that can resemble schizophrenia (locura manganica), and neurologic disorders similar to Parkinson's disease (Waldbott 1978; Gough et al. 1979). Chronic exposures mainly effect the central nervous system and result in

memory and emotional disorders. Bowen (1979) reports that 10 to 20 mg/d of manganese is toxic to rats.

Manganese occurs in soils at concentrations such that under low pH conditions it can become mobilized at concentrations sufficient to produce toxicity in plants. Concentrations on the order of 2 to 8 ppm in the soil solution have been reported as toxic to potatoes and cotton (Berger and Gerloff 1947; Foy et al. 1969). Generally, dry weight concentrations on the order of 400 to 1000 ppm in plant tissue are associated with toxicity.

2.6.8.7 Nickel

Nickel is a ubiquitous metal that constitutes about 0.008% of the earth's crust (National Research Council 1975). Average concentrations range from 8 to 12,000 ppm in rock (Vinogradov 1959) and from 40 to 50 ppm in soil (Vinogradov 1959; Bowen 1979). Nickel is resistant to oxidation and corrosion and is used in the production of steel alloys (primarily stainless steel) and white gold, electroplating, nickel-cadmium batteries, and electronic components. Releases to the environment occur primarily around mines, smelters, fabrication plants, and incinerators. Nickel carbonyl, $Ni(CO)_4$, is used in nickel plating, nickel refining, and in the petroleum industry. It can also be produced during incineration of nickel-containing products. Nickel carbonyl is the only organic nickel compound that has been recognized as a systemic human toxicant (National Research Council 1975). It is a recognized carcinogen, and if inhaled, it can be extremely toxic or lethal.

Although nickel is essential for many plants, its toxicity to plants can occur at relatively low concentrations. Soil solution concentrations as low as 2 ppm nickel have been reported by a number of investigators as toxic (Gough et al. 1979). Bowen (1979) reports that 0.5 to 2 ppm in solution is toxic to plants. Dry weight concentrations anywhere from 12 to 250 ppm in leaf tissue have been associated with toxicity in tomato, corn, and tobacco (Sauchelli 1969; Soane and Saunder 1959).

Nickel is probably essential for animal nutrition, and studies of nickel deprivation in experimental animals have produced growth and liver abnormalities (National Research Council 1975). The toxicity of nickel to animals is relatively low, but nickel salts can irritate the mucosal lining of the stomach if ingested. Also, contact dermatitis with symptoms of tiny highly itchy nodes or blebs is a common result of skin contact with nickel (Waldbott 1953). Nickel competes with calcium in nerve and muscle tissue, strongly binds to reactive proteins, and generally prolongs action potentials of these tissues. In high doses, inhalation of nickel compounds has been associated with cancer of the sinuses and lungs in nickel refinery and furnace workers in Wales, Canada, Norway, and Russia (National Research Council 1975). Nickel has also been found to induce cancer in rats, mice, rabbits, guinea pigs, and cats (National Research Council 1975).

2.6.8.8 Lead

Lead is by far the most widespread toxic metal contaminant of the environment. It occurs naturally at average concentrations ranging from 3 to 24 ppm in rocks and from 8 to 35 ppm in soil (Vinogradov 1959;

Haley 1969; Bowen 1979). At such concentrations natural lead poisoning of plants and animals is extremely rare. However, man has been responsible for its global distribution. Murozumi et al. (1969) showed that global lead contamination significantly increased beginning with the industrial revolution of the nineteenth century and increased exponentially with the introduction of tetraethyl lead additives to gasoline in 1923. World production of lead is estimated at 3.2×10^9 kg/y (Dyrssen 1972), and until recently lead was added to petroleum in amounts on the order of 3×10^8 kg/y (Bowen 1979).

Historically, lead has been used for water pipes, cooking vessels, in paint pigments, and in fungicides. These uses have been linked with the decline of the Roman Empire (Gilfillan 1965) and even the deaths of the impressionist artists Goya and Van Gough (Niederland 1972). Leaded gasoline and paints have been responsible for significant contamination of urban areas. Lead can comprise up to 5% (50,000 ppm) of roadside dusts and concentrations up to 2000 ppm in soils have been found near houses with flaking paint (Waldbott 1978).

Lead is fairly immobile in soils and the food chain, and toxicity to plants has not been observed (Gough et al. 1979). However ingestion of lead-contaminated soil by livestock or foods and feeds contaminated by lead dusts and aerosols has led to many instances of lead poisoning of animals and humans. Occupational exposures among miners, smelter operators, automobile finishers and mechanics, traffic policemen, foundry and storage battery workers, and painters have resulted in numerous instances of chronic lead poisoning or plumbism. Children, particularly inner city children, have been particularly susceptible to

plumbism. Their habit of consuming soil, flaking paint, and plaster ("pica") and chewing toothpaste tubes and pencils leads to elevated blood lead levels often requiring treatment or special care. Bowen (1979) states that 1 mg/d lead is toxic and 10 g/d is lethal to man.

Lead accumulates in bones, teeth, and nervous tissue where it replaces calcium. Lead poisoning gives rise to blood disorders, including anemia, nervous disorders, and kidney and heart problems. In early stages of plumbism anemia, headaches, and muscle pains are felt. Later, kidney disorders, jaundice, and gout can occur. In more advanced stages nervous disorders, including drowsiness, loss of balance, lethargy, and epileptic convulsions can occur. In the most advanced stages brain damage and blindness occur. Lead poisoning of children may result in learning disabilities and mental retardation.

2.6.8.9 Selenium

Selenium is not a metal, but it occurs as a by-product in the refining of copper, lead, nickel, gold, and silver ores, and certain selenium compounds (e.g., H_2Se) are extremely poisonous. Selenium is widely distributed with concentrations averaging 0.03 to 0.09 ppm in rock and averaging 0.4 ppm in soil (Waldbott 1978; Bowen 1979). Higher concentrations of selenium can be found in volcanic sulfur deposits, carbonaceous siltstones, and phosphate rock. Superphosphate contains roughly 20 ppm selenium (Oelschlager and Menke 1969), and its application as a fertilizer tends to enrich agricultural soils with selenium.

Selenium is essential to some plants and all vertebrates (Bowen 1979). It is necessary for the function of light receptors in the

retina, involved in decarboxylation processes, and important in fat metabolism. Naturally occurring selenium toxicity to plants has not been observed (National Research Council 1976), but excess soil selenium (primarily in arid regions of the world) may prevent plants without tolerance from growing on high selenium soils. Bowen (1979) reports that soil solution concentrations of 1 to 2 ppm are toxic to plants. Certain plants growing in high selenium soils may accumulate the element to levels toxic to grazing livestock (Gough et al. 1979). Selenium poisoning in the western United States has been widely reported. Gough et al. (1979) report that chronic selenium poisoning occurs in animals consuming grasses containing 5 to 30 ppm selenium. Bowen (1979) reports 1 to 2 mg/d selenium (IV) is toxic to rats, and 5 mg/d selenium is toxic to man.

Selenium toxicity resembles that of arsenic. Under occupational exposures to fumes containing selenium, victims develop nasal congestion, nose bleeds, dizziness, eye irritation, and eventually lung fibrosis. Under chronic selenosis, symptoms include mental depression, pallor, jaundice, weakness, nervousness, dizziness, gastrointestinal disorders, dental caries, and excessive perspiration with a garlic-like odor (Waldbott 1978). Eventually selenium toxicity adversely affects the kidneys, liver, and spleen.

2.6.8.10 Zinc

Zinc occurs in nature in trace quantities, usually in the sulfide form (ZnS) associated with lead and iron. Average concentrations in rock range from 20 to 500 ppm and in soil from 50 to 90 ppm (Vinogradov 1959; Bowen 1979). It is an essential trace element in both plants and

animals and functions in the synthesis of nucleic acids and proteins. It is essential for growth and cell reproduction and plays a part in the development of skin and skeleton. Its uses include, primarily, die-casting alloys and the galvanization of iron and steel, but also, corrosion protection, plating, paint pigments, wood preservatives, algicides, fire retardants, dyes and glazes, antiseptics and astringents, electroplating, deodorants, and rat poisons (National Research Council 1979). As an environmental pollutant it is often encountered in association with other metals, including copper, iron, cadmium, and lead near metal mining, refining, and fabrication industries.

Natural zinc toxicity to plants has been observed, but often effects of other metals in association with zinc are difficult to distinguish (Gough et al. 1979). Most often zinc toxicity to plants occurs in acid soils or contaminated areas near mine spoil areas, industrial areas, and waste disposal sites (National Research Council 1979). Bowen (1979) reports 60 to 400 ppm in soil solution is toxic to plants. Dry weight plant tissue concentrations of zinc in excess of 300 ppm are often associated with toxicity (National Research Council 1979).

There are no recorded instances of zinc toxicity to animals under natural conditions (Gough et al. 1979). Zinc compounds are relatively non-toxic to animals, especially mammals. However, Bowen (1979) reports that 150 to 600 mg/d of zinc in the diet is toxic to man.

Under occupational exposures inhalation of zinc produces a malaria-like illness that causes chills, high fever, depression, nausea,

vomiting, and head and muscle aches. More serious pulmonary disease occurs with massive inhalation of zinc chloride by welders and military personnel using zinc smoke screen compounds. It is reported that the particle size of the zinc oxide and zinc chloride inhaled is responsible for the type and degree of respiratory symptoms (U.S. Department of Health, Education, and Welfare 1968). Excessive ingestion of zinc (e.g., in acid drinks from galvanized containers) produces intestinal disorders, including vomiting, diarrhea, and bowel disorders (Brown et al. 1964).

3. ALTERNATIVE REMEDIAL ACTIONS FOR THE CLEANUP AND RECLAMATION OF CONTAMINATED AREAS

3.1 TERRESTRIAL SYSTEMS

Cleanup of hazardous contaminants on land may involve dispersal, removal and storage, stabilization, or treatment. Dispersal of the contaminant (e.g., flushing a soluble contaminant from soil with large quantities of water) may alleviate a local contamination problem, but if the contaminant is persistent in the environment, then dispersal merely exacerbates a regional or global problem. Removal of the contaminant, usually by containment in barrels and storage in land fills, may simply shift the problem from one geographic location and time frame to another. In both dispersal and removal/storage the hazardous chemicals are made less of an immediate threat to health and environmental effects, but additional management techniques may eventually be necessary. Stabilization is a more permanent method for ultimately handling hazardous materials. Stabilization involves engineering methods to physically alter the hydrology of the contaminated area to isolate the contaminant or to control its dispersal through resuspension by wind and movement by water, thereby preventing subsequent transport into the biosphere. Treatment, however, is the most environmentally "friendly" approach to management of hazardous chemicals. Treatment involves biological, chemical, and physical approaches to detoxify or destroy the hazardous chemicals. The following sections detail the above options for cleanup and decontamination of contaminated land.

3.1.1 Cleanup by Dispersal

Moein (1978) reports that in the southeast United States (Region IV) almost 98% of reported spills of hazardous chemicals involve transportation accidents and the largest number and volume of spilled chemicals are water-soluble substances such as acids, bases, and salts. Many of these substances, at the high concentrations usually associated with a spill, can pose immediate health risks and environmental hazards. Often the response taken is dispersal of the chemical using water jets or firehoses to dilute and remove it from the contaminated area. Spills that contaminate streams or sewers often only require the application of a neutralizing agent to the water because dilution and dispersal are a consequence of downstream transport. Spills on land can be dispersed by flooding the area with the proper flushing agent (usually water) and monitoring seepage subsequent to the flushing through the use of shallow wells. Wright and Caretsky (1981) maintain that flushing of contaminated soil is practical only when the depth of contamination is shallow and the area contaminated is small. The major advantages to dispersal of a hazardous substance are that it is cheap and easily implemented. The major disadvantage is that the substance is spread over a larger area (Unterberg et al. 1981) and possibly transported to an aquatic environment.

3.1.2 Cleanup by Removal and Storage

The most common method of handling hazardous waste and contaminated soil, vegetation, and structures is placement of the material in drums and transportation to a dump site for long-term or

permanent storage (Tucker and Carson 1985). In 1979 the EPA estimated that as much as 52 billion kilograms of hazardous waste are generated in the United States each year (EPA 1979). Approximately 80% of this material is disposed of in nonsecure ponds, lagoons, and landfills. Many of these dump sites are now continuing sources of pollution of groundwater, surface water, air, and food and pose a potential for direct poisoning of man and livestock because of poor judgment in site location, improper design and operational practice, or failure to monitor during operation or after closure (Kiang and Metry 1982). Examples of improper storage and dumping of hazardous substances abound (e.g., Love Canal, Kentucky's "Valley of the Drums," the Lowell, Massachusetts dump site, and Stringfellow acid pits near Riverside, California). It is beyond the scope of this review to adequately address the problems associated with illegal or improper disposal of hazardous materials. However, we will address proper disposal as an option for cleanup of contaminated land.

Landfills operate on two principles: (1) utilization of the absorptive capacity of soils to isolate waste and (2) storage of wastes to isolate them from direct contact with man (Powers 1976). Federal and state regulations govern the design and operation of secured landfills. Although specifics cannot be detailed in this report, each properly sited landfill should have the following characteristics (Powers 1976):

* located in areas of low population density, low alternative land use value, and low groundwater contamination potential,
* away from flood plains, natural depressions, and excessive slopes,
* protected from unauthorized intrusion,

* located in soils with high clay content for reduced permeability and high absorptive capacity,
* near transportation routes,
* near the source of the hazardous material,
* far from water supplies,
* in areas with low rainfall and high evapotranspiration rates, and
* located well above the groundwater table.

Liners, caps, and encapsulation of the hazardous materials may be necessary, depending on regulations or characteristics of the site. Steel drums (55-gallon), alone, with plastic liners, or with polyurethane foam coating are most commonly used to encapsulate hazardous substances prior to storage in secured landfills (Powers 1976); however, encapsulation in concrete, molten asphalt, or plastics is also practiced.

Because of the numerous problems of environmental contamination from landfills, lagoons, and dumps, and the often unpredictable behavior of hazardous substances in the landfill environment, it appears prudent to use the storage option as a temporary solution to cleanup and reclamation of contaminated land areas. The practice has caused numerous environmental problems that are ameliorated only with a great deal of difficulty. Furthermore, dumping hazardous chemicals into landfills or waste sites is increasingly seen as an ineffective and expensive option when costs are examined over the long term (Piasecki 1984). A better alternative is to destroy, detoxify, or recycle hazardous chemicals and remove them permanently from the biosphere.

3.1.3 Decontamination through Stabilization

Stabilization in situ of hazardous chemicals on land is a viable method of preventing transport to subsurface areas and groundwater. It may be the only practical alternative when the contaminated land areas are large, and alternative methods of cleanup or decontamination are too costly. Such stabilization methods involve the control of wind and water, which are the primary mechanisms of contaminant dispersal. Control of dispersal may include surface water runoff control, impermeable barriers, and capping or surface sealing (Wright and Caretsky 1980).

Control of surface water runoff may include drainage or diversion channels, canals, culverts, and dikes; stabilization with vegetation or fine-grained soil cover; impermeable caps; and subsurface drains. Surface water diversion may require construction of channels or canals to divert runoff water around the contaminated area. The Russians apparently employed this stabilization method to a large area of 25 to 1000 km^2 (exact area not known) in the eastern Ural Mountains after the area was heavily contaminated with fission product radionuclides in the winter of 1957-1958 (Trabalka et al. 1980). After 1958, two new reservoirs and a network of canals and dams were constructed to divert water from the Techna River around two contaminated lakes, divert drainage water away from the contaminated land area, and prevent sediment from the contaminated lakes from entering the Techna River.

Stabilization with surface soil and vegetative cover will not prevent surface water runoff, but will reduce erosion and resuspension of dusts. Wright and Caretsky (1980) maintain that a slope of 2 to 5%

will ensure that incident precipitation will runoff to drainage facilities with minimal surface erosion. Application of impermeable clay, cement, or asphalt caps will prevent infiltration by surface water. Any land areas stabilized via this approach would require adequate drainage because the finished surface is impenetrable and undercutting of soil at the edges by precipitation could threaten the integrity of the cover (Smith and Lambert 1978). Subsurface drains (e.g., perforated pipes) will intercept infiltrating precipitation and divert flow to a collection pond. Such drains should be located above the contamination zone, but below the land surface (Wright and Caretsky 1980).

3.1.4 Decontamination by Biodegradation

Biological decontamination of hazardous chemicals is not a new technology. Composting, a form of aerobic digestion, has been practiced for centuries. Today many municipal waste treatment plants commonly use a variety of biological decomposition processes for water and sludge treatment, including activated sludge, trickling filters, aerated lagoons, waste stabilization ponds, anaerobic digestors, and composting. However, recent developments in biological decontamination methods include the genetic engineering of new strains of microorganisms capable of rapidly degrading specific organic compounds.

The biological treatment of hazardous chemicals consists of inoculating soil or other media with microorganisms capable of metabolizing the contaminant into less hazardous products. This process is limited to organic compounds, although inorganic compounds

may be converted to less toxic forms (e.g., valence change) or made less available through their incorporation into the cell walls of the microbes (Kiang and Metry 1982). Often, microorganisms capable of performing the decontamination process are already present in the soil, water, or waste product. The process of biological decontamination, then, involves optimization of the microbe's environment to enhance degradation rates. This optimization may include controls on oxygen levels, addition of nutrients, and control of the microbial populations (Kiang and Metry 1982).

Biological decontamination of hazardous chemicals may be accomplished under either aerobic or anaerobic conditions. Generally, aerobic decontamination proceeds faster than anaerobic decontamination, and results in larger quantities of microbes and microbial waste products. Oxygen is essential for the decomposition of long-chain and aromatic hydrocarbons (Kiang and Metry 1982). Under anaerobic conditions only relatively simple organics, including carbohydrates, proteins, alcohols, and acids, can be decomposed.

The microorganisms decompose organics through the process of dissimilation or catabolism. Dissimilation is an exothermic (energy producing) process that involves oxidation and hydrolysis. Under complete dissimilation, the end products are carbon dioxide and water; under incomplete dissimilation, the end products are lower molecular weight organics, alcohols, aldehydes, and acids. The energy requirements for biological decomposition of hazardous organic compounds are modest. This is due to the fact that the carbon in the compounds to be decomposed is the main source of energy for the microbes. Other

essentials include water, nitrogen, phosphorus, sulfur, potassium, calcium, magnesium, and essential micronutrients. Often these essentials are present in the soil or waste itself.

Many of the techniques to enhance the natural ability of the soil to degrade organics are derived from experience with composting. These techniques involve the addition of essential nutrients and maintenance of the proper carbon-nitrogen-phosphorus ratio, pH and moisture control, maintenance of mixed, acclimated microbial populations, and aeration of the soil. Nutrients may be readily added through addition of municipal waste sludges, manure, and wood chips. If pH levels are kept neutral-to-alkaline, then toxic metals present in the waste or contamination are likely to be present as oxide, hydroxide, or carbonate precipitates (Kiang and Metry 1982). In solution, excess quantities of toxic metals can inhibit microbial metabolism rates, but under proper composting conditions metal inhibition of microorganisms has not been observed (Kiang and Metry 1982). Mixed, acclimated microorganism cultures are more resistant to toxic metals and more rapidly degrade organics compared with pure, unacclimated cultures. Thus, inoculation of wastes or soils with microbial populations from previously contaminated areas can speed up degradation rates. It is important to maintain aerobic conditions, and, therefore, mixing of the soil through plowing or disking is essential. Also addition of crushed lime or wood chips can provide additional porosity to the soil. Moisture control is also important. Excess moisture restricts aeration, but too little moisture can restrict microbial enzyme activity. Studies on municipal composting have established a moisture content of between 63 to 79% as

optimum (Kiang and Metry 1982). Higher moisture contents can be accommodated by adding porous media such as straw, wood chips, manure, or crushed limestone.

3.1.5 Decontamination by Physical and Chemical Processes

The decontamination of contaminated lands by physical and chemical processes involves treatments to detoxify, deactivate, or destroy the contaminant. Such processes might include photodegradation, oxidation, hydrolysis, and incineration.

3.1.5.1 Photodegradation

Photolysis or photodegradation is the process whereby chemical bonds are broken by light energy. In the photolysis reaction light energy intercepted by the compound raises electrons to a higher energy state, and the compound may then undergo a chemical reaction. The effectiveness of light in degrading organic compounds is dependent on the compound structure, light wavelength and energy, and the medium in which the photolysis reaction occurs. According to Kiang and Metry (1982) the effectiveness of photolysis is dependent on three criteria: (1) the radiation source must be sufficiently energetic to produce electron transitions in the target molecule, (2) the radiation must be absorbed by the target, and (3) the breakdown products must be less toxic than the parent molecule.

Dioxin is readily destroyed by sunlight under special conditions (Kriebel 1981). When 2,3,7,8-TCDD is suspended in a thin film of an organic solvent it is broken down by sunlight with a half-life of as little as an hour (Crosby and Wong 1977). However, if the organic solvent is not present, photolysis is dramatically slowed or stopped.

3.1.5.2 Chemical treatment

Chemical treatments to hazardous wastes and soils contaminated by hazardous wastes are designed to physically or chemically transform hazardous materials into less hazardous forms. Such transformations involve oxidation, reduction, dechlorination (hydrogenation), or degradation of the hazardous components of the waste or soil. The techniques employed can range from simply neutralizing strong acids and bases to complex thermal, electrochemical, or microwave techniques. The simpler processes, such as acid or base neutralization, are readily performed in the field as remedial action. The more complex processes are of limited use in situ for reclamation of contaminated lands. These processes would require construction of special facilities on or near the contaminated site. Such specially constructed facilities would result in high cleanup costs in the near term. However, treatment offers the advantages of (1) permanently removing the contaminant from the biosphere and (2) eliminating remedial action costs in the long term should short-term fixes fail to contain or isolate the hazardous materials from the environment. Furthermore, some costs may be recovered if the treatment products can be recycled or sold.

All of the following chemical treatments are primarily targeted at organic materials, but also include methods to alter highly toxic chromium VI to less toxic chromium III. The various methods include the following (Tucker and Carson 1985):

1. neutralization (adding acids to bases and vice versa),

2. oxidation, including, wet oxidation, ozonation, molten salt combustion, microwave plasma oxidation, and electrochemical oxidation,
3. reduction, including treatment with formaldehyde and catalytic reduction with metal powder,
4. dechlorination via catalytic hydrogenation and other techniques, and
5. hydrolysis.

A waste is considered corrosive if it has a pH less than 2 or greater than 12 (Tucker and Carson 1985). Spills involving strong acids [e.g., hydrochloric (HCl), sulfuric (H_2SO_4), nitric (HNO_3), phosphoric (H_3PO_4), and hydrofluoric (HF)] or bases [e.g., ammonia (NH_3), sodium hydroxide (NaOH), and potassium hydroxide (KOH)] are almost always ameliorated in situ via the application of an appropriate neutralizing agent to achieve a near neutral pH. Compounds most extensively used on acids include sodium hydroxide, lime (CaO), periclase (MgO), and magnesite ($MgCO_3$). Hydrochloric and sulfuric acids are most often used on strong bases.

Wet oxidation processes are used to destroy or degrade hazardous chemicals in solid wastes and in waste water streams. In wet oxidation, compounds are destroyed in aqueous solution under high temperatures (175 to 345°C) and pressures (between 2.0×10^6 and 2.0×10^7 Pa) with or without the aid of a catalyst (Tucker and Carson 1985). Often air or oxygen is bubbled through the solution. The Cu^{2+} ion is an effective catalyst for destruction of a variety of organic compounds. Oxidation products include carbon dioxide, alcohols, ketones, carboxylic acids,

chloride, and sulfates. The alcohols, ketones, and carboxylic acids are easily biodegraded. The chlorines and sulfates are derived from chlorinated hydrocarbons and sulfur compounds, respectively, and can be recovered for future economic use.

Ozone is a strong oxidant that can destroy carbon-carbon bonds and aromatic rings. At sufficient quantities it can oxidize any organic hydrocarbon to carbon dioxide and water. Its uses include the electroplating industry for destroying copper, nickel, and zinc cyanides; sewage treatment and rendering plants for destruction of phenols and odors, and the paint and plastics industries for reducing odors (Tucker and Carson 1985). Ozonation has also been used to oxidize organic lead compounds in waste waters into their insoluble oxide forms prior to filtration and removal. Ozone is particularly useful in destroying 2,3,7,8-TCDD (dioxin) with a reported efficiency of 97% (Tucker and Carson 1985). Ultraviolet light radiation increases the reactivity of ozone and can improve its oxidation efficiency.

Molten salt combustion involves oxidation of the hazardous compound below the surface of a salt such as sodium carbonate (Na_2CO_3) or sodium sulfate (Na_2SO_4) at temperatures between 800 and 1000°C. The hazardous organic chemicals and air are fed into a chamber below the surface of the melt, and the heat produced during oxidation is usually sufficient to maintain the molten state of the melt. The primary oxidation products formed are carbon dioxide and water. Hydrochloric acid and sulfur dioxide are also oxidation products that form during oxidation of chlorine- and sulfur-containing compounds. These two products, however, react with the sodium carbonate and are trapped in

the molten salt. Tucker and Carson (1985) report that greater than 99.9% destruction efficiencies have been achieved with molten salt processes for DDT, Malathion, chlordane, and mustard gas.

Under acidic conditions formaldehyde will reduce chromium VI to chromium III. Under basic conditions it will convert free cyanide to substituted acetates. Thus, formaldehyde is used extensively in the tannery and electroplating industries. However, formaldehyde use is of potential concern because of its reported carcinogenic properties. Therefore, other reducing agents, including sulfur dioxide and sodium hydroxide, are commonly used to reduce chromium VI to chromium III. Metal powders of aluminum, iron, and zinc can also be used to reduce organic compounds, including PCBs, chlordane, Kepone, atrazine, and N-nitrosodimethylamine (Tucker and Carson 1985).

Polychlorinated hydrocarbons may be made less toxic by replacing chlorine atoms with hydrogen atoms. This hydrogenation process can be achieved with certain metal catalysts at high temperatures and pressures and is effective for treatment of PCBs and DDT (Tucker and Carson 1985). A mixture of molten sodium metal and polyethylene glycol in the presence of air or oxygen will dechlorinate PCBs, DDT, Kepone, and pentachlorophenol.

Microwave radiation of oxygen results in a plasma that can degrade a variety of substances. The plasma consists of free electrons that disassociate molecular oxygen (O_2) into atomic oxygen, ions, and neutral species. The atomic oxygen reacts vigorously with organic compounds breaking carbon-carbon bonds. Efficiencies of destruction of greater than 99% have been reported for microwave plasma treatment of

Malathion, Arochlor 1242 and 1254, phenylmercuric acetate, and Kepone (Tucker and Carson 1985). Reaction products include carbon dioxide, carbon monoxide, water, and chlorides and sulfates.

Alkaline hydrolysis has been used to degrade a large number of organophosphate and carbamate pesticides. Tucker and Carson (1985) report success of this process for Malathion, parathion, methyl parathion, DDVP, and carbaryl. A 0.5 N sodium hydroxide solution containing 0.05% laundry detergent will hydrolize captan, an imide used as a fungicide for seed corn.

3.1.5.3 Incineration

Powers (1976) defines incineration as "a controlled process that uses combustion to convert a waste to a less bulky, less toxic, or less noxious material." The principal products of incineration are carbon dioxide, water vapor, and ash; minor effluents include sulfur-, nitrogen-, and halogen-containing products that may be of significant environmental concern. Often secondary treatment of these potentially hazardous by-products is accomplished through use of afterburners, scrubbers, and filters. Solid (ash) and liquid by-products of secondary treatments often constitute a hazardous waste, which must be properly treated or stored. Ottinger et al. (1973) list ten types of incinerators:

* open pit incinerators, which are used for trash, tars, and sludges and provide little control over atmospheric emissions of particulates and gasses;

* open incineration, which uses no enclosures to contain the combustion process, is used primarily for waste material on open land and destruction of explosives, often results in incomplete combustion of waste materials, and results in uncontrolled emissions of gasses and particulates;
* multiple chamber incinerators, which provide primary combustion of wastes and secondary combustion of gasses;
* multiple hearth incinerators (Herreshoff furnaces), which are commonly used for sewage, sludges, tars, solids, gasses, and combustible liquids, provide for complete destruction of the waste, and produce inert, sterile ash;
* rotary kiln incinerators, which are used for solids, liquids, and gasses and provide for high efficiency destruction of wastes because of the mixing provided by the rotation of the cylindrical combustion chamber;
* fluidized bed incinerators, which use forced air to agitate a heated sand bed, providing for complete combustion of wastes and minimal production of nitrous and sulfur dioxides;
* liquid combustors, which atomize liquids, heat them, and combust the wastes in gaseous form;
* catalytic combustors, which are used to destroy low concentration combustible materials in the gaseous state (see section 3.1.5.2);
* gas combustors (or direct-flame thermal incinerators), which are utilized to dispose of low concentration combustible gaseous waste; and
* flare combustors, which have been utilized extensively in the petroleum and petrochemical industries to burn off combustible gasses into the open air.

Incineration is capable of destroying a very large variety of organic compounds and degrading some inorganic chemicals (Ottinger et al. 1973). However, often secondary treatment techniques will be necessary when the material contains inorganic salts, halogen compounds, sulfur compounds, and nitrogen compounds (Powers 1976). Also, solid and liquid incineration by-products will require additional handling and storage. However, recycling of combustion by-products and waste heat offers the potential for some economic recovery of initial investment and operational costs.

The end product gases, liquids, and solids of incineration are a function of the material combusted and the incineration temperatures. If the hydrocarbons combusted contain halogens, then hydrofluoric acid (HF), hydrochloric (HCl), and chlorine gasses may be produced. Also, incomplete destruction of complex organic molecules through insufficient temperatures or incomplete oxidation may lead to production of by-products that are more toxic than the original material. Furthermore, there is a potential for toxic compounds to form during incineration of highly complex wastes. In Denmark it has been estimated that municipal incinerators are the major source of dioxins and furans entering the Danish environment (Connett 1985).

3.2 GROUNDWATERS AND SURFACE WATERS

Contaminants can enter both surface water and groundwater from a variety of sources. Surface water can receive input from domestic/municipal treatment systems; industrial discharges; airborne contaminants; erosion of pesticides, herbicides, and both natural and

chemical fertilizers from agricultural land; and erosion of mineral resources such as coal and toxicant-bearing end products such as flyash (Pye and Patrick 1983).

3.2.1 Factors Influencing Contaminant Dispersion

The extent of transport and dispersion of contaminants in surface waters depends, in part, on the flow in the receiving water body. The precipitation and amount of contaminant-bearing runoff entering the surface water system and the recharge of groundwater from surface water or from groundwater also influence the availability of various contaminants. In urban areas, stormwater drainage may mobilize a variety of organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and deposit them in surface waters. If recharge from surface waters occurs, contaminants in surface water may infiltrate groundwater aquifers. Unconfined aquifers are the most susceptible to contamination because they are not overlain by impermeable material and are recharged by material seeping through the soil. Confined aquifers, however, may become contaminated when they are tapped for use, when contaminating activities are sited in their recharge areas, or when water leaks into the aquifer from a shallower unconfined aquifer or a deeper saline aquifer (Pye and Patrick 1983).

Schwarzenbach et al. (1983) found that in Switzerland surface water recharge of groundwater was a major source of groundwater pollution. These authors found that volatile organic compounds such as hexachlorobenzene, chloroform, 1,1,1-trichloroethane, trichloroethylene,

and tetrachloroethylene passed through the soil and entered groundwater unchanged. Other compounds (C_1-C_4-benzenes, naphthalene, methyl-naphthalenes, and 1-4-dichlorobenzene) were biotransformed during infiltration and reached groundwater at levels below detection limits. Page (1981) found that the patterns of contamination were very similar in groundwater and surface waters in New Jersey. Groundwater was found to be at least as contaminated with toxic and carcinogenic substances as were surface waters.

3.2.2 Factors Influencing Contaminant Availability

The proximity of chemical use and disposal to surface and groundwaters and the introduction onto and movement of chemicals through the soil medium determines the availability of these chemicals for uptake and dispersion through water. The flow and volume of surface waters determine the hydraulic residence time and greatly influence the concentration of chemical contaminants introduced either from the land surface or directly into surface water by accidental spills or releases. Attenuation of contaminants flowing in the unsaturated zone is generally greater than below the water table because there is more potential for aerobic degradation, adsorption, complexing, and ion exchange of organics and inorganics. The availability of contaminants in both surface water and groundwaters in bound and free forms determines the potential for land contamination from various land and water use practices.

3.2.2.1 Physical and chemical factors

After contaminants have reached groundwater, many physical and chemical processes may operate to reduce their concentration in the water. These processes include (Page 1981):

* dilution,
* buffering of pH,
* precipitation by reaction of water with indigenous wastes or solids,
* precipitation due to hydrolysis,
* removal due to oxidation or reduction,
* mechanical filtration,
* volatilization and loss as a gas,
* biological assimilation or degradation,
* membrane filtration, and
* sorption.

The rate of purification of groundwater is influenced, however, by the rates of movement of both groundwater and the introduced contaminant, which determine the amount of mixing and the extent of contact of the contaminant with geological material. Sorption of contaminants to both geologic and organic material affect the movement of contaminants and thus their rate of dispersion and potential effects (McCarty et al. 1981).

3.2.2.2 Biological factors

Natural biodegradation of trace organics in groundwater may occur rapidly; however, if sufficient organic material is not available to support microorganisms, the time necessary for biotransformation may

range from a few days to a few years (Mackay et al. 1985). While biotransformation in groundwater may occur, there is no assurance that the compounds have been converted to harmless or even less hazardous compounds. Biotransformation of such compounds as PCE, TCE, and TCA can result in the formation of such intermediates as vinyl chlorides, which cannot be further transformed under prevailing conditions (Mackay et al. 1985).

3.2.3 Remedial Measures

Various remedial measures have been or are being developed to remove hazardous chemicals from surface water and groundwaters. These include containment, removal, treatment, and in-situ rehabilitation.

3.2.3.1 Surface waters

While both surface waters and groundwaters may remain contaminated for long periods of time following the introduction of toxic metals or toxic organic compounds, surface waters are more amenable to reclamation or detoxification because, in part, the location of the introduced material is more accessible for sampling, the direction of flow of the surface water is known, and the rate of downstream movement and flow rates are known. Toxic contaminated sediments, where localized, may be dredged from surface waters and deposited in approved land disposal sites (Henningson and Thomas 1981). This process is complicated by the toxic nature of many compounds and the danger of resuspension and downstream transport. Alternatives to this are in-place destruction or in-place fixation. In-place destruction could potentially involve use of ultraviolet radiation/ozonalysis; biodegradation, chemical oxiation,

gamma radiation, and electron beam radiation; however, most of these methods are in the developmental stage and are not currently suitable for field application (Dawson 1981). In-place fixation has been used in the marine environment where silicate-based agents were mixed with bottom sediments to create a cement-like substance; however, information is not yet available on the long-term stability or subsequent releases from these fixed sediments (Dawson 1981).

Floating contaminants may be removed from surface waters by containing and removing them, destruction by biodegradation or combustion, or by dispersal throughout the water column (Dawson 1981). The method employed would depend upon the nature of the chemical and which method would have the least environmental effect. Compounds suspended throughout the water column may be removed by filtration or by the addition of material that will sorb the chemical and then be removed from the water body. In the case of the Kepone contamination of the James River, the proposed clean-up alternatives varied from stabilizing sediments with molten sulfur, to dredging, to using retrievable sorbents. The huge estimated cost, in excess of $3 billion, coupled with the fact that almost any mitigation measures taken would have severe biological impacts on the river, resulted in the decision to let nature take its course (Huggett and Bender 1980). As long as the substrate remains fairly stable and is not resuspended by extreme flows or by dredging, contaminants such as PCBs, Kepone, DDT, mercury, and dioxins become continually sequestered in the sediment and can decrease in their effect and potential for dispersion over time.

3.2.3.2 Groundwaters

Before contaminated aquifers can be restored, the contaminants present, the source(s) of contamination, and the rate and extent of movement of contaminants within the aquifer must be identified. The investigation of groundwater contamination is complex and uncertain because the hydrogeologic environment is not easily observed and varies both spatially and temporally. The rate, direction, and pathways of contaminant movement in groundwater cannot be described or predicted with absolute confidence. In addition, there is uncertainty about which contaminants are present, where they are moving, how fast they are moving, and their concentration as they move (U.S. OTA 1984) (see also Section 3.2.2).

Information to help minimize the uncertainties associated with the movement and presence of contaminants is obtained from sampling wells. In general, the greater the number of sampling points, the less uncertainty about the rate, direction, and pathways of movement of contaminants in the groundwater. Because of differences in patterns of movement within aquifers and differences in the binding affinities of different contaminants to organics, samples must be taken at different locations within the aquifer to get a clear picture of constituents present.

Determination of the contaminants present and their distribution will determine which methods may be used to either restore the aquifer or to minimize the spread of the contaminant(s) within the aquifer. The greater the extent of aquifer contamination, the greater the potential for introduction of the contaminants onto the land surface. There are

a number of corrective action alternatives that may be employed to minimize contaminants in aquifers:

1. containment,
2. withdrawal,
3. treatment, and
4. *in situ* rehabilitation.

Within each of these categories, there are a number of alternatives that were summarized by The Office of Technology Assessment (U.S. OTA 1984).

Pumping groundwater from a contaminated aquifer is the most widely used and most reliable means of reducing the contaminant concentration in groundwater. If the area of the aquifer that is contaminated is small, pumping may be an effective means of contaminant removal. However, if the contaminant is widespread or if the source of contamination has not been identified or eliminated, the distribution of the contaminant within the aquifer may be unaffected by pumping (U.S. OTA 1984). The injection of steam, chemicals, or other additives into the aquifer has been done on an experimental basis to enhance pumping extraction of groundwater; however, this technique has proven effective only for oil recovery. Use of enhanced recovery techniques for aquifer restoration may result in the introduction of additional chemical contaminants into groundwater or volatiles from the aquifer into the atmosphere (U.S. OTA 1984). Pumping groundwater to the surface is a proven technology for the removal of contaminated groundwater; however, once groundwater is pumped to the surface, it must be decontaminated prior to disposal, use, or reinjection. The primary means of decontamination is by filtration.

Treatment of contaminated groundwater may involve physical means such as skimming floating contaminants from groundwater, filtration, reverse osmosis, or either air or steam stripping. Precipitation, ion exchange, or either chemical or biological transformation may also be used to treat groundwater. Use of these treatment methods assumes that the groundwater has already been withdrawn from the aquifer. Treatment can then take place at the source, at the site of contamination, prior to distribution of the groundwater for surface use, or at the site of actual use.

Filtration methods involve physical retention and removal of contaminants either as suspended solids or as dissolved solids, metals, hydrocarbons, and other high molecular weight substances passed through semipermeable membranes. Depending upon the characteristics of the groundwater, pretreatment to remove substances such as iron and magnesium may be necessary for filtration to be effective (Lamarre et al. 1983). Stripping involves the introduction of either air or steam to volatilize organics and such substances as hydrogen sulfide (H_2S) to the atmosphere (U.S. OTA 1984). Some of these treatment methods (e.g., ultrafiltration, ion exchange, and steam stripping) are in developmental stages and lack performance data.

Many chemical methods involve the introduction of additives to coagulate, or sorb selected ions or compounds to the chemical additive. The chemical additive, along with the associated or sorbed contaminant, must be removed from the water and placed in an approved land disposal area (see also Section 3.1.2). Transformation of contaminants to less

toxic substances may be undertaken either by chemical or biological agents or by incineration (U.S. OTA 1984) (see also Section 2.1.4 and 3.1.5.3).

In-situ rehabilitation using chemical or biological degradation has been applied only in research situations and narrowly defined site conditions. Natural biological degradation of groundwater is limited by the availability of adequate nutrients as a primary organic substrate to sustain microorganisms that feed on secondary (contaminant) constituents. There appears to be a minimum concentration to which a single organic material can be decomposed under steady-state conditions. This concentration is a function of the growth and decay coefficients of the bacteria, which in turn are dependent upon temperature, pH, bacterial species present, and the availability of electron acceptors (McCarty et al. 1981).

3.2.4 Engineering Measures for Containment

Containment is designed primarily to prevent contamination or spread of contaminants in groundwater.

3.2.4.1 Diversions and trenches for runoff control

Diversions and trenches are measures designed to limit contaminant mobility and prevent the further spread of contaminants. Slurry and sheet pile barrier walls are constructed in-place, usually below the water table, to limit the horizontal migration of contaminants in the saturated zone, facilitate withdrawal, or channelize groundwater flow. The use of diversions and trenches for surface water runoff control is discussed in Section 3.1.3.

Surface sealants are designed to limit the movement of contaminants from soil either by surface water runoff, mobilization and transport from the site, or by surface water infiltration into contaminated soil. Surface sealants are designed to limit contaminant mobilization and subsequent transport of the contaminants into groundwater. Surface sealants may be clay, concrete, asphalt, or silicon-based covers over the contaminated soils (Wright and Caretsky 1980).

3.3 COMPARATIVE COSTS OF ALTERNATIVE MEASURES

The actual costs of contaminated land cleanup will depend upon the type (composition) and quantity of contamination; its geographic location and extent, the features and accessibility of the contaminated area; and the size, expertise, and experience of the contractor performing the cleanup. In general, the costs per hectare of area cleaned up will be higher for small areas compared with large areas (Powers 1976). Costs will also be significantly higher for highly toxic or hazardous contamination cleanup than for more moderately toxic or hazardous contamination (Cahill and Holman 1981). Costs will include (Powers 1976):

* personnel,
* equipment and fuel,
* maintainence and repair,
* land rental or purchase,
* depreciation or amortization,
* materials,

* administration and overhead,
* miscellaneous tools,
* utilities, and
* insurance.

For landfills, wages are approximately 40 to 50% of total costs, and cover material, administration and overhead, and miscellaneous amount to approximately 20% of the total cost (Powers 1976). Also included in costs will be economic loss of the land. Smith and Lambert (1978) estimate that the market value of farmland in the United States ranges between $160 and $5200 per hectare. Average economic loss per hectare per year would be expected to be the following: $420 for crops, $6500 for commercial forests, and $770 for farmland (Smith and Lambert 1978). These costs represent the average value of crops, timber, and farmland, respectively.

In general, cleanup by dispersal or removal and storage are less than by chemical and physical treatment processes. Cahill and Holman (1981) state that

> "... technologies designed to destroy the waste (e.g., high-temperature incineration) are more expensive than those that are, in actuality, no more than long-term storage techniques (e.g., secure landfills). Thus it costs more money to have the satisfaction of knowing there will be no nightmares in the future."

Much of this additional cost for treatment is due to the high price of capital investment in the treatment facility. For example, a median-sized incineration facility may cost up to $10 million (Cahill and Holman 1981). Additional costs would include operation and fuels.

Table 3.1 compares approximate costs for several methods for cleanup of contaminated land that involve isolation or stabilization of the contaminated land. By far the most inexpensive methods of in situ treatment are fencing off the land and flushing or flooding with water. Application of soil, asphalt, or plastic covers are the most expensive alternatives. Table 3.2 compares approximate costs for removal and storage of contaminated soil and vegetation. Various costs for 55-gallon drums and foam encapsulation of the material and drums are also included. Table 3.3 compares approximate costs for various treatments to degrade or detoxify contaminated soil and vegetation. The least expensive option is composting. Incineration requires the greatest investment in construction costs.

Table 3.1. Costs associated with *in situ* stabilization of contaminated land[a]

Method of cleanup	Average cost ($/ha)	Range ($/ha)
Flushing/neutralization[b]	1800	820-2800
Fencing off land	2700	860-8200
Asphalt cover (0.16 cm)	2700	
Asphalt cover (1.27 cm)	13,000	
Chemical binder covers		490-69,000
Loam cover (10 cm)		3700-8200
Topsoil cover (10 cm)		8200-14,000

[a]Based on Smith and Lambert (1978).
[b]2.54-cm (1.0-in.) depth assumed.

Reference:
Smith, C. B. and J. A. Lambert. 1978. *Technology and Costs for Cleaning Up Land Contaminated with Plutonium*, U.S. Environmental Protection Agency, Office of Radiation Programs, Washington, D.C.

Table 3.2. Costs associated with removal of contaminated vegetation and soil and subsequent storage[a]

Method of cleanup	Average cost ($/ha)	Range ($/ha)
Clearing/grubbing:		
non-wooded areas	1200	
sparsely wooded areas	3100	
wooded areas	4900	
Soil removal and storage:		
55-gallon drum[b]	2	
Foam encapsulation[c]	23	
Clay liner[d]	2900	
Asphalt liner[d]		15,000-30,000
Rubber or hypalon liner[d]		27,000-54,000
PVC liner[d]		12,000-24,000
Offsite disposal:		
Nonretrievable	310,000	270,000-470,000
Retrievable	410,000	370,000-580,000
Federal repository	1,300,000	90,000-1,500,000

[a]Based on Smith and Lambert (1978) unless indicated otherwise.
[b]Cost per each based on Powers (1976).
[c]Cost per m^3 based on Powers (1976).
[d]Powers (1976).

References:

Powers, P. W. 1976. How to Dispose of Toxic Substances and Industrial Wastes, Noyes Data Corporation, Park Ridge, New Jersey.

Smith, C. B. and J. A. Lambert. 1978. Technology and Costs for Cleaning Up Land Contaminated with Plutonium, U.S. Environmental Protection Agency, Office of Radiation Programs, Washington, D.C.

Table 3.3. Costs associated with various types of treatments to detoxify contaminated land[a]

Treatment method	Capital cost ($)	Operating cost ($/MT)[b]
Composting[c]		110
Wet oxidation	100,000	870
Reduction	230,000	570-760
Hydrolysis	320,000	75-110
Ozonation	330,000	1.50-3.80
Incineration[d]	10,000,000	50-1000

[a]Kiang and Metry (1982) unless otherwise indicated.
[b]MT = metric ton (1000 kg).
[c]Total cost, including capital costs.
[d]Cahill and Holman (1981).

References:

Cahill, L. B. and W. R. Holman. 1981. "Siting waste management facilities," in Peirce, J. J. and P. A. Vesilind (eds.), Hazardous Waste Management, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan.

Kiang, Y. H. and A. A. Metry. 1982. Hazardous Waste Processing Technology, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan.

4. ASSESSMENT OF POTENTIAL LONG-TERM IMPACTS OF CONTAMINATED AREAS

4.1 NEEDS FOR ASSESSMENT MODELS

There are thousands of individual and many more combinations of chemical compounds that comprise the 250 to 275 million metric tons of hazardous wastes produced annually in the United States. The ecotoxicological evaluation of each existing chemical and each newly produced chemical is an expensive and time-consuming process. Commercial laboratories offer acute toxicity tests with aquatic vertebrates at costs typically on the order of $1500. Costs increase by an order of magnitude for relatively simple laboratory bioconcentration studies with aquatic vertebrates (e.g., $14,000 to $15,000 for BCF studies using fish). Comparable costs ($20,000 to $70,000) can be expected for simple determinations of chemical toxicity to small birds (ducks, quail, poultry). However, costs can increase dramatically for bioconcentration tests with larger terrestrial vertebrates (e.g., ruminants and wildlife). The number of chemicals of environmental concern, in combination with the expense involved in ecotoxicological studies, precludes the possibility of undertaking comprehensive research on the environmental fate and effect of all chemical constituents of hazardous wastes.

In lieu of extensive field studies, computer simulation models can be developed to assess the potential environmental impact of a toxic substance. Computer models can be implemented at a fraction of the cost required to conduct site specific field investigations on contaminant mobility in food chains and toxicological studies on contaminant effects

in biota. Eschenroeder et al. (1980) present an example of the level of sophistication that can be achieved to describe contaminant fate and effects by modeling. However, the authors point out that there are immense difficulties in satisfying the very large data requirements of sophisticated environmental transport and effects models. Data needed for large-scale environmental modeling of a single compound would typically include measurements of photodegradation, oxidation, hydrolysis, biodegradation, sorption to soil and sediment, volatility, bioaccumulation, and elimination from biota (Mill 1980). Again, due to costs, computer simulation models appear to be useful only for a limited number of well-studied hazardous substances. Their principal value would be for the prediction of the amount of a chemical in a given environmental compartment (i.e., air, water, or soil) as a result of increased or decreased release rates to the environment.

Because of constraints on the testing and modeling of potentially hazardous chemicals, there has been considerable interest in recent years in defining a set of minimum information required for assessing the environmental impact of existing or newly synthesized compounds. Daniels et al. (1985) have recently identified six axiomatic principles of risk assessment based on experience with the Toxic Substances Control Act (TSCA). The first principle deals with the types of data needed to assess the environmental risk of a chemical substance. Three basic questions that must be answered in the evaluation of risk are:

1. What is the chemical's direct exposure to living things?
2. What is the chemical's environmental fate leading to indirect routes of exposure?

3. What are the toxic effects of the chemical on living things related to their exposure?

The second principle states that an evaluation of the manufacturing process and the projected uses of a chemical are important considerations that indicate the extent of data required for environmental assessments. Less data are needed for chemicals produced or used in closed systems as compared to chemicals intended for public dispersal through the commercial market. The third principle is, "Risk assessment is an interactive and interdisciplinary thought process." This is also to say that the process involves considerable common sense in the formation of an informed judgement as to the environmental risk of a chemical. Such judgements often form the basis of preliminary hazard assessments.

4.2 AVAILABLE SCREENING MODELS AND LIMITATIONS

There are two types of simple models currently in popular use for preliminary assessment of the ecotoxicological hazard of a chemical based on a minimum amount of data; they are the "benchmark" approach and an approach using quantitative structure-activity (QSAR) relationships (Haque et al. 1980).

The benchmark approach involves the selection of one or more chemicals, for which considerable environmental data already exist, to represent an important general class of chemicals. Risk assessment for a newly synthesized chemical substance then involves comparison with the benchmark compound in the same chemical class and a prediction of

environmental fate based on known behavior of the reference chemical. Experience has shown that this approach is of limited use because (1) data (toxicity, persistence, solubility, bioaccumulation, etc.) used in environmental risk assessments are often highly variable (and of variable quality) for individual chemicals, and (2) chemicals can rarely be placed in discrete groups, based on chemical structure or other properties, for hazard assessment purposes (Daniels et al. 1980). As stated by Daniels et al. (1980) in their sixth axiomatic principle of risk assessment, "there are very few similarities among chemicals with regard to magnitudes of specific data values ...." Despite this fact, a classic example of the benchmark approach is found in the classification of insecticides into environmentally persistent organochlorines and nonpersistent organophosphates. It can generally be expected that newly synthesized organophosphate insecticides will be quickly degraded based on a number of benchmark compounds, while all organochlorines can be suspected of persistence in soil and bioaccumulation in food chains.

Although intended for a more limited use than the benchmark method, the QSAR approach has found wide application to the preliminary evaluation of environmental risk from hazardous substances. QSAR is based on correlation and the development of a predictive relationship between some empirical measure of biological activity (e.g., toxicity or bioaccumulation) and a simply measured or calculated physicochemical parameter like lipophilicity. Table 4.1 presents a summary of studies that have shown correlations between physicochemical parameters and either bioaccumulation potential or environmental persistence.

Table 4.1 Correlation coefficients for quantitative structure-activity relationships between environmental and physicochemical parameters.

Environmental parameter	Physicochemical parameter	Correlation coefficient	Number	Reference
Bioaccumulation				
Ruminants	Octanol:water	0.58	66	1
		0.79	23	2
	Water solubility	-0.73	53	1
		-0.82	23	2
Nonruminants	Octanol:water	0.59	56	1
	Water solubility	-0.70	37	1
Birds	Octanol:water	0.73	47	1
	Water solubility	-0.69	33	1
Fish	Octanol:water	0.76	36	3
		0.91	84	4
		0.78	100	5
	Water solubility	-0.66	50	3
		-0.81	71	1
	Molecular connectivity	0.97	20	6
Soil Persistence				
Sorption	Octanol:water	0.86	45	3
		0.71	41	1
	Water solubility	-0.84	106	3
		-0.72	64	1
	Molecular connectivity	0.97	37	7
Degradation	Octanol:water	0.32	106	1
	Water solubility	-0.39	143	1

References:

1. Garten, C. T., Jr. and J. R. Trabalka. 1983. "Evaluation of models for predicting terrestrial food chain behavior of xenobiotics," Environ. Sci. Technol. 17:590-595.
2. Kenaga, E. E. 1980. "Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties," Environ. Sci. Technol. 14:553-556.
3. Kenaga, E. E. and C. A. I. Goring. 1980. "Relationships between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota," pp. 78-115, in Eaton, J. G., P. R. Parrish, and A. C. Hendricks (eds.), Aquatic Toxicology, ASTM TP 707, American Society for Testing Materials, Washington, D.C.

References for Table 4.1 (Continued):

4. Veith, G. D., K. J. Macek, S. R. Petrocelli, and J. Carroll. 1980. "An evaluation of using partition coefficients and water solubility to estimate bioconcentration factors for organic chemicals in fish," pp. 116-129, in Eaton, J. G., P. R. Parrish, and A. C. Hendricks, (eds.), Aquatic Toxicology, ASTM STP 707, American Society for Testing and Materials, Washington, D.C.
5. Trabalka, J. R. and C. T. Garten, Jr. 1982. Development of Predictive Models for Xenobiotic Bioaccumulation in Terrestrial Systems, ORNL-5869, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
6. Sabljic, A. and M. Protic. 1982. "Molecular connectivity: a novel method for prediction of bioconcentration factor of hazardous chemicals," Chem. Biol. Int. 42:301-310.
7. Sabljic, A. 1984. "Predictions of the nature and strength of soil sorption of organic pollutants by molecular topology," J. Agr. Food Chem. 32:243-246.

Two physicochemical parameters that are commonly used as independent variables for QSAR are water solubility and the octanol-water partition coefficient (K_{ow}). However, the empirical nature of both these parameters limits their usefulness as independent variables for making predictions about environmental fate based on QSAR. Water solubility and K_{ow} are difficult to precisely determine for hydrophobic chemicals due to the effects of chemical purity, solvent purity, interactions with container surfaces, and differences in measurement techniques. Given these contraints, reported water solubility data may only be accurate within an order of magnitude for some chemicals (Trabalka and Garten 1982). Octanol-water partition coefficients have not been determined for many chemicals. However, they can be predicted from correlations with water solubility (Kenaga and Goring 1980) or calculated from chemical structure based on well established techniques (Leo et al. 1975; Hansch and Leo 1979). However, errors in calculated values can arise because of difficulties in predicting the effects of some steric or electronic factors based on molecular theory. Experimental determinations of K_{ow} by standard batch techniques are difficult for lipophilic chemicals with log K_{ow} values greater than 4 (Veith et al. 1979b), and this is one reason why calculated and experimentally determined values of K_{ow} for the same chemical may vary by one to two orders of magnitude (Kenaga and Goring 1980; Garten and Trabalka 1983; Sabljic and Protic 1982). New experimental techniques for direct measurement of K_{ow}s for highly lipophilic chemicals, however, have been introduced (Woodburn, Doucette and Andren 1984).

Low precision in the determination of octanol-water partitioning or water solubility data, along with orders of magnitude variability about predictions based on regression equations, have been recognized as shortcomings to the present QSAR approach for forecasting environmental fate of potentially hazardous organic chemicals (Kenaga and Goring 1980; Kenaga 1980; Sabljic and Protic 1982; Garten and Trabalka 1983). For example, actual and predicted values of bioaccumulation based on regressions against water solubility or octanol-water partitioning can differ by approximately an order of magnitude or more (Kenaga 1980; Kenaga and Goring 1980).

The imprecision of QSAR when considering large numbers of heterogeneous and dissimilar chemicals has led to admonitions against overdue reliance on this approach, in lieu of traditional and well established, although expensive, methods for determining bioaccumulation of organic chemicals in terrestrial vertebrates (Garten and Trabalka 1983). Caution must be exercised in the use of QSAR for predicting the environmental fate of organic chemicals that are ionizing, or the bioaccumulation potential of organics, like methyl mercury or PAHs, that covalently bind to proteins. The latter compounds exhibit bioaccumulation factors that are substantially higher or lower than those expected on the basis of their octanol-water partitioning. In addition, their toxicological properties are not directly related to bioaccumulation in animal fat, but rather accumulation in other body tissues.

Problems with QSAR models may be reduced by the use of less empirical parameters upon which predictions of bioaccumulation or

biological activity are based. Sabljic and Protic (1982) have proposed the use of molecular connectivity indices for QSAR in place of parameters like K_{ow} or water solubility. Molecular connectivity indices are based on molecular topology (the number and types of atoms and chemical bonds). The indices are calculated for chemicals, thereby eliminating many uncertainties associated with measurements. Molecular connectivity indices are reported to be highly correlated with soil sorption coefficients for nonionic organic chemicals (Sabljic 1984) and also highly correlated with bioaccumulation of organics in fish (Sabljic and Protic 1982). Molecular connectivity is a promising approach to circumvention of some precision problems associated with present QSAR methods.

The imprecision of regression equations between bioaccumulation factors and physicochemical properties has also led to an alternative proposal of screening levels for determining the bioaccumulation potential of organic chemicals. A screening level model is used to classify a chemical into a nonhazardous or potentially hazardous category, and does not involve the same requirements of precision and accuracy inherent in statistical models. For example, Garten and Trabalka (1983) reported that a log K_{ow} greater than or equal to 3.5 can be used to identify compounds with high bioaccumulation potential. In mammals and birds, compounds with a log K_{ow} less than 3.5 do not exhibit bioaccumulation factors in fat greater than 0.3. In fish, compounds with log K_{ow} less than 3.5 exhibit bioaccumulation factors (from water to fish) less than 1000 (Trabalka and Garten 1982). This screening level does not successfully identify compounds such as methyl

mercury, which is an example of a "false negative" classification, or wrongly classifying a compound as nonbioaccumulating. Methyl mercury has a log K_{ow} of 1.48 and an observed bioaccumulation greater than 0.3 in brain, liver, and kidney tissue. Methyl mercury accumulates by binding to certain proteins, rather than by partitioning into lipids; therefore, an index of lipophilicity (K_{ow}) does not reflect its actual bioaccumulation potential. Experience shows that the frequency of "false positives" (wrongly classifying a compound as hazardous) is approximately 20 to 40% with the adoption of a screening level for bioaccumulation of log K_{ow} equal to 3.5 (Trabalka and Garten 1982; Garten and Trabalka 1983).

The same screening level that will identify compounds that potentially bioaccumulate in mammals, birds, or fish will also identify compounds that migrate through soil. Schwarzenbach et al. (1983) reported that persistent organic chemicals with log K_{ow} values less than about 3.7 exhibited rapid transport from river water into groundwater. Nonetheless, the use of a single physicochemical parameter to identify potential problem chemicals oversimplifies the many other aspects in evaluations of environmental hazard.

4.3 MULTIVARIATE MODELS FOR HAZARD ASSESSMENT

A screening level model for assessing potential ecotoxicological effects based on a minimum set of several simple chemical properties has been suggested by Gillett (1983). Briefly, this model proposes that testing requirements for a chemical can be determined by knowledge of three properties: environmental persistence, bioaccumulation, and

volatility. Major categories of ecotoxicological hazard in Gillett's screening model are defined based on degradation half-time, octanol-water partitioning, and Henry's law constant (H_c). Chemicals of serious concern for persistence and bioaccumulation are those that have the following combination of properties: log K_{ow} greater than 3.5, persistence half-time greater than 14 d, and log H_c less than -2.86 (many chemicals with log H_c greater than 2 are gaseous). Persistent chemicals with log K_{ow} values less than 3.5 and log H_c less than -2.86 may also be of concern from the standpoint of mobility in soil and plant uptake. Compounds with persistence half-times less than 0.1 d or with log K_{ow} values greater than 7 or with log H_c values greater than 2 are classified as being of low ecotoxicological concern (Gillett 1983). This model does not apply to organometallic, highly ionized, gaseous, polymeric, and/or covalently reacting chemicals. Beyond these limitations, Gillett's screening system can be applied with minimum data requirements for the purpose of determining if a chemical is of ecotoxicological concern and what testing needs to be considered in its hazard evaluation.

A shortcoming of all existing methods for hazard assessment is that chemicals are evaluated as single compounds independent of other substances in waste mixtures. Although this approach overlooks the possibilities of environmental problems resulting from reactions or interactions of chemicals in soil and biota, current methods are not sophisticated enough to evaluate the ecotoxicological hazard of wastes as mixtures. Nonetheless, in a chemical mixture, all other chemicals have the potential to become variables affecting the ecotoxicological

properties of a single constituent. Past research has shown that the environmental behavior of single compounds can be modified by the presence of other chemicals. For example, Stojanovic et al. (1972) found that mixtures of pesticide formulations were more biodegradable in soil than single compounds when at least one of the chemicals in the mixture was rapidly degraded. Although not well studied, ecotoxicological interactions between chemicals may be less frequent than expected. For example, Nash and Harris (1973) tested 165 combinations of pesticides in soil on oats and cucumbers and found that only 13 combinations indicated the occurrence of a phytotoxic interaction between chemicals on at least one of the plant species. More research is needed to determine the potential for interactions between chemicals in waste mixtures, the ecotoxicological consequences of such mixtures, and to determine to what extent the environmental behavior of single chemicals can be modified by the presence of other chemicals.

5. SUMMARY AND CONCLUSIONS

5.1 SOURCES OF CONTAMINATION

The annual production of nonradioactive hazardous wastes by manufacturing industries in the United States exceeds 67 million metric tons. Hazardous chemicals can contaminate land, surface water, and groundwater from a variety of sources, including transportation accidents or spills, domestic and municipal waste treatment discharges, industrial accident and routine discharges, erosion of pesticides, herbicides, and chemical fertilizers from agricultural land, and erosion of mineral resources such as coal and toxicant-bearing products such as flyash. Many of the hazardous wastes of current environmental concern are organic chemicals, including pesticides, nitrosoamines, polynuclear aromatics, halogenated hydrocarbons, aromatic phenols, amines, nitroles, aromatics, and hydrocarbons (acids and esters). The types of releases into the environment include:

1. accidents in storage and handling (e.g., PBB contamination of dairy feed in Michigan),
2. industrial accidents (e.g., the dioxin accident at a chemical plant near Seveso, Italy),
3. illegal or accidental disposal or dumping (e.g., dioxin contamination of soils in Missouri from waste oil that was sprayed on unpaved roads and in dirt arenas to control dust),
4. hazardous waste dumps and landfills (e.g., Love Canal in New York),
5. land use of waste water and sludge,

6. agricultural uses, and
7. industrial products [e.g., polychlorinated biphenyls (PCBs) and phthalic acid esters (PAEs)].

In this report several categories of toxic contaminants are considered, including hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorinated dioxins and furans, polychlorinated hydrocarbon pesticides, polybrominated biphenyls (PBBs), and toxic metals. Briefly, sources of these contaminants are the following;

* Hexachlorobenzene occurs as an industrial waste product in the manufacture of chlorinated solvents and pesticides and is a fungicide used on seed grains. It is globally distributed.
* Polychlorinated biphenyls are industrial chemicals that are widely used for heat transfer fluids, protective coatings, solvents, dielectric fluids in transformers and capacitors, and for improving the resistance of plastics, paints, and rubbers. Sewage outfalls, industrial disposal into rivers, and leachate from dumps and landfills are the major sources of PCB entry into the environment. PCBs are globally distributed.
* Polychlorinated dioxins and furans are toxic impurities that are formed during the production of commercial chlorophenols and herbicides. They have been in use since the 1930s as bactericidal and fungicidal agents; wood, paper, and leather preservatives; and sanitizing agents. Dioxin (TCDD) is a trace contaminant of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), which was one

constituent of chemical defoliants widely used in Vietnam from 1962 to 1971. TCDD has also been found in the environment adjacent to abandoned chemical dump sites, such as Love Canal in New York.

* Chlorinated hydrocarbon pesticides (e.g., DDT) are ubiquitous in the environment because of their former widespread production and agricultural use, as well as their chemical stability and persistence.
* Polybrominated biphenyls are used as fire retardants. In 1973, there was a mixup in handling of the fire retardant "Firemaster" and the nontoxic magnesium oxide feed additive "Nutrimaster" at a Michigan chemical company, resulting in the incorporation of 225 to 450 kg of PBBs into livestock feed.
* Polycyclic aromatic hydrocarbons consist of three or more fused benzene rings. Electric power generation by fossil fuel plants, in addition to forest and agricultural fires, are the most significant contributors to the global PAH inventory.
* Phthalic acid esters are water insoluble, lipophilic, colorless liquids, with high boiling points (>200°C), which are commonly used as plasticizers to promote the durability and flexibility of plastic products. Waste dumps and municipal landfills are a primary source of PAE contamination of the environment because many plastics are eventually disposed of in landfills.
* Arsenic can be found in naturally high concentrations in some soils in England, New Zealand, and Switzerland, but high concentrations in soils and sediments are typically associated with smelting or lead arsenate insecticide applications. Lead arsenate applications to

fruit orchards in the United States have rendered some soils phytotoxic.

* Cadmium occurs in nature in association with sulfide deposits that also contain copper, lead, and zinc; therefore, cadmium contamination often occurs near lead and copper mines, refineries, and smelters. Cadmium is also used in electroplating, batteries, electrical equipment, manufacturing of polyvinyl chloride plastics and fertilizers, and in automobile engines and tires. It has been estimated that incineration of scrap steel, electrical equipment, and automobile parts is responsible for over half of the cadmium released to the environment in the United States each year.
* Chromium is widely used as a metal plating because of its resistance to corrosion and its high lustre. It is also used in producing steel alloys and in cement. It is most commonly released to the environment from chrome-plating industries.
* Copper is found in high environmental concentrations around mines, refineries, and smelters. Copper toxicity to plants is severe, and agricultural use of copper is approximately 70,000,000 kg/y. A mixture of copper sulfate and lime (Bordeaux) is widely used as a fungicide in vineyards. Because copper is negligibly translocated to aboveground plant parts, it is also widely used to clear sewer lines and septic tanks of encroaching plant roots.
* Mercury is widely distributed in nature. Approximately 2.7 million kilograms of mercury are released from coal combustion throughout the world each year. Mercury has many medical, agricultural, and industrial uses. Mercury compounds are used as diuretics, and

mercury amalgams are extensively used as fillings in teeth. In agriculture mercury compounds have been widely used as fungicides under the trade names Ceresan, Argosan, and Upsulan. Alkylmercury compounds are used for the treatment of wheat and barley seeds. Methylmercury seed dressings, marketed under the name of Panogen, have been used extensively in Sweden.

* Manganese is used in fertilizers, steel alloys, manufacturing of dry cell batteries and glass, welding, and as an additive in gas and oil. Releases to the environment occur in the vicinity of steel manufacturing plants and near manganese mines. Manganese occurs in soils at (natural) concentrations such that under low pH conditions it can become mobilized at concentrations sufficient to produce toxicity in plants.
* Nickel is used in the production of steel alloys, including stainless steel, white gold, electroplating, nickel-cadmium batteries, and electronic components. Releases to the environment occur primarily around mines, smelters, fabrication plants, and incinerators. Nickel carbonyl, $Ni(CO)_4$, is used in nickel plating, nickel refining, and in the petroleum industry. It can also be produced during incineration of nickel-containing products.
* Lead is by far the most widespread toxic metal contaminant of the environment. It has been used for water pipes, cooking vessels, in paint pigments, and in fungicides. Leaded gasoline and paints have been responsible for significant contamination of urban areas. Lead can comprise up to 5% (50,000 ppm) of roadside dusts and concentrations up to 2000 ppm in soils have been found near houses with flaking paint.

* Selenium occurs as a by-product in the refining of copper, lead, nickel, gold, and silver ores. High concentrations of selenium can be found in volcanic sulfur deposits, carbonaceous siltstones, and phosphate rock. Superphosphate contains roughly 20 ppm selenium, and its application as a fertilizer tends to enrich agricultural soils with selenium.
* Zinc occurs in nature in trace quantities associated with lead and iron. Its uses include, primarily, die-casting alloys and the galvanization of iron and steel, but also, corrosion protection, plating, paint pigments, wood preservatives, algicides, fire retardants, dyes and glazes, antiseptics and astringents, electroplating, deodorants, and rat poisons. As an environmental pollutant it is often encountered in association with other metals, including copper, iron, cadmium, and lead near metal mining, refining, and fabrication industries.

5.2 HEALTH AND ENVIRONMENTAL IMPACTS

Hazardous nonradioactive chemicals are classified as toxic, reactive, or corrosive. Toxic hazardous chemicals are carcinogenic, mutagenic, teratogenic, or lethal and are a threat to humans and wildlife because of their potential for bioaccumulation in food chains, or their persistence in soils, sediments, or water. Reactive hazardous chemicals may be explosive, flammable, or capable of undergoing spontaneous reaction upon exposure to air, water, or other chemicals. Corrosive wastes are either strongly acidic or basic. Hazardous wastes typically involve complex mixtures of chemicals.

The potential risk to man and the environment of toxic substances is a function of their concentration, environmental persistence, inherent toxicity, and food-chain bioaccumulation potential. Persistence on land is dependent on volitility; leachability, which depends on sorbing capacity of the soil, water solubility, and moisture regime of the area; and degradation rate. In aquatic systems, persistence depends on volatility; degradation rate; and volume, mixing, and flow rate of the receiving water body.

Typically, persistence is measured in terms of the environmental half-time, $T_{1/2}$, or the time required for 50% of an initial amount of chemical to disappear. Disappearance of organic contaminants from soil or sediment often proceeds rapidly in the first few days following contamination due to volatilization and then more slowly weeks following contamination due to biodegradation of the material.

The factors that affect the persistence and fate of hazardous organic chemicals in soil and sediment are the chemical's structure and properties, including water solubility, affinity for lipids, molecular charge, and volatility; soil and sediment properties such as pH, percent organic matter, and clay content; the climate of the area, especially temperature and moisture; the number and type of microflora and fauna; and the form of application. Structure and chemical properties determine sorption, leachability, food-chain transport characteristics, and degradation rates. Soil and sediment properties affect sorption and degradation rates. Temperature affects volatility and both temperature and moisture affect the rate of biological activity, which

results in degradation. Volatility is also affected by the depth of placement. Granular forms of chemicals usually persist longer in soil than liquid forms.

Organic matter is an important absorbant for many organic chemicals in soil and sediment. Un-ionized, nonpolar, and lipophilic compounds can be adsorbed to varying degrees by soil organic matter. Phytotoxicity generally decreases and retention of foreign compounds generally increases with increasing organic matter.

Electrical charge on a compound is one of the most important properties influencing the adsorption and deactivation of organic chemicals in soil. Positively charged or cationic organics are usually very persistent in soils because of their strong adsorption to clay and organic matter, which have net negative surface charges. In the normal soil pH range of 5 to 7, anionic organic chemicals (net negative charge) are not strongly adsorbed by soil. These compounds are more readily leached to groundwater. Such compounds exclude the organochlorines, which are weakly adsorbed by soil organic matter but are poorly leached from soils due to their low water solubilities. For this reason chlorinated hydrocarbons are among the most persistent of all chemicals in soil.

Microbial degradation involves dehalogenation, oxidation, reduction, hydrolysis, and ring cleavage. Since these reactions are biologically mediated, microbial degradation is slowest in cold, dry soil. High concentrations of hazardous organic chemicals in the soil or sediment can alter the composition of microbial populations, favoring the survival of one group over another. Metabolic adaptation, by induction of enzymes needed to metabolize a chemical, often produces an

"enrichment" effect that results in a more rapid degradation of subsequent applications of the chemical.

Organic chemicals that have the greatest likelihood of being bioaccumulated by plants are polar, water soluble compounds. Nonpolar molecules tend to sorb onto the root surface rather than pass into the plant. Thus, plants do not bioaccumulate very nonpolar organic compounds such as chlorinated hydrocarbons beyond levels found in soil. However, it is not necessary for an organic contaminant to accumulate in plant tissue via root uptake and translocation to aboveground tissues. Volatilization is an important pathway for the movement of organic chemical compounds directly from the surface soil to aboveground plant parts.

Bioconcentration or bioaccumulation of organic chemicals is animal-specific because of dietary, behavioral, and physiological differences among species. In general, predators are at the greatest risk of bioaccumulating lipophilic organic contaminants through food chains because of higher concentrations found in their diets. However, ingestion of soil by grazing herbivores or animals that feed on soil invertebrates may result in significant bioaccumulation of toxic chemicals. Some foreign organic chemicals are bioaccumulated in animals in direct proportion to dietary intake, but some organics, including some chlorinated hydrocarbons, bioaccumulate in inverse proportion to intake. Given a constant concentration in the diet, small animal species tolerate less of a toxic compound than larger species. Gender can also be important. Fat levels differ by sex, and egg and milk production are contaminant-voiding processes.

Bioconcentration of organic chemicals is also compound-specific, but is related to the tendency of a chemical to dissolve in body fat. This lipophilic property is commonly measured by the n-octanol:water partition coefficient, K_{ow}. Bioaccumulation factors for organic chemicals in fat are negatively correlated with water solubility and positively correlated with K_{ow}.

The health and environmental impacts of the categories of toxic contaminants examined in detail are briefly summarized below.

* Hexachlorobenzene is highly toxic in humans and produces a wide variety of pathological conditions in animals. Although HCB is volatile and does not persist on surface soil, it is known to accumulate in bottom sediments of rivers, estuaries, and marine systems. Although HCB is slowly metabolized, it is lipophilic, accumulates in animal fat, and exhibits biomagnification in food-chain transfers from fish to birds. Milk is the major route of HCB elimination in cows.
* Polychlorinated biphenyls have a low acute toxicity, compared to organochlorine pesticides; however, PCB mixtures often contain highly toxic impurities, such as chlorinated dibenzofurans. They are environmentally persistent because of their chemical inertness and low water solubility. The more chlorinated forms are more soluble in lipids, more resistant to degradation, and less volatile.
* Polychlorinated dioxins and furans are highly toxic and have been extensively used as herbicides. Toxicity generally increases with the level of chlorination. The most infamous dioxin, 2,3,7,8-TCDD,

is highly chlorinated, persistent in soil, nonpolar, and devoid of biologically labile functional groups. Its uptake by plants is negligible, but TCDD bound to soil is bioavailable.

* Chlorinated hydrocarbon pesticides have been responsible for the reduced reproductive performance and population decline of certain raptors. They are characterized by low water solubility, long persistence times in soil, and high bioaccumulation in animal fat.
* Polybrominated biphenyls are water insoluble, lipophilic compounds used as fire retardants. They do not bioaccumulate to the same extent as PCBs in animal fat, but appear to have a great affinity for avian fat. They show negligible plant uptake and are extremely persistent in soils and sediment.
* Polycyclic aromatic hydrocarbons are aromatic hydrocarbons consisting of three or more fused benzene rings that are very environmentally stable, have variable lipid solubilities, and show some carcinogenic and mutagenic properties. Both biological metabolism and photolysis of PAHs result in production of carcinogenic, mutagenic, or toxic products. These metabolites and decomposition products are of long-term environmental concern. PAHs are poorly taken up by plants, but surface-applied PAHs readily penetrate into plants and dissolve into plant oils.
* Phthalic acid esters are water insoluble, lipophilic, colorless liquids, with high boiling points. PAEs are of low acute toxicity to animals and do not appear to be carcinogens. However, they appear to be teratogenic and mutagenic at low concentrations and to reduce reproduction rates in aquatic insects and fish. They are lipophilic

and have potential to bioaccumulate in animals, but metabolism rates for PAEs in terrestrial organisms are fairly rapid. Plant uptake of PAEs from soil is negligible. In aquatic systems they are metabolized slowly and show long-term persistence.

* Arsenic compounds are extremely toxic to plants and animals. The trivalent arsenites are far more toxic than the pentavalent arsenates. Additionally, arsenic may be carcinogenic. High concentrations in soils and sediments are usually associated with smelting or lead arsenate insecticide applications. Plant uptake of arsenic is very low. High concentrations of arsenic have been reported in seafood, and contaminated water is the most common form of arsenic poisoning in man.

* Cadmium is toxic to all body systems and functions of mammals, and this toxicity is likely associated with cadmium's ability to replace zinc, and other essential elements in several sulfur-containing organic radicals. Mammmals have no homeostatic mechanism for elimination of cadmium from the body, so it accumulates in the liver and kidneys. Cadmium is found naturally in association with copper, lead, and zinc sulfide deposits. Thus, cadmium contamination occurs near lead and copper mines, refineries, and smelters. Excess cadmium has been associated with arterial hypertension, renal tubular dysfunction and softening of the bones ("itai-itai" disease), teratogenic effects, and cancer.

* Chromium is an essential element for sugar and fat metabolism and for the action of insulin, and chromium deficiency produces diabetes-like symptoms, heart disease, and high blood cholesterol. Chromium is

found naturally in the trivalent form, which is stable and relatively nontoxic; the hexavalent forms are irritating, corrosive, and very toxic to plants and animals. Chromium VI is also carcinogenic.

* Copper is essential in trace quantities to both plants and animals. Over 30 copper metalloenzymes are known, and these enzymes function in electron transport during photosynthesis and respiration, as dioxygen reducers, as oxygen carriers, and as catalysts in the oxidation of iron in mammalian blood. Copper toxicity to plants is severe, and it is widely used as a herbicide and fungicide. Copper is the most commonly found toxic metal in aquatic organisms. Sheep appear to have a high sensitivity to copper, but its toxicity to man is moderate. Excessive levels of copper can build up in the liver and central nervous system, and the metabolic inability of the body to excrete copper is the fundamental cause of Wilson's disease.

* Mercury is a widely distributed toxic metal used in fungicides, anaseptics, and diuretics. Mercury compounds include both inorganic and organic forms. Inorganic mercury salts are fairly insoluble in water and poorly taken up from soil by plants. Metal mercury is very volatile and contaminates food directly from the air. The important organic forms of mercury are aryl, alkyl, and alkoxyalkyl mercury, which are many times more toxic to animals than inorganic forms. Inorganic mercury can be transformed into organic forms by anaerobic bacteria in sewage sludges and lake sediments. Inorganic mercury compounds accumulate in the liver, intestinal lining, and kidneys, where it damages the tubules that readsorb salts and sugars from the urine. In the brain, mercury interferes with mental functions and

coordination, causing characteristic tremors. Severe poisoning can lead to disintegration of brain cells.

* Manganese is essential in both plants and animals. Manganese enzymes function in photosynthesis in plants, and in animals they are important in cartilage and bone formation. Deficiencies in animals are associated with retardation of growth, abnormal bone formation, and disturbances in the reproductive and central nervous systems. Releases to the environment occur in the vicinity of steel manufacturing plants and near manganese mines. Exposures to manganese dusts and fumes can result in pneumonia, nasal congestion, nose bleeds, and severe psychiatric and neurologic disorders. Under low soil pH conditions manganese can become mobilized at levels sufficient to produce toxicity in plants.
* Nickel is carcinogenic and nickel carbonyl is recognized as a systemic human toxicant that, if inhaled, can be extremely toxic, or lethal. The toxicity of nickel to plants is severe, but to animals is relatively low. Nickel salts can irritate the mucosal lining of the stomach if ingested and produce contact dermatitis on contact with the skin. Inhalation of nickel compounds has been associated with cancer of the sinuses and lungs. Nickel has also been found to induce cancer in rats, mice, rabbits, guinea pigs, and cats.
* Lead is immobile in soils and the food chain, and toxicity to plants has not been observed. However, many instances of lead poisoning in animals and man have been reported. It accumulates in bones, teeth, and nervous tissue where it replaces calcium. Lead poisoning gives rise to blood disorders, anemia, nervous disorders, kidney and heart

problems, brain damage, and blindness. Lead poisoning of children results in learning disabilities and mental retardation.

* Selenium is essential to some plants and to all vertebrates for the function of light receptors in the retina, decarboxylation processes, and fat metabolism. Naturally occurring selenium toxicity to plants has not been observed, but excess soil selenium may prevent the growth of plants without tolerance in such areas. Plants growing in high selenium soils may accumulate levels toxic to grazing livestock. Selenium toxicity resembles arsenic toxicity. Victims can develop nasal congestion, nose bleeds, dizziness, eye irritation, mental depression, pallor, jaundice, weakness, nervousness, dizziness, gastrointestinal disorders, dental caries, excessive perspiration with a garlic-like odor, and lung fibrosis. Eventually, selenium toxicity adversely affects the kidneys, liver, and spleen.
* Zinc is an essential trace element in both plants and animals and functions in the synthesis of nucleic acids and proteins, growth and cell reproduction, and development of skin and skeleton. Natural zinc toxicity has been observed in plants, but not in animals. Zinc toxicity to plants most often occurs in acid soils or contaminated areas near mine spoil areas, industrial areas, and waste disposal sites. Zinc compounds are relatively nontoxic to animals, especially mammals. Under occupational exposures, inhalation of zinc produces chills, high fever, depression, nausea, vomiting, and head and muscle aches. Excessive ingestion of zinc produces intestinal disorders, including vomiting, diarrhea, and bowel disorders.

In addition to the contaminants described above, there are thousands of individual and many more combinations of chemical compounds which comprise the 250 to 275 million metric tons of hazardous wastes produced annually in the United States. The number of chemicals of environmental concern, in combination with the expense involved in ecotoxicological studies, precludes the possibility of undertaking comprehensive research on their environmental behavior and fate. Thus, computer simulation models are used to assess the potential environmental impact of these chemicals because they can be implemented at a fraction of the cost required to conduct site-specific field investigations on contaminant mobility in food chains and toxicological studies on contaminant effects in biota. The data needed for these models typically include measurements (or estimates) of photodegradation, oxidation, hydrolysis, biodegradation, sorption to soil and sediment, volatility, bioaccumulation, and elimination from biota. Since this type of data is usually lacking for the vast majority of chemicals to be assessed, three approaches, based on minimum data requirements, can be taken. These are the "benchmark," quantitative structure-activity relationship (QSAR), and screening level approaches.

In the benchmark approach one or more chemicals, for which considerable environmental data already exist, are selected to represent a general class of chemicals. Comparison with the benchmark compound is then made to predict the environmental fate based on known behavior of the reference chemical. This approach is limited because chemicals can rarely be placed in discrete groups, based on chemical structure or other properties, and when they are, chemical properties are as

variable within a group as among groups. As a result the benchmark approach allows for qualitative, rather than quantitative, descriptions of environmental fate and behavior.

The QSAR approach is based on correlation and predictive relationships between empirical measurements of biological activity and easily measured physicochemical parameters. Two parameters commonly used as independent variables for QSAR models are water solubility and the octanol-water partition coefficient (K_{ow}). Water solubility is difficult to precisely determine for chemicals with very low solubility and may be accurate only within an order of magnitude. Octanol-water partitioning can be calculated from chemical structure or predicted from correlations with water solubility. Experimental determinations of K_{ow} by batch techniques are difficult for liphophilic chemicals with log K_{ow} greater than 4, and experimentally determined K_{ow}s for a chemical can vary by one to two orders of magnitude. Thus, low precision in the determination of K_{ow} or water solubility and orders-of-magnitude variability about predictions based on regression equations are shortcomings to the QSAR approach.

A screening level model classifies a chemical as either nonhazardous or potentially hazardous. Its use does not require precise or accurate data; thus, danger exists in wrongly classifying a chemical as not bioaccumulating ("false negative"). Methyl mercury is an example. A log K_{ow} equal to 3.5 identifies compounds with high bioaccumulation potential in mammals, fish, and birds, but methyl mercury has a log K_{ow} of 1.48 and accumulates in brain, liver, and kidney tissue. Nevertheless, a screening level model was used to

predict the following based on degradation half-time ($T_{1/2}$), octanol-water partitioning (K_{ow}), and Henry's law constant (H_c):

* <u>Chemicals that persist and bioaccumulate in animal fat</u>

$$\log K_{ow} > 3.5,$$
$$T_{1/2} > 14 \text{ d, and}$$
$$\log H_c < -2.86.$$

* <u>Chemicals that are mobile in soil and taken up by plants</u>

$$\log K_{ow} < 3.5 \text{ and}$$
$$\log H_c < -2.86$$

* <u>Chemicals of low ecotoxicological concern</u>

$$\log K_{ow} > 7 \text{ and}$$
$$T_{1/2} < 0.1 \text{ d or}$$
$$\log H_c > 2.$$

The model does not apply to organometallic, highly ionized, gaseous, polymeric, and/or covalently reacting chemicals. The frequency of "false positives" or wrongly classifying a compound as hazardous is approximately 20 to 40% with the screening level of log K_{ow} equal to 3.5 to assess bioaccumulation.

None of the three types of models are sophisticated enough to evaluate the ecotoxicological hazards of chemical mixtures. More research is needed to determine the potential for interactions between chemicals in waste mixtures, the ecotoxicological consequences of such mixtures, and to determine to what extent the environmental behavior of single chemicals can be modified by the presence of other chemicals.

5.3 COUNTERMEASURES AND COSTS

Cleanup of contaminated land and waters may include dispersal, removal and storage, stabilization and containment, or treatment. Dispersal may alleviate a local contamination, but exacerbate a regional or global problem. Removal and storage shifts the problem from one geographic location and time frame to another. In situ stabilization or containment is a more permanent solution, and involves engineering methods to alter local hydrology or isolate and control contaminant dispersal by wind and water. Treatment involves biological, chemical, or physical detoxification or destruction of the chemical. Surface waters are more amenable to treatment than groundwaters because they are more accessible and flow rate and direction are known. Cleanup of groundwater contamination is complex and uncertain because the hydrogeologic environment is not easily observed and varies both spatially and temporally.

Spills of soluble substances on land or in streams may be addressed through dispersal with water and neutralizing agents. The advantage is that it is inexpensive, roughly $540/ha, and easily implemented; the disadvantage is that contamination is spread over a larger area and potential exists for groundwater contamination. Compounds most extensively used on acids include sodium hydroxide (NaOH), lime (CaO), periclase (MgO), and magnesite ($MgCO_3$). Hydrochloric and sulfuric acids are most often used on strong bases.

The most common method of handling contaminated materials is placement in drums for transportation to and storage in landfills. In terrestrial environments, collection of vegetation and soil is

accomplished through sweeping, scraping, grubbing, or bulldozing. In aquatic environments, sediment may be dredged; floating contaminants may be contained and skimmed; soluble substances may be precipitated, coagulated, or collected via ion-exchange gels and filtered; and suspended solids may be removed by filtration or addition and collection of sorbent material. Contaminants may be removed from small aquifers by pumping and filtering groundwater. Injection of steam, chemicals, or other additives into aquifers to enhance pumping efficiencies has been done experimentally for oil recovery. Enhanced recovery techniques, however, may introduce additional chemical contaminants into groundwater or volatiles from the aquifer into the atmosphere.

Landfills utilize the absorptive capacity of soil to isolate waste and provide storage to prevent direct contact with man and the environment. Properly sited landfills are

* located in areas of low population density, low land use value, low groundwater contamination potential, and low rainfall;
* located in areas where evapotranspiration rates are high;
* away from flood plains, natural depressions, and excessive slopes;
* protected from unauthorized intrusion;
* located in soils with high clay content for reduced permeability and high absorptive capacity and well above the groundwater table;
* near transportation routes and the source of the material; and
* far from water supplies.

However, many landfills are not properly sited. Numerous problems of environmental contamination from landfills, lagoons, and dumps have occurred because of the often unpredictable behavior of hazardous substances in the landfill environment. Therefore, it seems prudent to use landfill storage as a temporary solution to cleanup and reclamation of contaminated land areas until a more permanent solution can be found.

Costs for clearing and grubbing areas prior to removal and storage in landfills are between $1200 and $5000 per hectare. Fifty-five-gallon drums cost approximately $2 each, and encapsulation of the material in foam costs about $23/m^3 of material. Landfill liners to prevent leachate from contaminating groundwaters cost between $3000 and $54,000 per hectare covered. Total costs for offsite disposal of contaminated materials ranges between $270,000 and $1.5 million per hectare.

In situ stabilization of contaminated land may be the only practical alternative when the area involved is large and alternative methods of cleanup or decontamination are too costly. Stabilization prevents transport to subsurface areas and groundwater through control of wind and water, which are the primary mechanisms of contaminant dispersal. Control may include surface water runoff control, impermeable barriers, and capping or surface sealing.

Surface water runoff control may include drainage canals, culverts, and dikes; stabilization with vegetation or fine-grained soil cover; impermeable caps and; subsurface drains. Surface water diversion may require construction of channels or canals to divert runoff water around the contaminated area. Stabilization with surface soil and vegetative cover will not prevent surface water runoff, but will reduce erosion and

resuspension of dusts. A slope of 2 to 5% will ensure that incident precipitation will runoff to drainage facilities with minimal surface erosion. Application of impermeable clay, cement, or asphalt caps will prevent infiltration by surface water. Costs of these covers range from $500 to $69,000/ha for chemical binder covers, to $2700 to $13,000/ha for asphalt covers, to $3700 to $14,000/ha for soil covers.

In situ biological degradation of organics and fixation of toxic metals occurs naturally. However, this treatment process can be augmented by optimizing the microbe's environment to enhance degradation of the contaminant through controls on oxygen levels, moisture, and addition of nutrients. Often, microorganisms capable of performing the decontamination process are already present in the soil, water, or waste product, but degradation rates can be sped up through inoculation of the contaminated area with microorganisms that have already acclimated to the contaminants.

Microorganisms decompose organics through dissimilation, which is an energy producing process that involves oxidation and hydrolysis. Food requirements are the organic contaminant, water, nitrogen, phosphorus, sulfur, potassium, calcium, magnesium, and essential micronutrients. Under aerobic conditions, more complex organics can be treated, and decomposition is faster and more complete than under anaerobic conditions. Therefore, plowing or disking soil or adding crushed lime or wood chips to provide additional porosity enhances degradation rates. Excess moisture restricts aeration, but too little retards enzyme activity. A moisture content between 63 and 79% is optimum and can be achieved by adding mulch, straw, wood chips, manure,

or crushed limestone. Soil pH should be neutral-to-alkaline so that toxic metals will be in unavailable forms and not inhibit microbial activity.

Physical and chemical treatments of contaminated land detoxify, deactivate, or destroy the contaminant. These treatments include photolysis, oxidation, reduction, dechlorination, hydrolysis, and incineration. Such processes are impractical in the field and require construction of special facilities on or near the contaminated site, resulting in high initial cleanup costs. However, treatment permanently removes the contaminant from the biosphere and eliminates potential future remedial action costs. Some costs may be recovered if treatment by-products can be recycled or sold. Briefly the treatments are described below:

* Photolysis or photodegradation breaks chemical bonds by elevating electrons to higher energy states, inducing a chemical reaction in the target compound. Its effectiveness is dependent on the compound structure, light wavelength and energy, and the medium in which the photolysis reaction occurs.
* Wet oxidation of compounds occurs in aqueous solution under high temperatures and pressures with or without the aid of a catalyst such as the Cu^{2+} ion. Oxidation products include carbon dioxide, alcohols, ketones, carboxylic acids, chloride, and sulfates. Wet oxidation treatment plants have been reported to cost $100,000 to construct and operate at a cost of $870 per metric ton of waste. Ozonation can destroy carbon-carbon bonds and aromatic rings and

oxidize any compound to carbon dioxide and water. It will destroy 2,3,7,8-TCDD (dioxin) with an efficiency of 97%. Ozonation plants have been reported to cost $330,000 to construct and operate at a cost of $1.50 to $3.80 per metric ton of waste. Molten salt oxidation occurs below the surface of a salt such as sodium carbonate (Na_2CO_3) or sodium sulfate (Na_2SO_4) at temperatures between 800 and 1000°C. The primary products are carbon dioxide and water with destruction efficiencies as high as 99.9% for DDT, Malathion, chlordane, and mustard gas. Microwave plasma oxidation breaks carbon-carbon bonds with destruction efficiencies of greater than 99% for Malathion, Arochlor 1242 and 1254, phenylmercuric acetate, and Kepone.

* Reduction through use of aluminum, iron, and zinc powders can degrade organic compounds, including PCBs, chlordane, Kepone, atrazine, and N-nitrosodimethylamine. Under acidic conditions formaldehyde reduces chromium VI to chromium III. Sulfur dioxide and sodium hydroxide also reduce chromium VI to chromium III. Treatment plants using reduction techniques have been reported to cost $230,000 to construct and operate at a cost of $570 to $760 per metric ton of waste.

* Dechlorination reduces the toxicity of chlorinated hydrocarbons. The replacement of chlorine atoms with hydrogen atoms can be achieved with metal catalysts at high temperatures and pressures and is effective for treatment of PCBs and DDT. A mixture of molten sodium metal and polyethylene glycol in oxygen will dechlorinate PCBs, DDT, Kepone, and pentachlorophenol.

* Alkaline hydrolysis has been used to degrade a large number of organophosphate and carbamate pesticides, including Malathion, parathion, methyl parathion, DDVP, and carbaryl. Hydrolysis treatment plants have been reported to cost $320,000 to construct and operate at a cost of $75 to $100 per metric ton of waste treated.
* Incineration utilizes combustion to compact, detoxify, and destroy noxious material. The products of incineration are carbon dioxide, water vapor, and ash and sulfur-, nitrogen-, and halogen-containing products, which may require secondary treatment via afterburners, scrubbers, filters, handling, and storage. It has been reported that initial capital costs for construction of an incinerator are $10,000,000 and operating costs range from $50 to $1000 per metric ton of waste incinerated. However, recycling of combustion by-products and waste heat offers the potential for some economic recovery of initial investment and operational costs.

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