

FATE AND PERSISTENCE IN SOIL OF  
SELECTED TOXIC ORGANIC CHEMICALS

PEI Associates, Incorporated  
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FATE AND PERSISTENCE IN SOIL OF  
SELECTED TOXIC ORGANIC CHEMICALS

by

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## FOREWORD

The Exposure Assessment Group (EAG) of EPA's Office of Health and Environmental Assessment has three main functions: 1) to conduct exposure assessments; 2) to review assessments and related documents; and 3) to develop guidelines for Agency exposure assessments. The activities under each of these functions are supported by and respond to the needs of the various EPA program offices. As part of the third function, EAG sponsors projects aimed at developing or refining techniques used in exposure assessments. This study, which is one of these projects, was done for the Office of Emergency and Remedial Response.

In recent years EPA has focused much attention on halogenated organic compounds, which tend to be toxic and refractory and to bind tightly to soil. The degree of persistence of these compounds in soil can be a key variable in estimating ecological and human exposure when they are disposed of or spilled in the environment. This report focuses on an evaluation of the sorptive tendencies for soil of halogenated benzenes, azobenzenes, cyclohexanes, dibenzofurans, dibenzo-p-dioxins, biphenyls, and naphthalenes. The evaluation also addresses how soil characteristics and environmental factors may influence the persistence of these compounds in soil.

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## ABSTRACT

This report reviews the environmental fate and behavior of several toxic organic materials. It summarizes the chemical and physical properties of these materials and discusses how these properties affect their persistence and behavior in the soil/water/air systems.

In general, the organic carbon content of a soil has the greatest effect on the behavior of hydrophobic toxic organic compounds. The organic compounds sorb strongly to the organic matter in the soil. Several equations have been derived that define water solubility relationships. These are partition coefficients between octanol/water and organic matter/water.

Persistence of the toxic organic compounds depends on several environmental factors, including soil organic matter, total precipitation and intensity, temperature, sunlight intensity, and soil texture. Organic chemicals are subject to one or more of seven possible fates: 1) sorption, 2) volatilization, 3) microbial degradation, 4) photodecomposition on the soil surface, 5) translocation to plants, 6) chemical degradation, and 7) leaching to ground water. Some of these fates are directly related to the degree of sorption; i.e., very little of a material that is strongly sorbed will be in solution and available for degradation or movement by the other processes.

Some generalities are presented regarding the environmental conditions and chemical/physical properties that affect persistence and mobility; however, the reader should bear in mind that there are always exceptions to the rule.

Disregarding any interactions between environmental conditions, the following effects might be expected:

- 1) Temperature--The warmer the temperature is, the greater the volatility, the lower the organic matter content of the soil, the more active the microbial population, and the higher the rate of evapotranspiration. The result is a decrease in pesticide persistence.
- 2) Moisture--There is an optimum level of soil moisture for microbial activity. If a soil is too wet or too dry, activity slows down. Volatility is also affected by moisture content; the nature of the effect depends on the solubility of the chemical. The total amount, the intensity, and the frequency of rainfall or irrigation water received affect the movement of chemicals in soil (Bailey 1966).

- 3) Light--Photochemical reactions are directly proportional to the number of photons absorbed by a chemical. Nearness to the equator or an increase in altitude will accelerate photochemical reactions.
- 4) Soil texture--Soil texture is an important factor. Soil organic matter is directly influenced by the soil texture. Coarse (i.e., sandy) soils will normally be low in organic matter; therefore, water percolation will be rapid and the leaching potential of chemical compounds will be high regardless of  $K_{ow}$  or  $K_{oc}$  values. The opposite is true for heavy (i.e., clayey) soils.

The property that affects persistence and mobility most directly is water solubility. Within a class of compounds (e.g., dioxins or PCB's), the higher the degree of chlorination or bromination is, the lower the water solubility and, therefore, the greater the persistence.

Low-molecular-weight compounds with low chlorine content (e.g., chlorobenzene, dichlorobenzene, naphthalene) will be subject to a greater degree of biodegradation, photodecomposition, volatilization, and leaching than will high-molecular-weight compounds with higher chlorine or bromine content (e.g., hexachlorobenzene, dibenzodioxins and dibenzofurans, PCB's, PBB's, and DDT and its related compounds).

The literature search revealed a sparsity of information on many of the compounds discussed in this document, and gaps were numerous. No information was found on biphenylenes and azoxybenzenes.

Half-life estimates between compounds were difficult to compare because of the differences in experimental and/or environmental conditions. If a standard set of conditions were adopted, and half-life estimates were developed for a well-studied compound (e.g., DDT) under each set of conditions, other compounds could be studied under these same standard conditions and half-life estimates could then be calculated relative to the standard materials. These relative half-lives could then be compared and used to predict behavior based on similarities and differences among other compounds of interest.

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## SECTION 1

### INTRODUCTION

The implementation of environmental programs to clean up organic chemicals that have been released onto and contaminated soils requires an understanding of the long-term risk associated with leaving the soil in place or transporting it to an ultimate disposal site. Currently available information on the persistence of highly toxic organic chemicals is too sparse to allow development of exposure assessments with the degree of confidence needed by the regulator or by the public. The U.S. Environmental Protection Agency (EPA) recognizes the need for guidance materials to assist in the determination of long-term human health risks posed by persistent toxic compounds.

The objective of the guidance material in this document is to provide information needed to support procedures for estimating the environmental half-life of compounds having a high affinity for soils. Specific compounds discussed herein were selected from the following groups:

Chlorinated benzenes	Halogenated biphenyls
Chlorinated azobenzenes	Halogenated biphenylenes
Chlorinated azoxybenzenes	Chlorinated naphthalenes
Chlorinated cyclohexanes	Halogenated dibenzofurans
Halogenated dibenzodioxins	

Also identified for investigation were toxaphene, DDT, and hexachlorobutadiene.

Selection of representative compounds or mixtures (e.g., toxaphene, polychlorinated biphenyls) was based on their potential for human toxicity and the availability of information on their behavior in soil (Table 1). Some compounds (e.g., DDT and  $\gamma$ -hexachlorocyclohexane) have been studied by many investigators; therefore, much information is available. Other

compounds, however, including the entire groups of biphenylenes and azoxybenzenes, have not been studied. Because information is sparse on these latter compounds, they are not addressed here.

TABLE 1. REPRESENTATIVE ORGANIC COMPOUNDS SELECTED FOR REVIEW BASED ON POTENTIAL TOXICITY IN THE ENVIRONMENT

Group	Compound
Chlorinated benzenes	Hexachlorobenzene 1,2-Dichlorobenzene
Chlorinated azobenzenes	3,3',4,4'-Tetrachloroazobenzene (TCAB)
Chlorinated cyclohexanes	$\gamma$ -Hexachlorocyclohexane (HCH)
Halogenated dibenzofurans	2,3,7,8-Tetrachlorodibenzofuran (TCDF)
Halogenated dibenzodioxins	2,3,7,8-Tetrachlorodibenzodioxin (TCDD)
Halogenated biphenyls	Polychlorinated biphenyls (PCB's) Polybrominated biphenyls (PBB's)
Chlorinated naphthalenes	Polychlorinated naphthalenes
Related compounds	Toxaphene Hexachlorobutadiene DDT

Before the primary objective of this guidance material could be achieved, several lesser objectives had to be identified and addressed. For example, this study addresses how soil characteristics, physical/chemical processes, biological processes, chemical structure, microorganisms, and interactions influence the persistence of compounds in soils. It also evaluates the influences of various environmental factors (including solar radiation, temperature, moisture, pH, Eh, and the presence of other chemicals) on persistence in and affinity for soils.

Wherever possible, the report includes information on the behavior of toxic organic compounds under varying soil and climatic conditions throughout the United States. Factors responsible for half-life variability under various conditions are also identified.

A method for estimating the half-life of compounds for which no such data are available is discussed. This method uses the  $K_{oc}$  partition coefficient to place compounds with unknown half-lives in a position relative to those whose half-lives are predicted with some degree of certainty. Finally, the relative soil adsorptive characteristics, persistence, and toxicity of the selected organic compounds are presented.

Section 2 of the report provides a review of soil and its physical/chemical properties, including composition and texture, water content, pH, organic matter, cation exchange capacity, and temperature. Section 3 describes each of the major pathways of chemical loss from the soil. Section 4 presents an explanation of partitioning in the environment and includes information on determining the likelihood of each chemical's fate. Section 5 provides information on the persistence, toxicity, and half-life of the specific organic compounds selected for investigation.

The materials used for this report were drawn from an existing literature data base. The sources are cited in the text and included in a list of references. A bibliography of other available sources is also included for the reader's convenience.

## SECTION 2

### SOIL PROPERTIES

This section presents a general review of major soil properties and their interrelated effects. An understanding of the physical and chemical properties of soil is vital to a discussion of the persistence of toxic compounds in that medium.

#### 2.1 COMPOSITION

Soil is a three-dimensional product of nature that has resulted from destructive processes such as the weathering of rock and primary/secondary minerals, microbial decay of organic material, and synthetic processes (e.g., the formation of clays and the development of characteristic compositional layering patterns) (Brady 1974). Soil consists of four major components: 1) inorganic mineral material, 2) organic matter, 3) water, and 4) air. These components exist in solid, liquid, and vapor phases and are finely subdivided and intimately mixed. The ratio of one component to another differs substantially from one location to another.

The inorganic mineral material present in soil consists primarily of quartz, feldspars, silicate clays, and iron and aluminum oxides and hydroxides. Organic matter forms and may accumulate as a result of the decay and synthesis of plant and animal residues. The water and air components of soil are held in the maze of pores located between the inorganic and organic solids. Air moves into those pores that are not filled with water.

Soils that are predominantly mineral in composition generally contain approximately 1 to 5 percent organic matter. In contrast, soils from bogs, swamps, and marshes contain 80 to 95 percent organic matter.

The three recognized broad soil textural classes (classified by the varying size of soil particles) are sand, loam, and clay. Sand refers to soil containing at least 70 percent sand-sized particles (between 0.05 and

2.0 mm in diameter). Sand has a low organic matter content and a high bulk density. (Bulk density is a weight measurement that takes into account pore spaces as well as soil solids.) A high bulk density indicates that the particles generally lie in close contact with each other. Clay refers to soil that has at least 35 percent clay-sized particles (less than 0.002 to 0.005 mm in diameter). Finely textured clay soil has a low bulk density and a relatively high organic matter content. Loam refers to soil that has a relatively even mixture of sand and clay particles (Brady 1974).

The voids between individual soil grains are referred to as soil pores. Their size, shape, and orientation affect the movement of air and water through the soil. The volume of pores in soil (porosity) is expressed as a percentage of a given soil volume.

## 2.2 ORGANIC MATTER

Climate, topography, and vegetation control the levels of organic matter and the rate of its decomposition in soil. The organic matter content of soil has widely ranging effects on the soil's capacity to affix or degrade organic chemical compounds that have been added. Factors affecting the amount of organic matter in soil include soil temperature, soil moisture, the presence of oxidizing agents, and the rate of incorporation. For example, the rate of decomposition of organic matter is restricted in cooler climates; thus, if all other factors are similar, the organic content of soils in cooler northern climates tends to be greater than that in warmer areas.

Organic matter content affects soil microbial activity, cation exchange capacity (CEC), and buffering capacity. Organic soils develop an even lower pH than do acidic mineral soils. Organic matter accounts for a large portion (20 to 70 percent) of the CEC of a soil. The magnitude of the CEC, in turn, determines buffering capacity. Therefore, organic soils show a marked resistance to pH changes compared with that shown by mineral soils.

The introduction of additional organic matter to soil increases soil porosity and decreases bulk density. The additional organic matter also increases the soil's water-holding capacity by increasing the number of small pores, and greater force is necessary to drain small pores than large pores (Bohn et al. 1985, Brady 1974, Khaleel 1981).



Organic matter content is the best single indicator of a soil's ability to adsorb nonionic hydrophobic organic chemicals. It is the primary soil constituent responsible for chemical sorption, and its role is similar in different soils. Table 2 summarizes some pertinent information about the effects of organic matter on the characteristics of soil.

## 2.3 WATER CONTENT

Cohesion (the attraction of water molecules to one another), adhesion (the attraction of water molecules to solid surfaces), and soil porosity affect how a soil retains water and controls its movement and utilization. Generally, stable, coarse-textured soils with large interconnected pores (i.e., sand) have lower adhesive capabilities than fine-textured, unstable soils and thus have a faster water conduction rate. Clay minerals and clay-sized particles tend to clog connecting pore channels, which increases adhesion and reduces water movement. As water movement is reduced, the water content of the soil increases.

The rate of water movement in unsaturated soils is slower than in saturated soils because the air that partially fills many pores must be displaced before the water can move.

The tendency of dry soils to retain organic compounds is stronger, and the amount retained is greater than in wet soils because water molecules compete with and displace sorbed compounds from organic matter present in the soil. As a soil dries out, the hydrophobic organic molecules may become trapped within collapsing clay lattices and not be available for leaching. The tendency of a compound to be adsorbed is inversely related to its tendency to be leached. Compounds that are strongly adsorbed are generally not leached to a significant degree (Bohn et al. 1985, Brady 1974).

## 2.4 SOIL TEMPERATURE

The temperature of the soil affects chemical and biological reaction rates and the absorption and transport of water. Soil temperature depends directly or indirectly on 1) the net amount of heat absorbed by the soil, 2) the heat energy required to bring about a given change in soil temperature, and 3) the energy used to evaporate water.

TABLE 2. GENERAL PROPERTIES OF SOIL ORGANIC MATTER<sup>a</sup>

Property	Remarks	Effect on soil
Color	The typical dark color of many soils is caused by organic matter.	May facilitate warming (by solar radiation).
Water retention	Organic matter can hold up to 20 times its weight in water.	Helps prevent drying and shrinking; improves moisture retention in sandy soils.
Combination with clay minerals	Organic matter joins soil particles into structural units called aggregates.	Permits gas exchange; stabilizes structure; increases permeability.
Chelation	Organic matter forms stable complexes with $\text{Cu}^{+2}$ , $\text{Mn}^{+2}$ , $\text{Zn}^{+2}$ , and other polyvalent cations.	Buffers the availability of trace elements to higher plants.
Solubility in water	Insolubility of organic matter results partially from its association with clay; salts of divalent and trivalent cations with organic matter are also insoluble; isolated organic matter is partly soluble in water.	Little organic matter is lost by leaching.
pH relations	Organic matter buffers soil pH in the slightly acid, neutral, and alkaline ranges.	Helps to maintain a uniform reaction (pH) in the soil.
Cation exchange	Total acidities of isolated fractions of organic matter range from 3,000 to 14,000 mmoles/kg	Increases the cation exchange capacity (CEC) of the soil; from 20 to 70 percent of the CEC of many soils is caused by organic matter.
Mineralization	Decomposition of organic matter yields $\text{CO}_2$ , $\text{NH}_4^+$ , $\text{NO}_3^-$ , $\text{PO}_4^{-3}$ , and $\text{SO}_4^{-2}$ .	Is a source of nutrient elements for plant growth.
Combination with organic molecules	Organic matter affects bioactivity, persistence, and biodegradability.	Modifies the application rate of pesticides for effective control.

<sup>a</sup> Stevenson 1982.

The amount of heat absorbed by the soil is determined primarily by the quantity of effective solar radiation reaching the Earth. Solar radiation levels are affected by latitude and climatic conditions. As latitude decreases, the Sun's rays become more direct and thus increase the amount of radiation reaching the soil level. If latitude is equal, climate affects solar radiation. For example, in a cloud-free arid region, 75 percent of the available solar radiation reaches the Earth's surface; whereas, in a cloudy humid region, only about 35 percent of the solar radiation reaches the Earth's surface.

Soil color, slope of the land, the altitude, and the vegetative cover also affect the amount of energy the soil absorbs. Dark soils absorb more energy than light soils. The closer the angle at which light strikes the Earth is to 90 degrees, the greater the heat that is absorbed. Increased altitude causes climatic changes similar to increased latitude, whereas vegetation has an insulating effect on the ground it covers.

Conduction of solar radiation into the soil is controlled principally by the amount of moisture available. Heat passes from soil to water 150 times more readily than from soil to air. As water content increases, air content decreases and heat transfer increases. In poorly drained soil, large amounts of radiant energy are required to raise the soil temperature. As heat input is increased, the resulting increase in molecular activity of the soil water causes the water to evaporate, which actually has a cooling effect at the soil surface.

Generally, changes in soil temperature occur slowly and lag behind those occurring at the soil-air interface. For example, in temperate regions, surface soil is cooler in winter and warmer in summer than the underlying subsoil.

## 2.5 CATION EXCHANGE CAPACITY (CEC)

Cation exchange capacity is the ability of soil materials to adsorb positively charged inorganic or organic chemicals or compounds. The CEC of different soils ranges from 2 meq/100 g of soil\* to as much as 150 meq/100 g of soil. The CEC differences result primarily from the amount of

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\* Milliequivalents per 100 grams of soil.

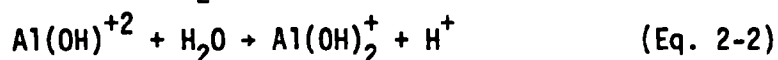
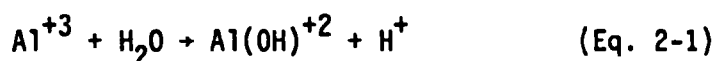
organic matter (20 to 70 percent), crystalline clay structure, and location of ionic substitution in the clay lattice.

Most soils have a slight negative imbalance that is offset by soluble cations. Exchangeable cations compete for sites on the soil solids, and uncharged hydrophobic organic molecules migrate to the organic matter or volatilize if the vapor pressure is high enough.

As the pH rises, hydrogen ions held by the soil are displaced by exchangeable cations and neutralized. Also, as discussed in the following subsection, the removal of aluminum hydroxy ions results in the formation of  $\text{Al(OH)}_3$  and the availability of additional exchange sites on the mineral colloids (Brady 1974, Theng 1974).

## 2.6 pH

Soil pH is controlled by the activity of hydrogen, and the hydrogen activity is influenced by cations present in the soil solution. Soil materials differ in their abilities to furnish hydrogen ions to the soil solution. Hydrogen ( $\text{H}^+$ ) and aluminum ( $\text{Al}^{+3}$ ) ions dominate acid soils. The  $\text{H}^+$  ions contribute directly to the concentration of hydrogen ions in solution. The  $\text{Al}^{+3}$  ions contribute indirectly through hydrolysis, as follows:



Basic pH conditions result from factors that encourage buildup or maintenance of a supply of cations (called exchangeable bases) other than  $\text{Al}^{+3}$  and  $\text{H}^+$  [e.g., calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na)]. Leaching encourages acidity by removing cations that would compete with  $\text{H}^+$  and  $\text{Al}^{+3}$  on an exchange complex.

### SECTION 3

#### CHEMICAL FATES

Complex physical and chemical interactions control the long-term persistence of organic compounds in the soil environment. Persistence is affected by the peculiar chemical and physical characteristics of both the compounds themselves and the soils in which they are found. These characteristics include but are not limited to the rate and amount of soil water movement, soil temperature, soil texture and organic matter content, and the chemical's water solubility, light intensity, vapor pressure, character, shape, molecular size, and configuration.

Organic chemicals entering soil are subject to one or more of seven possible fates: 1) sorption, 2) volatilization, 3) microbial degradation, 4) photodecomposition (on soil surface), 5) translocation to plants, 6) chemical degradation, and 7) leaching to ground water. The fate of a chemical in an environmental system depends greatly on its sorptive behavior. Various processes and factors, such as those listed above, control the extent of compound's entry into these pathways.

The single most important factor governing persistence of organic compounds in soil is the amount of organic matter contained in the soil. Organic compounds tend to be adsorbed to the organic matter in soil, thereby decreasing their availability to the six remaining pathways. Adsorption and desorption of a chemical to organic matter in the soil are referred to collectively as sorption. Factors such as chemical polarity, water solubility, and hydrophobicity affect the extent of the compound's sorption. Generally, the more hydrophobic, less polar, and less water-soluble a compound is, the greater the extent to which it will adsorb to the organic matter in the soil.

The amount of a chemical undergoing sorption governs the amount that is available to be subjected to the other six fates. This is because the movement of a chemical away from its initial deposition site is governed by the amount present in the soil solution and vapor phases. Any molecules that are

not adsorbed to soil organic matter remain in the soil solution. Soil solution is defined as the aqueous liquid phase of the soil and its solutes and consists of ions dissociated from the surface of soil particles and other soluble materials. Organic compounds within the soil solution are available to volatilize, biodegrade, photodecompose, translocate to plants, or leach to ground water. Table 1 presents a list of the organic chemicals selected for evaluation in this document. These chemicals are toxic to humans and appear to have a high affinity for and persistence in soil.

In addition to having an obvious effect on physical transport, sorption can be involved directly or indirectly in degradation. The chemical reactivity of a compound in a sorbed state may differ significantly from that in aqueous solution, both in extent and chemical pathway. Moreover, natural sorbents may indirectly mediate solution-phase processes by altering the concentration of the solution-phase compound or by controlling compound release into the aqueous phase, which may limit the rate of the solution-phase reaction. In addition, natural sorbents introduce into solution a buffered suite of inorganic and organic species that may significantly affect compound reactivity in the aqueous phase.

Because the compounds considered in this report have low polarity and water-solubility, soil pH, hydrolysis, charge distribution, polarizability, and cation exchange capacity are not considered important.

This section addresses the likely fate of each chemical. General conclusions on the likelihood of sorption, volatilization, and degradation by light or microorganisms are presented by groups of chemicals. The relative water-insolubility of these chemicals makes leaching an unlikely fate. Section 5 contains detailed experimental data on measured concentrations of the chemicals in soil, partition coefficients, half-life estimates, and background information, including structure, toxicity, applications, sources, and metabolites, for each individual chemical.

### 3.1 SOIL SORPTION

Natural sorbents may be biotic or abiotic, organic and/or inorganic, or chemical composites thereof. They may range in size from macromolecules to gravel. All the organic compounds of interest are only slightly water-soluble. This limited solubility allows the development of simplistic sorption models with some degree of theoretical legitimacy.

It has long been recognized that sorption of pesticides and related organic compounds on soils determines their fate and transport in the environment. Thus, a considerable amount of data has been collected over the past two decades to characterize sorption on soils and sediments. Since the EPA's development of a list of priority pollutants under the Clean Water Act, data have been and continue to be collected on sorption of organic compounds on soils and sediments.

A number of mathematical equations can be used to describe the convective, diffusive, and dispersive transport of organic compounds during transient water flow as functions of the soil bulk density, hydrodynamic dispersion coefficient, pore-water velocity, concentration in solution, concentration in the sorbed phase, time, and distance moved. Sinks for degradation and plant uptake are ignored.

Sorption/desorption processes can be described as a function of equilibrium or nonequilibrium conditions. For equilibrium conditions, linear and Freundlich isotherm models have been used most commonly for organic chemical sorption on soils and sediments. These equations can be stated as follows:

$$S=KC \text{ (linear)} \quad (\text{Eq. 3-1})$$

and

$$S=K_f C^N \text{ when } N \leq 1, \text{ (Freundlich)} \quad (\text{Eq. 3-2})$$

where  $S$  = Adsorbed-phase concentrations at equilibrium  
 $C$  = Solution-phase concentrations at equilibrium  
 $K, K_f$ , and  $N$  = Empirical constants specific to a sorbent-sorbate combination

For  $N=1$ , Equation 3-2 reduces to Equation 3-1. The values of  $K, K_f$ , and  $N$  are usually obtained by curve-fitting the two equations to measured data.

The value of the sorption coefficients  $K$  or  $K_f$  (also referred to as the partition coefficient) is a measure of the extent of chemical sorption on soils. These values may vary by one order of magnitude or more among several soils and sediments for a given chemical. Multiple regression analyses of  $K$  (or  $K_f$ ) with several physical chemical properties of soil suggest that the soil organic carbon content (OC) may be the single best predictor of sorption coefficients for nonionic and nonpolar compounds. For a given compound, most researchers report that the sorption coefficient normalized with respect to

soil's organic carbon content is essentially independent of soil type. This normalized sorption coefficient, designated as  $K_{oc}$ , is defined as follows:

$$K_{oc} = 100 K/OC \times 100 \text{ for linear isotherms} \quad (\text{Eq. 3-3})$$

and

$$K_{oc} = 100 K_f/OC \times 100 \text{ for nonlinear isotherms.} \quad (\text{Eq. 3-4})$$

The values of  $K_{oc}$  for a broad range of compounds may be found in reviews by Hamaker and Thompson (1972), Rao and Davidson (1980), Kenega and Goring (1981), and Karickhoff (1981). Recent work suggests that a  $K_{oc}$  value for a given compound is also independent of particle-size fractions within or among different soils and sediments (Karickhoff et al. 1979, Rao et al. 1982). All of these findings suggest that organic carbon is the principal sorbent of organic substances in soils and sediments. This does not imply, however, that inorganic soil constituents do not act as sorbents. Sorption on clay minerals is important for cationic pesticides (e.g., the herbicides paraquat and diquat). Because soil organic matter and clay minerals exist in soils largely as clay-metal-organic complexes (Stevenson 1976), however, separating the independent contributions of clay minerals and organic matter to compound sorption may be difficult. The  $K_{oc}$  concept is a practical and useful simplification for estimating sorption of nonionic organic compounds on a broad range of soils. Its use for estimating sorption coefficients  $K$  or  $K_f$  in soils with either very low or very high organic carbon contents, however, may be prone to introduce considerable errors (Hamaker and Thompson 1972).

Although the  $K_{oc}$  value for a given compound is fairly constant (within a factor of two) among different soils or sediments, the  $K_{oc}$  values for different compounds may vary more than several orders of magnitude. Helling and Dragun (1981) note that molecular properties that affect  $K_{oc}$  values include 1) structure and conformation, 2) acidic or basic dissociation constants, 3) aqueous solubility, 4) charge status, 5) polarity and polarizability, and 6) molecular size. These researchers further state that  $K_{oc}$  values reflect the relative affinity of the soil's organic carbon content for the compound and the compound-water interactions. For nonionic compounds, aqueous solubility and  $K_{oc}$  are usually inversely correlated.

Few researchers have investigated the rate at which sorption equilibrium is attained under nonequilibrium conditions. Under conditions of water flow



(in laboratory soil columns or field soil profiles), the contact time may be insufficient to achieve sorption equilibrium between soil-water or sediment-water phases. From batch experiments, Rao and Davidson (1980) concluded that about 60 to 80 percent of the sorption may be complete in less than a minute, whereas the remainder may take one to a few hours. For some compound-soil combinations, sorption may continue at a very slow rate for days or weeks. Although most batch experiments indicate essentially instantaneous or very rapid sorption, flow experiments with packed soil columns suggest that this may not be valid.

When the sorption reactions are instantaneous, equilibrium exists between the solution-phase and sorbed-phase concentrations and is specified by the adsorption isotherm  $S=KC$ . Various rate laws have been proposed to apply when sorption is not instantaneous, depending on how the processes responsible for sorption nonequilibrium were conceptualized. Conclusions regarding the sorption processes, however, are generally applicable to both transient and steady water-flow conditions. For solution concentrations associated with agricultural applications, linear sorption isotherms may be adequate. For applications dealing with waste disposal on land, however, the assumption of linear sorption isotherms may lead to serious underestimations of toxic organic compounds leaching in the soil.

Models based on chemical nonequilibrium or physical nonequilibrium are mathematically identical, and the solution to these models would be the same for given initial and boundary conditions. Nonequilibrium conditions are expected only when water movement through the soil is greater than 90 cm/h, a rate that is likely to occur only in sands.

The  $K_{oc}$  value is the best indicator of adsorption (affinity) across all soils (except those very low or very high in organic matter). Accordingly, the information presented in Table 3 indicates that 2,3,7,8-TCDD is very strongly sorbed, whereas dichlorobenzene may be only weakly sorbed.

The addition of chlorine atoms to a base compound decreases water solubility and increases  $K_{oc}$ . For example, Table 4 shows the effects on  $\log K_{oc}$  of increased chlorination of biphenyls and chlorobenzenes. An estimate of  $K_{oc}$  can be made for a highly chlorinated compound (e.g., 2,3,6,7-tetrachloronaphthalene) based on the  $K_{oc}$  of the base compound (naphthalene). Thus, the  $K_{oc}$  for chloronaphthalenes is probably greater than 10,000 ( $\log K_{oc}$

TABLE 3.  $K_{oc}$  VALUES FOR ENVIRONMENTAL ASSESSMENT OF TOXIC ORGANIC SUBSTANCES<sup>a</sup>

Compound	$K_{oc}$	$\log K_{oc}$
TCDD <sup>b</sup>	808,000	5.91
PBBs <sup>c</sup>	219,000	5.34
p,p'-DDT	181,000	5.26
o,p'-DDT	- <sup>d</sup>	
p,p-DDD	80,000	4.90
p,p'-DDE	55,000	4.74
Toxaphene	53,000	4.72
PCBs <sup>e</sup>	5,000	3.70
Hexachlorobenzene	3,900	3.59
Hexachlorocyclohexane	1,000	3.00
Tetrachlorodibenzofuran	-	
Dichlorobenzenes	170 to 251	2.23 to 2.40
Tetrachloroazobenzene	-	
Hexachlorobutadiene	-	
Other related chemicals		
2,4,2',4'-Tetrachlorobiphenyl	32,500	4.51
Naphthalene	6,000	3.78
2-Chlorobiphenyl	1,700	3.23
1,2,4-Trichlorobenzene	501	2.70
Chlorobenzene	223	2.35

<sup>a</sup> Sabljic 1984, Briggs 1981, Karickhoff 1985, McCall et al. 1983.

<sup>b</sup> 2,3,7,8-Tetrachlorodibenzodioxin.

<sup>c</sup> Polybrominated biphenyls.

<sup>d</sup> Information unavailable.

<sup>e</sup> Polychlorinated biphenyls.

TABLE 4. COMPARISON OF CHLORINE CONTENT AND MEASURED LOG K<sub>oc</sub> FOR  
SELECTED COMPOUNDS<sup>a</sup>

Compound	Number of chlorine atoms	log K <sub>oc</sub>
2-Chlorobiphenyl	1	3.23
2,2'-Dichlorobiphenyl	2	3.68
2,4'-Dichlorobiphenyl	2	3.90
2,4,2',4'-Tetrachlorobiphenyl	4	4.51
2,5,2',5'-Tetrachlorobiphenyl	4	4.67
2,3,4,2',5'-Pentachlorobiphenyl	5	4.50
2,4,5,2',5'-Pentachlorobiphenyl	5	4.63
2,3,4,2',3',4'-Hexachlorobiphenyl	6	5.05
2,3,4,5,6,2',5'-Heptachlorobiphenyl	6	5.95
Chlorobenzene	1	2.10
1,2-Dichlorobenzene	2	2.26
1,3-Dichlorobenzene	2	2.23
1,4-Dichlorobenzene	2	2.40
1,2,4-Trichlorobenzene	3	2.70
1,2,3,5-Tetrachlorobenzene	4	3.20
Pentachlorobenzene	5	3.50
Hexachlorobenzene	6	3.59
1,2-Dichloroethane	2	1.28
1,2-Dibromoethane	2 (bromine)	1.56

<sup>a</sup> Source, Sabljic 1984.

>4.0). The higher chlorinated biphenyls are likely to have  $K_{oc}$  levels greater than 50,000 ( $\log K_{oc} > 4.5$ ) because the  $\log K_{oc}$  of the 2,4,2',4'-isomer is 4.51 and the  $\log K_{oc}$  for the 2-chlorobiphenyl isomer is 3.23. Brominated compounds have higher  $K_{oc}$  values than related chlorinated compounds, as illustrated by the halogenated ethanes shown in Table 4. Therefore, brominated compounds have a greater affinity for soils or a greater tendency to leave the aqueous phase.

In addition to  $K_{oc}$ , several other measurements are used to model sorptive behavior of organic compounds in soil. These include  $K_{ow}$ , the octanol-water partition coefficient;  $K_d$ , the soil- or sediment-water partition coefficient; WS, water solubility; and BCF, the bioconcentration factor. Several formulas have been derived empirically to relate  $K_{oc}$ ,  $K_{ow}$ , WS, and  $K_d$  with compound movement within the soil profile and the potential for bioaccumulation in aquatic organisms (Briggs 1981). These relationships exist because all are related to hydrophobicity.

$$\log K_{oc} = 0.52 \log K_{ow} + 0.62 \quad (\text{Eq. 3-5})^*$$

$$\log WS = 0.01 - \log K_{ow} - (0.01 T_m - 0.25) \quad (\text{Eq. 3-6})$$

[ $T_m$  = melting point, °C]

$$\log (1/R_f - 1) = \log K_{ow} + \log OM - 1.33 \quad (\text{Eq. 3-7})$$

[ $R_f$  = mobility factor]

$$\log K_{oc} = 0.74 - 0.55 \log WS \quad (\text{Eq. 3-8})$$

$$\log BCF = 0.85 \log K_{ow} - 0.70 \quad (\text{Eq. 3-9})^*$$

In general, the less water-soluble the compound is, the higher the  $K_{ow}$ ,  $K_{oc}$ ,  $K_d$ , and BCF and the lower the potential for the chemical to move into the ground water phase. Only chemicals with a water solubility greater than 60 ppm are likely to reach ground water (Briggs 1981). Table 5 contains the values of the partition coefficients for each of the chemicals selected for investigation.

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\*Briggs 1981.

The equations and observed data were used to assemble Table 5 for the organic chemicals of interest. Various observed and/or calculated values were used to place each chemical in the appropriate position on the chart. Location is not necessarily precise, as all values for each constant may not fall into the same classification. The accuracy of the table is also limited by the quality of the data used.

### 3.2 VOLATILIZATION

Determining whether the compound of interest is likely to volatilize (diffuse) rapidly, leach downward, or move up and down in the soil profile in response to precipitation and evapotranspiration, requires consideration of the dominant fate or transport path of an organic chemical near the terrestrial-atmospheric interface via diffusion to the air, along with consideration of chemical and biological transformation. Simple diffusion transport models for volatile compounds have been developed with the following important assumptions (Bomberger et al. 1983):

- 1) No chemical transport by water movement occurs.
- 2) The diffusion coefficient is a constant.
- 3) Porosity correction is constant in both time and space.
- 4) Chemicals move between the three soil phases much more rapidly than they diffuse into the air phase. This means that they appear to be in equilibrium.
- 5) Sorption is reversible.
- 6) Soil stays wet.

The fourth and fifth assumptions are the most critical and are probably violated under field conditions. Smith et al. (1978) found that at least one-half hour (hours to days is more likely) was required to achieve adsorption equilibrium between a chemical in the soil water and on the soil solids. Solution of the diffusion equation (Bomberger et al. 1983) has shown that many volatile compounds theoretically have diffusion half-lives of days (e.g., toxaphene, 9 days), whereas those less volatile have diffusion half-lives of months to years. Under actual field conditions, the time required to achieve adsorption equilibrium will retard diffusion, and diffusion half-lives in the soil will be longer than predicted. Numerous studies have reported material bound irreversibly to soils, which also would cause apparent diffusion half-lives in the field to be longer than predicted.

TABLE 5. VARIOUS MEASURED AND ESTIMATED PARTITION COEFFICIENTS  
AND PROPERTIES FOR ENVIRONMENTAL ASSESSMENT OF  
SELECTED TOXIC ORGANIC SUBSTANCES

Compound	WS mg/liter	K <sub>d</sub>	log K <sub>oc</sub>	log K <sub>ow</sub>	Soil thin layer chromato- graphy, RF
Hexabromobiphenyl	0.02-0.006	500	5.34	7.00	0.002
Hexachlorobiphenyl	0.06	150	6.61	6.34	0.006
Tetrachlorodibenzo- p-furan	-	-	-	6.95	-
Tetrachlorobiphenyl	0.017	-	4.51	6.44	-
Tetrachlorodibenzo- p-dioxin	0.002	-	5.91	6.15	-
p,p'-DDT	0.02-0.085	-	5.26	3.98-6.19	-
o,p'-DDT	0.085	-	-	-	-
p,p'-DDD	0.02-0.10	-	4.90	5.06-5.99	-
p,p'-DDE	0.01-0.12	-	4.74	5.43-5.69	-
Hexachlorobenzene	0.006-0.32	6.0	3.59	5.57	-
Tetrachloroazo- benzene	Insol.	-	-	4-5 est.	0.02
Tetrachlorobiphenylene	0.6	50	3.30	5 est.	-
Hexachlorocyclo- hexane	0.15-17	12.4	3.11-3.59	3.80	-
Tetrachloro- naphthalene	-	-	-	-	-
Toxaphene	0.4-7.0	-	4.72	3.30-5.43	0.06
2-Chlorobiphenyl	6	15	3.23	4.72	-
Trichlorobenzene	19	-	-	3.97	-
Biphenyl	-	-	-	-	-
Naphthalene	31	-	3.78	2.38-3.36	-
Dichlorobenzene	100	14.8	2.26	-	-
Upper limit for systemic activity in plants on K <sub>ow</sub> scale					
Chlorobenzene	4	2.35	60	2.84	0.19
Upper limit for leaching of stable chemicals to ground water					
Benzene	1	1.70	600-1791	1	0.44
Dibenzofuran					

<sup>a</sup>Sabljić 1984, Briggs 1981; Karickhoff 1985; McCall et al. 1983; Verschueren 1983; Stratten et al. 1979; Nash CP File 1985; Callahan et al. 1979.

Another important underlying assumption is that the soil stays wet. It is well established that organics bind much more strongly to dry soil than to wet soil; thus, the  $K_{OC}$  of a compound increases when the soil dries out. Therefore, in a dry soil, the relationship defining the volume fraction of the compound in air and water is too low and the estimated diffusion coefficient is too large. Spencer and Cliath (1970) measured dramatic increases in sorption of lindane ( $\gamma$ -hexachlorocyclohexane) as soil moisture was decreased, and Ehlers et al. (1969) showed decreases in the effective soil diffusion coefficient as the soil dried. Because the soil can dry out under field conditions, predicted soil diffusion half-lives will almost always be longer than those that actually occur.

Because the compounds under consideration in this report have low vapor pressures, the following equation can be used to examine diffusion:

$$D_{soil}^W = D^W T_w / H \alpha, \quad (\text{Eq. 3-10})^*$$

where  $D^W$  = compound's diffusion coefficient in free water  
 $T_w$  = correction factor for the soil porosity  
 $H^W$  = Henry's constant  
 $\alpha$  = constant relating the volume fraction of soil that is surrounded by air or water, the fraction of organic carbon, Henry's constant, and soil bulk density.

Diffusion coefficients in water are much smaller than diffusion coefficients in air. For example, for oxygen,  $D^a$  (in air) =  $1.75 \times 10^{-1} \text{ cm}^2/\text{s}$ , but  $D^W$  (in water) =  $2.1 \times 10^{-5} \text{ cm}^2/\text{s}$ . Consequently, the predicted soil diffusion half-lives for volatile compounds range from hours to days, whereas the predicted half-lives for nonvolatile compounds range from weeks to months. This long diffusion half-life for nonvolatile compounds results in a violation of one of the derivation assumptions--that no transport occurs by water movement. Over several weeks a significant fraction of soil water will evaporate, and the movement of water through the pores becomes the principal transport mechanism for dissolved nonvolatile organics. The water evaporation rate determines the compound's mass transport rate, and overall volatilization rates will be slow.

In comparing the leaching potential with the volatilization potential for lindane and toxaphene, Bomberger et al. (1983) stated that lindane does not volatilize by diffusion, but rather by mass transport as a result of

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\* Bomberger et al. 1983.

water evaporation at the soil surface. Toxaphene, on the other hand, is strongly adsorbed and does not move in the soil profile. For toxaphene which is in solution, however, volatilization is predicted to be rapid. The fraction of toxaphene in air is greater than that of lindane in air (Table 6).

TABLE 6. DIFFUSION BEHAVIOR OF TOXIC ORGANIC COMPOUNDS IN A SOIL WITH 10 PERCENT MOISTURE<sup>a</sup>

	log K <sub>oc</sub>	H <sup>b</sup>	$\lambda_s^c$	$\lambda_a^c$	D <sub>soil</sub> , cm <sup>2</sup> /s	Half-life, days
Toxaphene	5.32 <sup>d</sup>	9.0	0.998	$1.4 \times 10^{-3}$	$3.0 \times 10^{-5}$	9
Lindane	3.11 <sup>d</sup>	$5 \times 10^{-5e}$	0.994	$1.2 \times 10^{-6}$	<sup>f</sup>	

<sup>a</sup> Taken from Bomberger et al. 1983.

<sup>b</sup> Henry's constant, estimate based on vapor pressure and solubility.

<sup>c</sup> Fraction of compound in either soil(s) or air(a) phase.

<sup>d</sup> Hamaker and Thompson 1972.

<sup>e</sup> Hamaker 1972.

<sup>f</sup> Not shown. The material cannot diffuse significantly in soil air because of low volatility.

Environmental conditions in and at the soil surface affect the volatility of organic compounds. Drying out the soil surface can cause the solubility of the diffusing organic to be exceeded and crystallization to occur. An increase in soil temperature increases random movement of molecules. In water or when sorbed to the soil surface, these molecules increase in energy as the temperature rises. As their energy increases, the amount escaping from the water or solid phase into the air in the soil also increases. In addition, the activity of the molecules already in the soil's air increases, and they escape into the atmosphere more rapidly.

Soil moisture affects volatility in that the pore volumes of the air and water in the soil change. Changing soil moisture from 10 to 25 percent increases soil half-lives by a factor of 6 for the volatility loss (Bomberger et al. 1983).

The loss by volatility of the organic compounds studied in this report will vary according to compound. Most loss by volatilization comes from the fraction of chemicals in the equilibrated water phase. As indicated earlier, water solubility for most of these chemicals is quite low; thus, little chemical is available for loss by volatilization. Significant amounts of DDT and its congeners are lost through volatilization, however.



Because the system is dynamic and only a small amount of a compound may be in the aqueous phase at any time, that mass in the aqueous phase that is lost will be replenished from the sorbed material. Hence, total mass transferred over a long time period may be significant.

### 3.3 MICROBIAL DEGRADATION

In general, microbial degradation is not significant among the compounds under consideration. The compound may degrade to an intermediate compound in the process and then ultimately degrade to carbon dioxide ( $\text{CO}_2$ ). As with many of the environmental reactions, water solubility seems to influence, either directly or indirectly, the extent of microbial degradation possible.

Lindane and dichlorobenzene, two of the compounds with the greatest water solubility, lowest  $K_{ow}$ , and lowest sorption to organic carbon, degrade much more rapidly than compounds with extremely low water solubility, such as DDT and TCDD.

Among the several factors affecting the potential of a compound to biodegrade are the organic matter content of the soil, additions of organic matter, moisture content, temperature, and degree of chlorination of the molecule. Addition of organic matter to a soil may dramatically increase the microbial population, and organic compounds may be co-metabolized as a result of this growth. Degradation rates are slow, however, and they do not increase with time (Alexander 1981).

Chemical and biological reaction rates are slow in cold soils. The rate of biodegradation also decreases in flooded soils because of lower soil temperature, slower decomposition of organic matter, less availability of nutrients, and slower absorption and transport of water and nutrients into plants. Some compounds, however, degrade under anaerobic conditions, and flooding enhances the degradation rate of these compounds.

Table 7 demonstrates the effect of chlorination on biodegradation rates. Monochlorobenzenes biodegrade rapidly, whereas other chlorobenzenes degrade less quickly. Hexachlorobenzene is particularly resistant to degradation (Freitag et al. 1974).

Microbial degradation of propanil results in the formation of 3,4-dichloroaniline. At high treatment rates, the dichloroaniline can form tetrachloroazobenzene (TCAB) or the oxygenated tetrachloroazoxybenzene (TCAOB) by

TABLE 7. RELATIVE BIOCONCENTRATION, MICROBIAL DEGRADATION, AND PHOTODEGRADATION OF SELECTED ORGANIC COMPOUNDS IN ACTIVATED SLUDGE<sup>a</sup>

Compound	BCF <sup>b</sup>	Microbial degradation, % CO <sub>2</sub> <sup>c</sup>	Photodegradation, % CO <sub>2</sub>
Benzene	1,700	29	15
Chlorobenzene	1,700	31.5	18
1,2-Dichlorobenzene	14,300	0.1	2
1,3-Dichlorobenzene	560	<0.1	5
1,2,4-Trichlorobenzene	1,400	0.1	10
Hexachlorobenzene	35,000	<0.1	2
Biphenyl	2,600	15.2	10
2,2'-Dichlorobiphenyl	6,300	0.1	4
2,4'-Dichlorobiphenyl	9,800	<0.1	3
2,5,4'-Trichlorobiphenyl	32,000	<0.1	6
2,4,6,2'-Tetrachlorobiphenyl	6,500	<0.1	4
2,4,6,2',4'-Pentachlorobiphenyl	27,800	0.3	5
DDT	14,000	<0.1	-
Hexachlorocyclohexane	820	0.1	
Hexachlorocyclopentadiene	2,400	-	50

<sup>a</sup> Source: Freitag et al. 1974.

<sup>b</sup> Bioconcentration factor.

<sup>c</sup> CO<sub>2</sub> represents the ultimate breakdown product, by microbial degradation or photodegradation, of the toxic organic compounds in soil. Percent CO<sub>2</sub> evolved from the soil represents a relative measure of the extent of degradation of the organic compounds. Stable intermediates may be present when the parent is gone and no CO<sub>2</sub> has been evolved.

bimolecular condensation. These compounds are similar in structure to TCDD and are resistant to further microbial degradation (Bordeleau and Bartha 1972). Tetrachloroazobenzene also may be present in technical propanil as a contaminant (Bunce et al. 1979). The PCB's, PBB's, and other organic compounds with high  $K_{ow}$  or  $K_{oc}$  values are also quite resistant to microbial degradation; 2,2'-dichlorobiphenyl degrades so slowly that no metabolites can be detected (Vockel and Korte 1974). Major degradation products of many chlorinated organic compounds are hydroxy analogs. These metabolites may react with existing organic matter to form bound residues. If the metabolite can never be removed, it becomes a part of the organic pool and eventually oxidizes to  $CO_2$  in a manner analogous to all soil organic matter.

### 3.4 PHOTODECOMPOSITION

Many organic chemicals introduced into the environment absorb sunlight and undergo transformations to new molecular species. Because ozone in the atmosphere absorbs ultraviolet light less than 285 nm, only those molecules that absorb energy above 285 nm are expected to undergo photochemical decomposition in sunlight.

The principle behind photodegradation is that it occurs only when a chemical (in its ground electronic state) absorbs a photon or an equivalent energy packet that converts it into a more energetic electronic state having a different electron distribution and thus a different chemistry. The energized molecule may lose energy by going completely or partially back to its initial ground state. Even though the partially energized states are less energetic, many photoprocesses occur from these partially energized states because their longer lifetimes (milliseconds) afford a better opportunity for bimolecular encounters.

Other chemicals can alter the course of photochemical reactions by creating other activated species that may interact with or transfer energy to the compound of interest. The reactions that occur depend on the physical state of the compound, the solvent, and the presence of other reactants (i.e., activators, oxygen, free radical donors, etc.). For example, 2,3,7,8-tetrachlorodibenzodioxin content in soil decreased 70 percent after irradiation with  $2 \text{ mW/cm}^2$ . The addition of xylene-ethyl oleate to the soil led to complete TCDD decomposition after 9 days. The amendments reduced TCDD

content by 50 percent in the subsoil (Liberti et al. 1978). Polychlorinated dibenzodioxins and polychlorinated dibenzofurans undergo photoreductive dechlorination with ultraviolet light irradiation in the presence of an effective hydrogen donor.

Photodecomposition reactions depend greatly on latitude, time of year, climate, and temperature, as these factors can affect the amount of energy that reaches the soil surface to initiate photodecomposition reactions. In soil, photochemical processes are generally not significant (Mill and Mabey 1985), especially if the compound is incorporated in the soil and none is on the surface that is exposed to sunlight.

### 3.5 TRANSLOCATION TO PLANTS

Translocation into plants is a function of the amount of a compound present in the soil solution. Because the compounds considered in this document are highly insoluble, only a small amount is present in soil solution to be absorbed by plant roots. Some solid/solid transfer is possible (i.e., soil organic matter directly to plant root). The amount found on the plant root and ultimately in the plant is a direct function of the  $K_{oc}$  and an inverse function of soil organic matter content. Inasmuch as only small amounts of these compounds have been found in plants, however, this process is not considered significant.

## SECTION 4

### PARTITIONING OF ORGANIC COMPOUNDS IN THE ENVIRONMENT

Having an understanding of sorption processes is an important key in the description of pollutant fate because sorption may significantly alter the physical transport and chemical reactivity of pollutants. Hydrophobic interactions are dominant in the sorption of uncharged organic chemicals to natural sorbents. For composite particulates (i.e., sediments/soils), organic matter is the primary sorbing constituent. Sorption partition coefficients, indexed to organic carbon ( $K_{oc}$ ), are relatively invariant for natural sorbents. The  $K_{oc}$ 's can be estimated from other physical properties of pollutants (aqueous solubility or octanol/water partition coefficients). Sorption tends to be affected by hydrophilic contributions under one or both of the following conditions: 1) high sorbate polarity, and 2) low organic carbon content of the sorbent, especially with coincident high clay content. Although a priori estimation techniques comparable to hydrophobic sorption are not currently available, estimates of hydrophilic contributions relative to  $K_{oc}$  can be based on chemical class and sorbent composition. Although sorption to sediment or soils is frequently viewed as a rapid process in environmental modeling, true sorption equilibrium may require weeks or months to achieve, as pollutant uptake and release kinetics are highly dependent on molecular size, sorbent cohesive properties, and solids concentration.

#### 4.1 PARTITIONING MODELS

Distribution of organic chemicals among environmental compartments<sup>\*</sup> can be defined in terms of simple equilibrium expressions. Partition coefficients between water and air, water and soil, and water and biota can be combined to construct model environments that will provide a framework for

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<sup>\*</sup> Air, water, soil, sediment, suspended sediment, biota.

preliminary evaluation of expected environmental behavior. This approach is particularly useful when few data are available, as partition coefficients can be estimated with reasonable accuracy from correlations between properties. In addition to identifying those environmental compartments in which a chemical is likely to reside (which can aid in directing future research), these models can provide a base for more elaborate kinetic models.

Because environmental partition coefficients are largely a measure of a chemical's tendency to partition between aqueous and organic media, correlations can be made between various combinations of partition coefficients. Water solubility has been related to n-octanol/water ratios, bioconcentration factors, and soil sorption constants. The ratio of a compound's solubility in n-octanol to its solubility in water (octanol/water partition coefficient,  $K_{ow}$ ) has been correlated with bioconcentration factors and soil sorption constants. More recently, Kenaga and Goring (1978) have given correlation equations for all combinations of these parameters.

The following correlation equations can be used in the estimation of partition coefficients (McCall et al. 1983):

$$\ln WS(\text{ppm}) = -1.7288 \ln K_{oc} - 0.01(\text{MP}-25) + 15.1621 \quad (\text{Eq. 4-1})$$

$$\ln K_{oc} = \ln K_{ow} - 0.7301 \quad (\text{Eq. 4-2})$$

$$\ln BCF = 0.935 \ln K_{ow} - 3.443 \quad (\text{Eq. 4-3})$$

The advantage of developing such correlations is that, once any of the parameters is known, it becomes a simple process to estimate the others.

In its simplest form, a partitioning model evaluates the distribution of a chemical between environmental compartments based on the thermodynamics of the system. The chemical will interact with its environment and tend to reach an equilibrium state among compartments.

A model is selected that predicts distribution patterns of chemicals in a simulated environment representative of a segment of the world. The goal is not to predict actual expected environmental concentrations, but to predict expected behavior by answering such questions as: To which phase is the substance likely to migrate? Will a compound applied to or spilled on soil leach or be volatile? Will a chemical accumulate in the biotic compartment? and so on.

A terrestrial model, a pond model, and an ecosystem model (which combines the first two models) can be described in terms of equilibrium schemes and compartmental parameters. The selection of a particular model will depend on the questions asked regarding the chemical. For example, if the partitioning behavior of a soil-applied pesticide were the item of interest, one would use the terrestrial model. The pond model would be selected if questions concerned aquatic partitioning, and the ecosystem model would be the choice if the overall environmental distribution were to be considered. The selection would also depend on whether the assessment is to be made on- or off-site. The problem of pesticide runoff would be assessed offsite, whereas the ground water impact would be assessed on site.

Partition coefficients can then be combined to describe the ecosystem, assuming all the compartments are well mixed so that equilibrium is achieved between them. This assumption is generally not true of an environmental system because exchange rates between compartments may be slower than transformation rates within compartments. Therefore, equilibrium is never really approached, except perhaps with very stable compounds. Such simplifications, however, indicate the compartments into which a chemical will tend to migrate and can provide a mechanism for ranking and comparing chemicals.

Table 8 presents a comparison of various models. Based on these models, if applied to soil, the three compounds shown would tend to remain in the soil; however, if they were applied to or reached an aqueous system, lindane would tend to stay in the aqueous phase, whereas the tetrachlorobiphenyl and DDT would migrate to the soil. In the ecosystem model, the DDT's sink is soil and sediment, whereas the tetrachlorobiphenyl and lindane tend to be volatile.

Fugacity is frequently used to estimate the behavior of organic compounds in model environments. Fugacity can be regarded as the "escaping tendency" of a chemical from a phase, and it is expressed in units of pressure. Equilibrium between phases is defined as occurring when their fugacities are equal. Fugacity,  $f(\text{Pa})$ , can be related to concentration,  $C(\text{mol/m}^3)$ , by using a fugacity capacity,  $Z (\text{mol/m}^3 \text{ Pa})$ , such that:

$$C = fZ \quad (\text{Eq. 4-4})$$

The  $Z$  values of a chemical can be estimated from knowledge of vapor pressure and solubility or the octanol/water partition coefficient.

TABLE 8. CHEMICAL DISTRIBUTION USING VARIOUS MODELS<sup>a</sup>  
(percentage of chemical in each compartment)

Compound <sup>b</sup>	Environmental compartment					
	Air	Water	Soil	Sediment	Suspended sediment	Biota
Terrestrial Model						
DDT	0.000014 (0.015) <sup>c</sup>	0.0067 (0.0007)	99.9 (2.11)			
Tetrachlorobiphenyl	0.014 (14.6)	0.031 (0.003)	99.9 (2.10)			
Lindane	0.0026 (2.68)	0.76 (0.080)	99.2 (2.09)			
Pond Model						
DDT		1.31 (0.000263)		98.6 (1.58)	0.099 (0.0000197)	0.081 (16.2)
Tetrachlorobiphenyl		5.77 (0.00115)		93.8 (1.50)	0.094 (0.0000188)	0.42 (84.2)
Lindane		60.6 (0.0121)		39.4 (0.63)	0.039 (0.00000788)	0.020 (3.94)
Ecosystem Model						
DDT	4.72 (0.00943)	0.65 (0.00042)	44.8 (1.86)	49.8 (2.65)	0.05 (0.0000332)	0.04 (27.3)
Tetrachlorobiphenyl	97.9 (0.196)	0.065 (0.0000435)	0.96 (0.023)	1.06 (0.057)	0.001 (0.000000071)	0.0048 (3.18)
Lindane	83.2 (0.166)	7.48 (0.00499)	4.41 (0.11)	4.86 (0.26)	0.004 (0.0000032)	0.0024 (1.62)

<sup>a</sup> McCall et al. 1983.

<sup>b</sup> DDT = dichlorodiphenyltrichloroethane.

<sup>c</sup> ( ) = concentration in compartment; air -  $\mu\text{g}/\text{m}^3$ ; others - ppm.



Several levels of fugacity models have been used to calculate the distribution between phases. Level I, the simplest, calculates the equilibrium distribution (Patterson 1985). The Level II model also calculates the distribution at equilibrium, but it is capable of including reaction or transformation and advection. Reaction includes photolysis, hydrolysis, biodegradation, and oxidation. The Level III fugacity model depicts a steady-state nonequilibrium system. This system, in which the fugacities in each phase are different, is produced by including transport between the compartments. The Level IV model is a dynamic version of Level III, in which emissions (and concentrations) vary with time. Several other models also have been developed to simulate or predict the behavior of toxic organic compounds in segments of the ecosphere. The inherent error in most models is that they assume instantaneous equilibrium between components of the system.

Table 9 shows the distribution of several organic compounds when the Fugacity I model was used. Compounds such as chlorobenzene and trichlorobenzene, which have a high Henry's constant and hence a low  $Z$  for water, partition mainly into air; however, the percentages in the soil and sediment increase with increasing  $K$ . Chemicals with low  $H$  and low  $K_{ow}$  remain primarily in water, whereas those with low  $H$  and high  $K_{ow}$  (e.g., DDT) partition mainly into the soil and sediment.

TABLE 9. PARTITIONING OF COMPOUNDS IN A UNIT WORLD WITH THE FUGACITY I MODEL<sup>a</sup>  
(percentage of chemical in each compartment)

Compound	Air	Water	Soil	Sedi- ment	Suspended sediment	Biota
DDT	0.275	0.281	51.4	48.0	0.080	0.032
2,4,2',4'-Tetra- chlorobiphenyl	5.10	0.300	48.9	45.6	0.076	0.031
2-Dichlorobiphenyl	69.6	4.78	13.2	12.4	0.021	0.0083
1,2,4-Trichloro- benzene	95.9	1.40	1.41	1.32	0.0022	0.00088
Chlorobenzene	99.1	0.815	0.045	0.42	0.00005	0.000028

<sup>a</sup> Patterson 1985.

## 4.2 ENVIRONMENTAL FATE MODELS

Numerous environmental fate models have been developed for specific situations that are more complex than the simple partitioning models just discussed. They generally treat situations where steady-state conditions are not applicable (e.g., rivers, ponds, transport in soil or ground water). A review of these models has been compiled (Dickson et al. 1983).

Two models, EXAMS and HydroQual, represent a complexity beyond the models considered in the preceeding subsection and are thus of interest in situations where the single partitioning models are not applicable.

### 4.2.1 EXAMS

The Exposure Analysis Modeling System (EXAMS), developed by a group at the U.S. Environmental Protection Agency (EPA) laboratory in Athens, Georgia (Burns et al. 1981), is one of the most successful and widely used models for assessing the behavior of chemicals in aquatic environments. The model system allows the user to specify volumes and compositions of water and sediment; equilibria are expressed by conventional partition coefficients; reactions such as photolysis, hydrolysis, and biolysis can be included; and transfer rates between compartments are quantified. The model can be run to calculate steady- or unsteady-state conditions. It can be applied to ponds or rivers, and validation can thus be obtained by comparing actual and calculated behavior.

### 4.2.2 HydroQual

HydroQual, Inc., in association with the Chemical Manufacturers Association, has developed a modeling system to describe the behavior of chemicals in lakes and rivers (Di Toro et al. 1982). The model is particularly strong in its treatment of interactions between the water column and sediments. Considerable effort has been devoted to expressing the key algebraic and differential equations in a simple form.

### 4.2.3 U.S. EPA Models

McDowell-Boyer and Hetrick (1982) developed the TOX-SCREEN model for the EPA as a multimedia screening-level model for assessing the potential for human exposure to chemicals released in the environment. The intent of this model is to identify chemicals that are most unlikely to present a problem. It is simplified and conservative in nature and makes use of data that are

typical of large areas of the United States rather than site-specific data. It includes intercompartmental transfer processes and equations for dispersion in air and water.

#### 4.2.4 ENPART

The Environmental Partitioning Model (ENPART) developed by Wood et al. (1982) is based on the fugacity equations of Mackay. This interactive or batch model has the ability to receive a minimum set of input data for the physical and chemical properties of a compound and to calculate other properties required by using correlations. It also has the ability either to receive input of degradation and transfer rates or to supply default values. This model thus provides a first-level screening analysis of a chemical and its partitioning in the environment. The interactive mode allows sensitivity analyses of various parameters of a substance to be performed quickly and easily.

#### 4.3 EFFECT OF CLIMATE ON CHEMICAL FATE

Climatic factors that affect the fate of toxic organic compounds are not simple; one factor influences another. Soil moisture and wind speed influence soil temperature, light intensity influences soil temperature, and many environmental influences affect soil organic matter. Table 10 shows the primary dissipation routes of toxic organic compounds in each of the six major climates of the United States.

TABLE 10. LIKELIHOOD OF ENVIRONMENTAL FATES OF TOXIC ORGANIC COMPOUNDS IN SIX MAJOR CLIMATES

Fate	Major climates <sup>a</sup>					
	1	2	3	4	5	6
Soil sorption	Medium	High	Medium	Low	High	Medium
Biodegradation	High	Medium	Medium	Low	Medium	High
Photodecomposition	High	Medium	Medium	High	Low	High
Volatilization	High	Medium	High	High	Low	High
Leaching <sup>b</sup>	Low	Low	Low	Low	Low	Low

- <sup>a</sup> 1 - Subtropical (Southern Coastal Pacific and Southeast).  
 2 - Temperate (Midwest, Mid-Atlantic, New England, Northern Coastal Pacific).  
 3 - Dry (Great Plains, Intermountain West).  
 4 - Desert (Southwest).  
 5 - Boreal (Rocky Mountains, Alaska).  
 6 - Tropical (Hawaii, island territories).

<sup>b</sup> Not significant in dissipation of hydrophobic toxic organic compounds.

Without regard for any interactions that may occur, the following rough effects might be expected:

- 1) Temperature--The warmer the temperature is, the greater the volatility, the lower the organic matter content of the soil, the more active the microbial population, and the higher the rate of evapotranspiration. The result is a decrease in pesticide persistence.
- 2) Moisture--There is an optimum level of soil moisture for microbial activity. If a soil is too wet or too dry, activity slows down. Volatility also is affected by moisture content; the nature of the effect depends on the solubility of the chemical. The total amount, intensity, and frequency of rainfall or irrigation water received affect the movement of chemicals in soil (Bailey 1966).
- 3) Light--Photochemical reactions are directly proportional to the number of photons absorbed by a chemical. Nearness to the equator or an increase in altitude will speed the rates of photochemical reactions.
- 4) Soil texture--Soil texture is a most important factor. Soil organic matter is directly influenced by the soil texture. Coarse (i.e., sandy) soils will normally be low in organic matter; therefore, water percolation will be rapid and the leaching potential of chemical compounds will be high regardless of  $K_{ow}$  or  $K_{oc}$  values. The opposite is true for heavy (i.e., clayey) soils.

#### 4.4 LIKELY CHEMICAL FATES

The fate of any particular chemical is governed by an interactive combination of water-solubility,  $K_{ow}$ , and Henry's Law Constant,  $H$ . Because chemicals with high  $K_{oc}$  or  $K_{ow}$  values are strongly sorbed onto the soil, they generally are not available for biodegradation, chemical decomposition, photodecomposition, volatilization, or leaching. However, they may adsorb on algae surfaces in aquatic systems where they are then subjected to photodecomposition. The following compounds fall into this category: hexabromobiphenyl; hexachlorobiphenyl; tetrachlorodibenzodioxin; p,p'-DDT; o,p'-DDT; p,p'-DDE; p,p'-DDD; and polybrominated biphenyls.

At the other extreme of the chemical scale, substances with higher water solubility and low  $K_{oc}$  are not sorbed strongly in soil and thus are slightly more available for biodegradation, photodecomposition, volatilization, and leaching. Chlorobenzene, dichlorobenzene, and naphthalene could fall into this category.

Toxaphene is apparently strongly adsorbed and does not move in the soil profile. This strong sorptive interaction with soils, however, may cause

some material to erode into surface waters during irrigation or precipitation events. There is no evidence to indicate the occurrence of oxidation, hydrolysis, or biodegradation; and photolysis is unlikely. Rapid volatilization (a characteristic that would normally cause toxaphene to be considered nonpersistent in the soil environment) is predicted, however. Nevertheless, field studies show that toxaphene is persistent. The difference between prediction and reality probably results from the fact that toxaphene is not a single compound, but a mixture of hundreds of component compounds. Although the overall mixture is strongly sorbed and not mobile in the soil, some individual components may be mobile and may leach deep into the soil, where diffusion to the surface would be slow. In addition, although the mixture is highly volatile, some components may be relatively nonvolatile and would therefore persist in the soil.

Volatilization calculations predict that lindane that has entered the soil profile does not volatilize by diffusion, but rather by mass transport as a result of water evaporation at the soil surface. On the other hand, the leaching calculations show that lindane is not highly mobile in the soil profile. There is no evidence to indicate oxidation, and because the aquatic hydrolysis half-lives are at least 6 months, hydrolysis rates in the soil will probably be slow. Photolysis is not expected, but biodegradation does occur. The results of studies of the biodegradation rates vary widely, and reported half-lives range from weeks to months. If lindane were applied to the surface in a climate where precipitation exceeded evapotranspiration, it could leach deeply into the soil over time and could contaminate ground water (if the biodegradation rate was slow). If evapotranspiration and precipitation or irrigation were in balance, lindane could move up and down in the soil profile with little net transport in either direction. The major loss route would be by biodegradation to  $\gamma$ -pentachlorocyclohexane (PCCH), followed by volatilization of the PCCH. Actual field experiments have confirmed this behavior (Clath and Spencer 1971).

Tetrachlorobiphenyl was predicted to partition into air (Table 8). Hexachlorobenzene, which is more water-soluble than lindane, might be expected to move within the soil profile in an analogous manner.

Given the interrelationships between the various aspects of behavior and the good general agreement between individual calculated and measured values, it is clear that chemicals having undesirable properties can be identified without extensive testing.

## SECTION 5

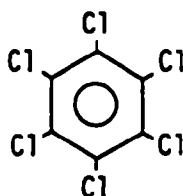
### INFORMATION ON SELECTED ORGANIC CHEMICALS

Preceding sections have presented general information about the chemical properties and environmental fates of several toxic organic compounds identified as having high affinity for soils. They also have attempted to impart knowledge to assist in an understanding of how certain properties can be used to determine long-term residence in various types of soils in various locations. This section provides detailed information on each of the compounds of concern.

The data on each chemical are organized in the following manner. Each subsection begins with background information on the compound's structure, sources, metabolites, applications, and toxicity. The subsection continues with information on water-solubility, volatilization, biotic and abiotic degradation, photodecomposition, partition coefficients, adsorption, and translocation to plants. Each subsection then concludes with discussions of experimental degradation measurements, detected levels in soil, and half-life estimates.

#### 5.1 HEXACHLOROBENZENE (HCB)

##### Structure and Physical Properties



The molecular weight of hexachlorobenzene is 284.79, and its melting point and boiling point are 230°C and 322°C (sublimate), respectively (CRC 1984).

### Sources

Large quantities of hexachlorobenzene, a highly stable compound, are formed as a result of the commercial production of chlorinated solvents and pesticides, including perchloroethylene, carbon tetrachloride, atrazine, propazine, simazine, and dacthal (Farmer et al. 1978). This compound is also a technical impurity in quintozone (Hankawa 1978, Beck and Hansen 1974).

### Metabolites

Hexachlorobenzene degrades to pentachlorophenol (Ballschmiter et al. 1977).

### Applications

Hexachlorobenzene has commercial application as a fungicide and is used as a seed dressing and wood preservative [World Health Organization (WHO) 1979]. It is also a byproduct of tetrachloroethylene production.

### Toxicity

Hexachlorobenzene is moderately toxic by ingestion, and it is a suspected carcinogen [U.S. Department of Health and Human Services (HHS) 1983, Sax 1984]. The LD<sub>50</sub> are presented below. The suggested allowable daily intake for man is 1 g/kg body weight (Verschuereen 1972).

<u>LD<sub>50</sub></u>	<u>Single dose mg/kg</u>
Mouse	4000
Rat	3500
Rabbit	2600
Cat	1700

### Water Solubility

Hexachlorobenzene is nearly insoluble in water--6.2 µg/liter at 23.5°C. Because of its low water solubility, HCB movement through the soil via mass flow is negligible (Farmer et al. 1978, 1980). Any factor that increases the water content of soil will decrease the amount of HCB flux through the soil.



## Volatilization

The vapor pressure of HCB is  $1.91 \times 10^{-5}$  mm Hg at 25°C (Farmer et al. 1980). Small amounts may be able to move through the soil by vapor phase diffusion and volatilization (Farmer et al. 1980).

Vapor-phase diffusion of HCB would occur through air-filled pores in the soil and would depend on the porosity of the soil. Increasing the bulk density of a soil will decrease the soil porosity and, consequently, HCB flux through the soil (Farmer et al. 1980).

Results indicate that air-filled porosity has an exponential effect on HCB diffusion through the soil. Farmer et al. (1978) showed that increasing the air-filled porosity of soil by 13.4 percent increased the apparent HCB diffusion coefficient by 45 percent.

Volatilization of HCB is a diffusion-controlled process. The rate of removal of HCB by volatilization is determined by the speed with which molecules diffuse upward through soil to the air. According to Farmer et al. (1978), volatilization increased exponentially with rising temperature. Each 10°C rise in temperature caused HCB volatilization to multiply by a factor of 3.5.

Farmer et al. (1978) used the following flux equation for steady-state diffusion to calculate the length of time required for 54.9 percent HCB by weight in soil to diffuse to the air-soil interface from a depth of 122 cm:

$$J = D_s(C_2 - C_s)/L \quad (\text{Eq. 5-1})$$

where  $J$  = Volatilization, or vapor flux,  $\text{ng}/\text{cm}^2/\text{day}$   
 $D_s$  = Apparent steady state diffusion coefficient,  $\text{cm}^2/\text{day}$   
 $C_s$  = Air concentration at soil surface,  $\text{ng}/\text{cm}^3$   
 $C_2$  = Air concentration at bottom of soil layer,  $\text{ng}/\text{cm}^3$   
 $L$  = Depth of soil layer, cm.

According to this equation and assuming no degradation within the soil, HCB would continue to volatilize from the soil at a maximum rate for several million years (Farmer et al. 1978). Volatilization is obviously not a significant pathway for HCB dissipation from the soil.

### Microbial Degradation

Hexachlorobenzene is resistant to microbial degradation (Farmer et al. 1978, Freitag et al. 1974). In a study by Haider (1980), HCB remained stable under both aerobic and anaerobic conditions and showed only slight dechlorination of 3 to 4 percent when incubated with Clostridium under anaerobic conditions and Pseudomonas under aerobic conditions. Clostridium and Pseudomonas are common, highly adaptive soil microbes.

### Photodecomposition

No information was available on photolysis of HCB.

### Partition Coefficients

Log  $K_{ow}$ 's for HCB have been estimated at 5.50, 5.57, 6.22, and 4.99 (NASH CP File 1985). The log  $K_{oc}$  is 3.59.

### Adsorption

Evidence indicates that a very high direct correlation exists between soil organic matter content and amounts of HCB adsorbed (Griffin and Chou 1980, 1981; Wallnoefer et al. 1975).

### Translocation to Plants

Significant amounts of HCB were taken up by carrots, spinach, radishes, young sugar beets, lettuce, and wheat (Freitag et al. 1974, Ogiso and Tanabe 1982, Wallnoefer et al. 1975, Scheunert et al. 1983b). German researchers claim that barley and wheat can metabolize hexachlorobenzene by enzymatic activity (Klein et al. 1983).

### Experimental Degradation Measurements

Several investigators found no significant decreases in the concentration of HCB in soil samples over periods of time ranging from 6 to 20 months (Hankawa 1978, Griffin and Chou 1980, Beck and Hansen 1974).

### Detected Levels in Soil

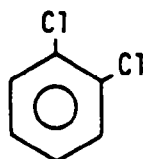
Hexachlorobenzene has been detected throughout the United States at 0.19 mg/kg, 0.11 mg/kg, 0-900  $\mu$ g/kg (wet weight basis), and 1677  $\mu$ g/kg (dry weight basis); in Belgium at 0.44 and 0.85 mg/kg; in Germany at 0.002-1.003 mg/kg; and in Italy at 40  $\mu$ g/kg (WHO 1979).

### Half-Life Estimates

No direct estimates have been made of the half-life of HCB in soil; however, based on its strong adsorption to soil organic matter and relative insolubility in water, it is expected to be strongly persistent, especially in soils with a high percentage of organic matter. Under most environmental conditions, it has a very low rate of degradation (HHS 1983).

## 5.2 1,2-DICHLOROBENZENE

### Structure and Physical Properties



The molecular weight of 1,2-dichlorobenzene is 147.01, and its melting point and boiling point are -17°C and 180.5°C, respectively (CRC 1984).

### Sources

1,2-Dichlorobenzene (o-dichlorobenzene) is produced as an intermediate in herbicide manufacture (WHO 1982).

### Metabolites

o-Dichlorobenzene degrades to a chlorophenol (Ballschmiter et al. 1977, Ballschmiter and Scholz 1980).

### Applications

o-Dichlorobenzene has commercial applications as an insecticide fumigant (WHO 1982).

### Toxicity

o-Dichlorobenzene is moderately toxic by inhalation and ingestion. It is the most toxic of all three dichlorobenzene isomers (Gosselin et al. 1984). In guinea pigs the LD<sub>50</sub> is estimated to be 1.5 g/kg.

### Water Solubility

The water solubility of o-dichlorobenzene is 100 mg/liter at 20 C°. Therefore, movement through soil in the water phase is likely to be significant.

### Volatilization

The vapor pressure of o-dichlorobenzene is a moderate 1.5 mm at 25°C (WHO 1982). Therefore, vapor phase diffusion and volatilization are probably significant pathways for the dissipation of this compound in soil.

### Microbial Degradation

Evidence suggests that o-dichlorobenzene is susceptible to microbial degradation. In one study, a mixed culture of soil bacteria was used to transform chlorobenzenes into chlorophenols (Ballschmiter et al. 1977). In another study, incubation of all three isomers of dichlorobenzene with soil species of *Pseudomonas* yielded dichlorophenols and dichloropyrocatechols (Ballschmiter and Scholz 1980). In a third study, dichlorobenzene was degraded under both aerobic and anaerobic conditions.

Wilson and McNabb (1983) explain that at reasonably high concentrations (e.g., greater than 100 µg/liter), microbial utilization of a pollutant can provide an ecological advantage in that it increases the number of microbes that metabolize the organic pollutant. At concentrations lower than about 10 µg/liter, use of the pollutant does not provide enough advantage to lead to enrichment of the active organisms. At concentrations greater than 1,000 to 10,000 µg/liter, metabolism of the pollutant may be limited by availability of oxygen and other metabolic requirements. Table 11 shows the likelihood of biotransformation of dichlorobenzenes in water-table aquifers (Wilson and McNabb 1983). This information was not available for pollutants in soils.

TABLE 11. PROSPECT OF BIOTRANSFORMATION OF DICHLOROBENZENES IN  
WATER-TABLE AQUIFERS <sup>a</sup>

Compound	Concentration of pollutant		Anaerobic water
	> 100 µg/liter	< 10 µg/liter	
o-Dichlorobenzene	Probable	Possible	None
p-Dichlorobenzene <sub>b</sub>	Probable	Possible	None
m-Dichlorobenzene <sub>b</sub>	Improbable	Improbable	None

<sup>a</sup> Wilson and McNabb (1983).

<sup>b</sup> The researchers did not explain why the likelihood of biotransformation of m-dichlorobenzene differs from that of o- and p-dichlorobenzene.

#### Photodecomposition

No information was available on photolysis of the dichlorobenzenes.

#### Partition Coefficients

Dichlorobenzene has an octanol/water partition log coefficient of 2.26 and a log  $K_{oc}$  of 2.23 (NASH CP File 1985).

#### Adsorption

Although no research data were found, the direct correlation shown between adsorption of hydrophobic organic compounds and soil organic matter content probably applies to dichlorobenzenes as well.

#### Translocation to Plants

No information was available on the uptake of any of the dichlorobenzenes by vegetation.

#### Experimental Degradation Measurements

No information was available on degradation measurements of the dichlorobenzenes.

#### Detected Levels in Soil

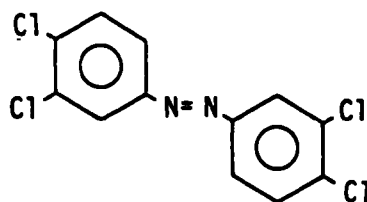
No information was available on detected levels of any of the dichlorobenzenes in soil.

### Half-Life Estimates

No direct estimates have been made for the half-life of o-dichlorobenzene in soil; however, based on its relative adsorption to soil organic matter and relative solubility in water, it is expected to be persistent, though not as persistent as compounds with higher octanol/water and organic carbon partition coefficients. Volatility, biodegradation, and leaching will be major loss routes for o-dichlorobenzene in solution.

### 5.3 3,3',4,4'-TETRACHLOROAZOBENZENE (TCAB)

#### Structure and Physical Properties



The molecular weight of TCAB is 320.02, and its melting point and boiling point are 68°C and 293°C, respectively (CRC 1984).

#### Sources

Numerous researchers have shown that 3,3',4,4'-tetrachloroazobenzene is a condensation product of 3,4-dichloroaniline (DCA). Burge (1972) and Bunce et al. (1979) have indicated that 3,4-DCA transforms microbially to TCAB. It further has been indicated that 3,4-DCA is itself a microbial breakdown product of the herbicide propanil [N-(3,4-dichlorophenyl)(propionamide)] (Helling 1971a, Hughes and Corke 1974). The electron-releasing substituents of anilines are highly susceptible to biochemical transformations, but they yield predominantly higher polymers rather than azobenzenes (Bordeleau and Bartha 1972). Researchers have also detected 3,3',4,4'-TCAB in soil treated

with the herbicide Swep [methyl-N-(3,4-dichlorophenyl)-carbamate] (Sprott and Corke 1971).

According to Canadian researchers, azobenzene formation is of greatest concern in sandy loam soils (Sprott and Corke 1971).

#### Metabolites

The probable decomposition of 3,3',4,4'-TCAB to organic radicals with the liberation of nitrogen, coupled with its insolubility in water, is suggestive of a chemical degradation process.

Evidence suggests that 3,3',4,4'-TCAB is a microbial breakdown product of 3,4-dichloroaniline, but no data are available to show the biodegradation of 3,3',4,4'-TCAB.

#### Applications

No information was available on applications of 3,3',4,4'-TCAB.

#### Toxicity

It has been confirmed that 3,3',4,4'-TCAB is a mutagen (Sax 1984).

#### Water Solubility

Because 3,3',4,4'-TCAB is relatively insoluble in water, its movement through the soil in the aqueous phase is negligible. Research data support this claim (Sprott and Corke 1971). Helling (1971b) used soil thin-layer chromatography studies to rate 3,3',4,4'-TCAB as completely immobile.

#### Volatilization

The vapor pressure of 3,3',4,4'-TCAB is moderately low (WHO 1975). Therefore, the mechanisms of vapor phase diffusion and volatility will not move large amounts of this compound through air-filled pores in the soil.

#### Photodecomposition

No information is available on photolysis of 3,3',4,4'-TCAB.

#### Partition Coefficients

No partition coefficients are available for 3,3',4,4'-TCAB. Because azobenzene has a log  $K_{ow}$  of 3.8 (Verschueren 1983), however, the log  $K_{ow}$  for TCAB is likely to be 4 to 5.

### Adsorption

The retarded mobility of 3,3',4,4'-TCAB may reflect the preferential adsorption of 3,3',4,4'-TCAB to active clay sites that become available through decreases in soil organic matter (Helling 1971a). This hypothesis has not been tested. It does partition readily into soil organic matter.

### Translocation to Plants

No information is available on the uptake of 3,3',4,4'-TCAB by vegetation.

### Experimental Degradation Measurements

In one study conducted in Canada, 3,3',4,4'-TCAB production was measured as a percentage conversion of dichloroaniline (Sprott and Corke 1971). Maximum concentrations of TCAB were detected at the end of 1 week; at the end of 3 weeks, TCAB could no longer be detected. These data indicate that when small amounts of TCAB are formed in Guelph loam, concentrations decrease rapidly after peak levels are reached. From this observation, researchers concluded that TCAB does not persist in Guelph loam. Table 12 shows the maximum concentrations of TCAB produced in the four different soils.

TABLE 12. 3,3',4,4'-TCAB PRODUCED IN ONTARIO SOILS<sup>a</sup>

	3,4 DCA added	TCAB produced	Percentage conversion of DCA to TCAB
Guelph loam	100 µg/g soil	0.075 µg/g soil	0.08
Peel clay	100 µg/g soil	0.00 µg/g soil	0.00
Lincoln clay	100 µg/g soil	0.024 µg/g soil	0.02
Vasey sandy loam	100 µg/g soil	0.60 µg/g soil	0.60

<sup>a</sup> Sprott and Corke (1971).

### Detected Levels

Detected concentrations of 3,3',4,4'-TCAB ranged from 0.01 to 0.05 ppm in 6 of 99 soil samples from rice-growing areas in Arkansas, California, Louisiana, Mississippi, and Texas (Carey et al. 1980).

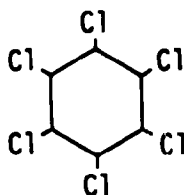


### Half-Life Estimates

The studies of Sprott and Corke (1971) suggest that TCAB does not persist in certain kinds of soil when present in small concentrations. It probably is dissipated by biodegradation. No other information is available on the half-life of 3,3',4,4'-TCAB in soil.

## 5.4 HEXACHLOROCYCLOHEXANE (HCH)

### Structure and Physical Properties



With regard to the persistence of HCH in soils, the gamma isomer has been by far the most widely studied of all the HCH isomers. Thus, this discussion is limited to  $\gamma$ -hexachlorocyclohexane (also known as lindane).

The molecular weight of lindane is 290.83, and its melting point and boiling point are 112°C and 323.4°C, respectively (CRC 1984).

### Sources

Hexachlorocyclohexane is a manufactured pesticide and scabicide.

### Applications

Lindane ( $\gamma$ -Hexachlorocyclohexane) is an insecticide.

### Toxicity

Hexachlorocyclohexane is highly toxic by ingestion and moderately toxic by inhalation or skin absorption. All the isomers of HCH are highly suspect as carcinogens (HHS 1983). The  $LC_{50}$  for 96-hour exposures of fish are >1.4 mg/liter.

### Water Solubility

The water solubility of HCH is 0.15-17 mg/liter (Guenzi et al. 1974; Verschueren, 1983). It is more mobile than most other chlorinated hydrocarbons. Because solubility rises with increasing temperature, HCH adsorption to soil decreases as it moves into the water phase.

### Volatilization

The vapor pressure of HCH is measured at  $9.4 \times 10^{-6}$  mm Hg at 20°C (Guenzi et al. 1974), and  $1.3 \times 10^{-4}$  mm Hg at 30°C (Cliath and Spencer 1971). It is one of the more volatile organochlorine insecticides.

Vapor diffusion is a significant pathway of HCH loss from the soil. Within an optimal range of soil moisture content (from about 4 to 20 percent) (Guenzi et al. 1974), 68 percent of an initial amount of lindane introduced could be lost in about 30 days (Jury et al. 1983).

Because small amounts of water can greatly increase the vapor density of HCH in soil, the volatility of HCH is much greater in wet soils than in dry soils. The displacement of the pesticide from clay surfaces increases the vapor density (Spencer and Cliath 1970). Very dry soil surface layers restrict HCH volatilization, which results in the creation of a relatively high concentration of pesticide in the upper 2-mm surface layer of the soil (Cliath and Spencer 1971).

The rate of volatilization decreases with time as the concentration of HCH rapidly decreases to a concentration below that required to give a maximum vapor density. Maximum volatilization rates obtained by Farmer et al. (1972) show losses of 202 kg/ha per year.

### Microbial Degradation

Evidence indicates that Bacillus coli and Clostridium sporogenes degrade HCH to benzene and monochlorobenzene, and that microbial activity is also responsible for the metabolism of HCH to  $\gamma$ -pentachlorocyclohexene (PCCH) (Guenzi et al. 1974, Cliath and Spencer 1971, Yule et al. 1967, Sethunathan et al. 1969).

Detection of the evolution of  $^{14}\text{CO}_2$  from soils treated with  $^{14}\text{C}$ -labeled lindane indicates that a ring cleavage mechanism is involved (Guenzi et al. 1974, MacRae et al. 1967).

One metabolite of lindane, PCCH, is probably more mobile than lindane, and a relatively large proportion of lindane lost to the atmosphere may be volatilized as PCCH.

Other evidence indicates that lindane stimulated the soil fungal population and did not inhibit dehydrogenase activity, which is thought to reflect the total range of oxidative activities of soil microflora (Tu 1981). Low levels of HCH, however, could not be used as a carbon source in microbial metabolism of soil organic matter (Suzuki et al. 1975).

Degradation of HCH by Flavobacterium sp., Agrobacterium sp., and Alcaligenes sp. was reported by Castro and Yoshida (1974) and degradation by a mixed anaerobic microbial culture was reported by Haider (1979, 1980). Other researchers observed that HCH degradation rates were quicker in nonsterilized soil than in sterilized soil and that degradation rates could be increased further by adding organics to the soil (Castro and Yoshida 1974). Higher degradation rates were noted in submerged unsterile soil (anaerobic) than in moist aerated soil (aerobic) or sterilized moist soil (aerobic) (Kohnen et al. 1975). Aerobic degradation occurred slowly, primarily by the formation of chlorinated aromatic compounds; however, rapid dechlorination and degradation occurred in anaerobic soils enriched with anaerobic bacteria such as Clostridium sp., Bacillus sp., and Enterobacteriaceae (Haider 1979). Japanese researchers observed growth of Clostridium rectum as HCH degraded (Ohisa and Yamaguchi 1978). Canadian researchers also noted biodegradation of lindane in an anaerobic sandy loam soil (Mathur and Saha 1975).

Degradation products include trichlorobenzenes, tetrachlorobenzenes, benzene, monochlorobenzene,  $\gamma$ -pentachlorocyclohexene, and trichlorophenol. A very small amount (less than 1 percent) has been shown to isomerize to the  $\alpha$ ,  $\beta$ ,  $\delta$ , and  $\epsilon$  forms of hexachlorocyclohexane (Waliszewski 1980).

#### Photodecomposition

The limited available information on photolysis of HCH indicates that it is stable in light under atmospheric conditions (WHO 1979), but is oxidized by ultraviolet light at 90°-95°C (Verschueren 1983).

### Partition Coefficients

The octanol/water partition coefficient,  $\log K_{ow}$ , of HCH is 3.80 and the log organic carbon partition coefficient is 3.00 (NASH CP File 1985).

### Adsorption

Lindane diffusion in Gila silt loam is strongly influenced by soil water content, bulk density, and temperature. Ehlers et al. (1969) and Spencer and Cliath (1970) found that decreasing bulk density and increasing temperature caused a greater proportion of the lindane to be in the vapor phase. No diffusion occurred when soil water content equaled zero percent, and the optimal water content was approximately 4 percent (Scheunert et al. 1983a).

Adams and Li (1971) found that variability in lindane sorption is due almost entirely to organic carbon. Evidence of lindane adsorption to organic matter is shown by the fact that movement is more pronounced in sandy loam than in silty clay (Guenzi and Beard 1967, Cliath and Spencer 1971). Desorption isotherms for lindane on Gila silt loam fit the Freundlich equation (Spencer and Cliath 1970). Adsorption of lindane on three different soil types increased with increasing concentration, following the Freundlich isotherm (Chopra and Goel 1971). In agreement with calculated results, when larger amounts of lindane were added, its concentration increased at each point in the soil column, but these larger amounts had no influence on the depth of maximum concentration or depth of penetration (Huggenberger 1972, Huggenberger et al. 1973).

Table 13 shows mobility factors developed by Fuhremann and Lichtenstein (1980) for lindane and metabolites. Only one metabolite, 2,4,5-trichlorophenol, was less mobile than lindane in a developing system that used a hydrophobic carrier.

TABLE 13. MOBILITY FACTORS FOR LINDANE METABOLITES<sup>a</sup>

Compound	Mobility factor, $R_f$
1,2,4,5-Tetrachlorobenzene	0.92
1,3,5-Trichlorobenzene	0.92
1,2,3,4-Tetrachlorobenzene	0.82
1,2,4-Trichlorobenzene	0.82
1,2,3-Trichlorobenzene	0.74
Lindane	0.22
2,4,5-Trichlorophenol	0.10

<sup>a</sup> Fuhremann and Lichtenstein (1980).

Adams and Li (1971) developed an equation to predict percent sorption of lindane in soil:

$$\text{Percent sorption} = 0.057 + 0.1607x - 0.0077x^2 \quad (\text{Eq.5-2})$$

where  $x$  = organic carbon content of soil

$x_2$  = square of the organic carbon content

These researchers showed that desorption of lindane is complete and that it is independent of all soil variables measured and the amount of lindane sorbed. Organic matter and moisture-holding capacity had the greatest influence on the sorption of organochlorine pesticides, including lindane. The findings of Wahid and Sethunathan (1979) support this conclusion. The influence of soil water is attributed to the inability of less polar compounds to compete with water for sorption sites. Adams and Li (1971) also showed that coarse-textured soils generally had the least affinity for lindane.

El Beit et al. (1981) suggested three possible operative factors in their observation that lindane adsorption decreased with increasing temperature:

- 1) Increasing the temperature increases the rate of water movement through soil and causes increased losses by leaching.

- 2) Increasing the temperature increases the rate of evaporation and degradation caused by decreased adsorption.
- 3) Adsorption is an exothermic reaction evolving heat. As temperature increases, the degree of adsorption decreases, particularly if adsorption mechanisms are physical.

Lindane adsorption may be affected by physical forces or hydrophobic bonds, or both. Decreased adsorption resulting from increased temperature and contact time and the rapid occurrence of adsorption after lindane is applied to soil support the physical theory. The hypothesis that lindane adsorption occurs through weak intermolecular forces at lipophilic sites on soil particles would support the hydrophilic theory. High unaccountable losses noted at high temperatures suggest that processes such as degradation and volatilization may be more operative at high temperatures and may cause decreased adsorption (El Beit et al. 1981).

Lindane is particularly prone to removal by leaching and runoff. The total proportion adsorbed at different concentrations was low compared with other organochlorine compounds investigated by El Beit et al. (1981). Lindane is moderately mobile, and these researchers suggested that physical leaching is probably more pronounced in light mineral soils than in heavy clay or organic soils. Brazilian investigators showed that lindane was more persistent in high-organic soils than in low-organic soils (Lord et al. 1978) and that it degraded more quickly in soil poor in organic matter than in organic-rich soil (Flores-Ruegg et al. 1980).

#### Translocation to Plants

Lindane has been detected in oat roots and tops and in potatoes (at 0.001 to 0.020 mg/kg), chickpeas, peas, carrots, corn, wheat, and soybeans (Fuhremann and Lichtenstein 1980, Uhnak et al. 1979, Kathpal et al. 1984, Lichtenstein 1975, Oloffs et al. 1971, Nash and Harris 1973).

#### Experimental Degradation Measurements

Numerous researchers have measured the degradation of HCH in a variety of soils and under various circumstances. One year after treatment, 70 and 82 percent of the original amounts of lindane applied to the soil were recovered from mixed and undisturbed soils, respectively (Guenzi et al. 1974). Of 117.3 kg/ha added to the soil between 1950 and 1953, 7.7 percent

remained in 1968 (Chisholm and McPhee 1972). Of lindane applied at 10 or 100 pounds per acre, 0.2 percent was recovered after 15 years. Eleven years after application, 94.7 and 99.5 percent of the original dosages had been lost. By the end of a single growing season, 57 and 45 percent of the applied lindane were lost from soils treated with 10 and 100 pounds per acre, respectively (Lichtenstein et al. 1971).

One month after spraying at 11.2 kg/ha, lindane residues were 31 ppm in the soil and 585 ppm in the surface litter. Lindane in the surface litter moved slowly into the soil, and the residue level in soil reached a high of 58 ppm 1.5 years after application. Five years after application, residues were 32 and 27 ppm in the soil and litter, respectively (Jackson et al. 1974).

Other investigators showed an average residue of 10 percent 14 years after two applications of 56 and 224 kg/ha; an average residue of 41 percent 11 years after applications of 0.3, 2.8, 5.6 and 11 kg/ha; and an average residue of 0.2 percent 15 years after applications of 11 and 112 kg/ha (Jackson et al. 1974).

Under favorable moisture conditions, all HCH added to soil at 700 µg/kg was completely degraded within 56 days (Zonglian et al., undated). After the use of lindane was prohibited in Japan, total HCH residue in one location decreased from 7.9 mg/kg in 1970 to 0.4 µg/kg in 1973. In another location, levels decreased from 0.06-1.12 mg/kg in 1970 to 0.013-0.848 mg/kg in 1972 (WHO 1979).

Table 14 shows the results of an 8-week-long radioactive lindane tracer degradation study. The least lindane was lost in moist organic soil, and the most was lost in submerged mineral soil.

TABLE 14. LINDANE RECOVERY AFTER EIGHT WEEKS<sup>a</sup>

Soil type	Percentage recovered
Moist organic soil	89
Submerged organic soil	86
Moist mineral soil	84
Submerged mineral soil	70

<sup>a</sup> WHO (1979).

Soil application of 10 kg/ha lindane resulted in losses of 99.4 percent in 180 days (Miles et al. 1978). Fifteen years after the last application of lindane to a sandy loam soil, 7.5 percent remained of the total amount applied (Stewart and Fox 1971). In 1972, seven air-dried soil samples contained 21.0 to 75.5 percent of the amount of lindane found in 1970 (Stewart and Chisholm 1971).

Lindane losses of 28.6 to 33.4 percent and 41.7 to 45.4 percent were noted in normal and alkaline soils, respectively, at the end of a 9-month period (Chawla and Chopra 1967). In India, initial residues of 2.89 ppm dissipated to 0.03 ppm in 100 days in chickpea soils; dissipation was "almost complete" in 148 days (Kathpal et al. 1984). Lindane loss was 53 and 88 percent at 1 and 5 months, respectively, after application (Pal and Kushwaha 1977). Indian researchers also measured lindane loss of 99.4 percent after 180 days (Agnihotri et al. 1977).

German researchers found 62 percent of the applied lindane remained after 105 days' incubation in moist aerated soil; 58 percent remained after 77 days in autoclaved submerged soil; and 76 percent remained after 105 days in autoclaved aerated soil (Kohnen et al. 1975).

In Nova Scotia, Stewart and Fox (1971) detected no lindane 12 years after its application in a sandy loam soil with 5.5 percent organic matter. Suzuki et al. (1975) observed rapid lindane decreases from spring to summer in flooded, biologically active conditions; high temperatures; and high humidity.

### Detected Levels

In South Bohemia, lindane has been detected in soil at 1  $\mu\text{g/kg}$  (WHO 1979), and in the United States, 13 out of 41 soil samples showed levels ranging from 0.001 to 0.35 ppm and averaging 0.01 ppm. (WHO 1974). Lindane was found in 8 of 50 agricultural soils tested in Colorado (Mullins et al. 1971). In Spain, levels of 0.003 to 0.0024 mg/kg were found (Simal et al. 1977); and in Taiwan, a level of 34.2 ppb was detected (Wang et al. 1981).

### Half-Life Estimates

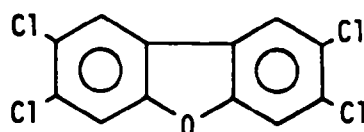
Because of its moderate water solubility, vapor pressure, and degree of adsorption to soil organic matter, lindane is not likely to persist in soils as long as TCDD, DDT, and hexachlorobenzene. Experimental results support



estimates that lindane is moderately persistent, especially under favorable moisture conditions. Jury et al. (1983) estimate a half-life of 260 days; Guenzi et al. (1974) estimate a half-life of 2 years. Volatilization and degradation are probably the primary pathways of loss.

## 5.5 2,3,7,8-TETRACHLORODIBENZOFURAN (TCDF)

### Structure and Physical Properties



There are 135 possible chlorinated isomers of dibenzofuran. No information is available on their behavior in soils. Because they are structurally and physicochemically similar to polychlorinated dibenzodioxins, however, one can draw tentative conclusions about dibenzofurans by extrapolating known information about dioxins.

The molecular weight of TCDF is 305.98. Although its melting and boiling points have not been measured directly, its melting point has been estimated by different methods at 107°, 139°, and 248°C; and its boiling point, at 346° and 510°C (EPA 1985).

### Sources

Chlorinated dibenzofurans are a pyrolysis breakdown product of PCB's and are often found as unintentional impurities in products derived from chlorophenols and chlorobenzenes (EPA 1982, 1983; WHO 1978).

### Applications

Polychlorinated dibenzofurans have no commercial applications.

### Toxicity

The three isomers considered to be the most toxic are 2,3,7,8-tetrachlorodibenzofuran; 2,3,4,7,8-pentachlorodibenzofuran; and

1,2,3,7,8-pentachlorodibenzofuran. Only 10 to 12 of the 135 possible polychlorinated dibenzofurans are expected to have significant toxicity (EPA 1982).

Furan itself has a toxicity rating of 6 out of a possible 6, which puts it into the class of the most severely toxic compounds (Gosselin et al. 1984). The toxicity of 2,3,7,8-tetrachlorodibenzofuran (TCDF) is believed to be one-fiftieth that of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

#### Water Solubility

The water solubility of TCDF is estimated to be 0.2 µg/liter at 25°C (EPA 1983). Dibenzofuran itself is slightly water-soluble at 3 mg/liter at 25°C, but increasing halogenation promotes lipid solubility and diminishes water solubility (EPA 1982). Although both TCDD and TCDF are comparatively insoluble in water, TCDF is slightly more soluble and it may be more readily leached from soils than TCDD is (EPA 1983).

#### Volatilization

No vapor pressures of chlorinated dibenzofurans have been measured directly. The vapor pressure of TCDF is estimated to be  $2.0 \times 10^{-6}$  mm Hg at 25°C (EPA 1982, 1983). With such a low vapor pressure, volatilization is not likely to be a major dissipation route from the soil.

#### Microbial Degradation-Metabolites

No direct evidence exists concerning microbial degradation of chlorinated dibenzofurans, but only 5 of the 100 strains tested showed any ability to metabolize TCDD (EPA 1982). Polychlorinated dibenzofurans can undergo photoreductive dechlorination in the presence of ultraviolet light and an effective hydrogen donor (EPA 1985).

#### Photodecomposition

Higher chlorinated dibenzofurans can be degraded by ultraviolet light. Polychlorinated dibenzofurans undergo photoreductive dechlorination in the presence of ultraviolet light and an effective hydrogen donor (EPA 1985).

#### Partition Coefficients

The log octanol/water partition coefficient of TCDF is estimated to be 6.95 (EPA 1985).

### Adsorption

No direct evidence was found regarding TCDF adsorption to soils. Even though TCDF is slightly more soluble than TCDD, it will not leach from soil.

The more chlorinated a dibenzofuran, the less polar it becomes; and the less polar it is, the stronger are the forces of adsorption to soil organic matter. Inasmuch as TCDD is strongly adsorbed to soil organic matter (Young 1980), it is logical to assume that TCDF also adsorbs strongly to soil organic matter.

### Translocation to Plants

No information is available on the uptake of chlorinated dibenzofurans by vegetation.

### Experimental Degradation Measurements

No experimental results are available on degradation of polychlorinated dibenzofurans in soil.

### Detected Levels

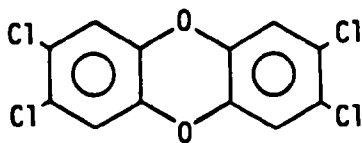
No information is available on levels of chlorinated dibenzofurans detected in soils.

### Half-Life Estimates

Based on the documented persistence of TCDD in soil, coupled with the structural similarity, low water solubility, low volatility, and high capacity for adsorption to organic matter of both chlorinated dioxins and chlorinated dibenzofurans, one can conclude that a strong possibility exists that research will eventually show that chlorinated dibenzofurans are strongly persistent in soils.

## 5.6 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN (TCDD)

### Structure and Physical Properties



The molecular weight of TCDD is 321.97. Its melting point has been measured directly at 305° to 306°C and has been estimated by different methods to be 305°C (Verschueren 1983) and 263°C (EPA 1985). Its boiling point has been estimated at 348° and 533°C (EPA 1985) by differing methods.

#### Sources

Found primarily as a contaminant in products derived from trichlorophenols (including 2,4-D and 2,4,5-T), TCDD is also formed as a byproduct of low-temperature incineration of wastes containing chlorinated precursors (Young 1980).

#### Applications

This compound has no commercial applications.

#### Toxicity

Known to be a carcinogen (WHO 1977), TCDD also is extremely toxic. Its toxicity rating of 6 out of a possible 6 indicates that it is in the class of most severely toxic compounds (Gosselin et al. 1984). It is estimated to be 50 times more toxic than tetrachlorodibenzofuran (EPA 1985).

The acute LD<sub>50</sub> is estimated at:

Guinea pig	0.6 µg/kg
Male rat	22 µg/kg
Female rat	45 µg/kg
Monkey	<70 µg/kg
Rabbit	115 µg/kg

#### Water Solubility

The water solubility of TCDD is estimated to range from 0.0002 µg/g at an unspecified temperature to 0.006 µg/g at 30°C (NASH CP File 1985). Helling (1971) reports the water solubility of TCDD to be 0.2 ppb at 25°C. Because of its low water solubility, movement of TCDD through the soil via mass flow is expected to be negligible (Young et al. 1976). According to the results of a long-term study in a natural ecosystem, no TCDD movement was detected despite an annual rainfall of 150 cm (Young 1980).

#### Volatilization

Researchers who conducted a long-term study in a natural ecosystem estimated that approximately 10 percent of TCDD volatilizes from the soil and

an estimated 5 percent is lost by volatilization each year (Young 1980). The estimated vapor pressure of TCDD is listed as 0.2 mPa (NASH CP File 1985).

#### Microbial Degradation - Metabolites

Although stable in the presence of heat, acids, and alkalis, TCDD undergoes photoreductive dechlorination in the presence of ultraviolet light and an effective hydrogen donor. Loss of chlorine atoms from the polychlorinated dibenzo-p-dioxins occurs preferentially from lateral positions on the carbon ring (EPA 1985). Two breakdown products of TCDD are 2,3,7-trichlorodibenzo-p-dioxin and dichlorodibenzo-p-dioxin (isomer unspecified) (WHO 1977).

Researchers disagree about the biodegradability of TCDD. One group has hypothesized that strong adsorption of TCDD to soil particles limits its bioavailability. They have concluded that situations in which herbicide residues are negligible, TCDD residues are in the form of a precipitate, and the overall soil organic matter is less than or equal to 1 percent are not conducive to TCDD biodegradation (Young 1980). One study that supports this view showed that only 5 of 100 soil microbe strains tested showed any ability to metabolize TCDD (WHO 1977); another showed that all efforts to biodegrade TCDD in soil were unsuccessful (Pocchiari 1978). Meanwhile, other researchers have concluded that TCDD is degradable by soil microbes, especially in the presence of other chlorinated hydrocarbons (Young et al. 1976). In two studies, application of 5,000 to 40,000 mg/kg of the herbicides 2,4-D and 2,4,5-T, which contained unknown amounts of TCDD, stimulated the growth of species of actinomycetes and fungi. It seems probable that the herbicides and TCDD were the carbon sources (WHO 1977).

Philipp et al. (1981) observed that in some experimental microbial cultures approximately 1 percent of TCDD transformed into a polar metabolite that may have been a hydroxylated derivative.

Massive concentrations of 2,4-D and 2,4,5-T did not sterilize soils, which indicates that microbial degradation of TCDD, a contaminant of these herbicides, remained a possibility (Young et al. 1983).

#### Photodecomposition

Some researchers suggest that TCDD can be broken down by ultraviolet light. Published data show a 70 percent decrease in soil TCDD content after

irradiation at an intensity of  $2\text{mW/cm}^2$  (Young et al. 1976, Liberti et al. 1978). Other results show photodecomposition of TCDD only when the TCDD is dissolved in an organic solvent, not in soil or water (Liberti et al. 1978, WHO 1977). Contaminated soils sprayed with xylene-ethyl oleate and exposed to solar radiation showed approximately 100 percent destruction of TCDD on the surface layer in 9 days and 40 to 60 percent destruction in the subsoil (Liberti et al. 1978). These investigators concluded that no increase in the decay rate of TCDD was observed when naturally occurring soil was exposed to sunlight.

#### Partition Coefficients

The  $\log_{10}$  octanol/water partition coefficient for TCDD has been calculated at 6.15, and the estimated organic carbon partition coefficient is 5.91 (NASH CP File, 1985).

#### Adsorption

Researchers believe TCDD is stable and immobile in soil and that it has a high capacity for adsorption to organic matter (Helling 1971, Briggs 1981). Soil thin-layer chromatography (TLC) results support this hypothesis (Helling 1971, Briggs 1981). The adsorption of TCDD to organic matter significantly increases its persistence in the soil (Young 1980). Philipp et al. (1981) demonstrated that a decrease in TCDD extractability over a long-term period of incubation with high microbial activity was a result of adsorption of the TCDD to soil material.

Distributed mostly in the upper 15 cm of soils, TCDD concentration decreases sharply with increasing depth (Di Domenico et al. 1980). The highest levels have been found between 0.5 and 1.5 cm and at not less than 0.5 cm (Di Domenico et al. 1980).

Little downward leaching of TCDD occurs, but lateral movement may occur by surface erosion (WHO 1977).

#### Translocation to Plants

Indications are that translocation of TCDD is either minimal or nonexistent. A maximum of 0.15 percent of TCDD in soil was translocated to aerial parts of oats and soybeans (WHO 1977).

### Experimental Degradation Measurements

Various measurements have been made of TCDD degradation in soils. Young (1980) found 10 to 1500 parts per trillion (ppt) in the top 15 cm of a soil 14 years after the last herbicide application at a site where 2.6 kg of TCDD had been applied to 37 ha between June 1962 and July 1964. Analysis of 61 soil samples showed that less than 1 percent of the original amount of TCDD remained on the test area.

Young et al. (1983) measured TCDD concentrations at 0.5 ppm (mg/kg), which tended to decrease over 3 years; however, no accurate estimate of persistence was possible.

Seventy-one percent of 100 mg/kg of TCDD in silty clay loam was recovered after 1 year; 56 percent was recovered from sand after the same period (WHO 1977). In another study, 1 percent of an initial amount of TCDD deposited at a depth ranging from 0 to 15 cm was detected at a depth below 30 cm after 414 to 557 days.

### Detected Levels

In soil samples of varying depths, TCDD was detected at concentrations ranging from less than 10 to 1500 ppt. The median concentration was 30 ppt and the mean was 165 ppt (Young et al. 1981). No TCDD was detected in 3-foot core samples from an area that received 2,4,5-T annually for 7 years (limit of detection equal to 1 ppb) (Woolson et al. 1973).

In Vietnam, TCDD concentrations equal to 1.2 to 2.3  $\mu\text{g/kg}$  were detected in soils sprayed aerially with 2,4,5-T. Of an estimated total of 100 kg of TCDD sprayed in Vietnam during the years 1966 through 1969, the average concentration in the top centimeters of soil averaged 40 ng/kg (WHO 1977).

### Half-life Estimates

In a soil with a high herbicide concentration that provided microorganisms with a readily available carbon source, the half-life of TCDD was measured at less than 200 days (Young 1980). In a dry climate (Utah), the measured half-life was 330 days; whereas in a warm and humid area (Florida), the half-life was approximately 190 days.

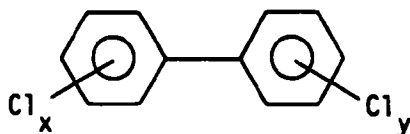
One month after an accidental release of TCDD in Seveso, Italy, the half-life was calculated to be approximately 1 year. Sixteen months later the half-life was recalculated to be more than 10 years. The TCDD concentration dropped to about half its original concentration in the first 5 months, after which no further decreases were detected (Di Domenico 1980). The 50 percent degradation of nanogram amounts of TCDD in 5 hours indicated that low levels of TCDD may degrade more quickly than high levels (WHO 1977).

In Missouri, TCDD concentrations of 0.12 to 0.85 ng/kg after 3 years indicated a half-life of 6 months. Estimates of TCDD half-life in soil fall consistently in the range of 0.24 to 1 year (WHO 1977).

These varying results indicate disagreement regarding the actual half-life of TCDD in soil. Perhaps the differences result from highly varying environmental conditions among experiments. The high  $K_{ow}$  of TCDD, however, suggests that it adsorbs strongly to soil organic matter and that it is extremely persistent.

## 5.7 POLYCHLORINATED BIPHENYLS (PCB's)

### Structure and Physical Properties



A total of 209 possible PCB isomers exist (WHO 1978). Isomers are normally found in mixtures; therefore, PCB's are a mixture of many isomers, all with different melting and boiling points.

### Source

Polychlorinated biphenyls are manufactured. They are often found as a blend with trichlorobenzenes.



### Metabolites

Although PCB's are virtually chemically inert, they form chlorinated dibenzofurans under extremely high temperatures (WHO 1978).

Because of their thermal stability, PCB's were once used as insulating fluid in electrical equipment (such as transformers and capacitors).

### Toxicity

Polychlorinated biphenyls are highly suspect as carcinogens (HHS 1983, Sax 1984), and they are severely toxic to animals and humans (Brinkman et al. 1981).

### Water Solubility

Most PCB's are virtually insoluble in water. Water solubility ranges from 0.04 to 0.2 mg/liter for the more common isomers (Table 5) and decreases with the addition of chlorines.

### Volatilization

No information is available on the vapor pressure of PCB's. Vapor pressure values of 1 mm Hg at 89.3°C and 1 mm Hg at 96.4°C were found for two monochlorinated biphenyls: 2-chlorobiphenyl and 4-chlorobiphenyl, respectively (Carey et al. 1980).

### Microbial Degradation

Polychlorinated biphenyls are highly resistant to biodegradation, and the higher the chlorine content of the PCB mixture, the greater the resistance (Kirk-Othmer 1984). When various microorganisms (including soil microbes, Azotobacter, Pseudomonas, lactic acid bacteria, yeast, fungi, and Neurospora) were incubated with 2,2'-dichlorobiphenyl, no metabolites were detected (Vockel et al. 1974). Microbial metabolism of certain dichloro-substituted rings of PCB's by biphenyl-oxidizing bacteria has been noted, however. These bacteria require an adjacent 2-3 position to form the first biphenyl metabolite, cis-2,3-dihydro-2,3-dihydroxybiphenyl (Jacobs et al. 1976).

### Photodecomposition

No information is available on photodecomposition of PCB's.

### Partition Coefficients

$\log_{10} K_{ow}$  values of 5.99, 6.34, and 6.73 have been calculated for 2,2',4,4',5,5'-hexachlorobiphenyl (NASH CP File 1985). Briggs (1980) obtained  $\log K_{ow}$  values of 6.30 and 6.84 (experimentally and by calculation, respectively) for pentachlorobiphenyl.

### Adsorption

Polychlorinated biphenyls adsorb strongly to soils (Brinkman et al. 1981). A very high direct correlation exists between soil organic matter content and the amount of PCB's adsorbed (Griffin and Chou 1981).

### Translocation to Plants

Research data show that PCB's are taken up by grass and beets, carrots, and sugar beets (WHO 1978, Monza et al. 1976).

### Experimental Degradation Measurements

According to some data, PCB's are very environmentally persistent. Norwegian researchers observed no change in PCB levels in orchard soils over a 2-year period (Kveseth et al. 1977). According to other data, however, some of the less heavily chlorinated biphenyls may be subject to loss by volatilization. German researchers applied  $^{14}\text{C}$ -labeled 2,2'-dichlorobiphenyl to a soil in which they grew carrots during one growing season and sugar beets during the following year's growing season. In the first year, 53.5 percent of the applied radioactivity was lost by volatilization; in the second year, an additional 25.2 percent was lost (Monza et al. 1976). In other work, Scheunert et al. (1983a) showed that the percentage of conversion products for 2,5,4'-trichlorobiphenyl and 2,2',4,4',6-pentachlorobiphenyl detected after one week was nearly the same as that detected after an entire growing period. From these data, Scheunert et al. (1983a) concluded that the conversion rate of PCB's is slow and time-dependent.

### Detected Levels

Various soil concentrations of PCB's have been reported. In Japan, they have been detected at levels ranging from 0.01  $\mu\text{g/g}$  to greater than 100  $\mu\text{g/g}$ . In Finland, levels were measured at 0.1  $\mu\text{g/g}$  (Rautapaa et al. 1976). Near a PCB manufacturing plant in Illinois, levels ranging from 130 to 20,700  $\mu\text{g/kg}$

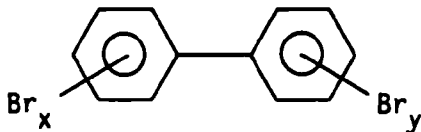
were measured in the soil. At a capacitor manufacturing site, levels ranged from 2.4 to 7.3  $\mu\text{g/kg}$ , and levels of 0.3  $\mu\text{g/kg}$  and 21  $\mu\text{g/kg}$  were measured at this site's new and old dumps, respectively. At another capacitor manufacturing site, levels ranged from 2.7 to 470  $\mu\text{g/kg}$  (Erikson et al. 1978). Brinkman et al. (1981) reported PCB levels of 0.160  $\mu\text{g/g}$  in one soil sediment sample and less than 0.030  $\mu\text{g/g}$  in four other samples. A study conducted by the EPA revealed that PCB levels measured near five metropolitan areas were higher than those measured in rural areas. The highest concentration reported in this study was 11.94  $\mu\text{g/g}$  (Carey et al. 1979).

#### Half-Life Estimates

No direct estimates have been made of the half-life of PCB's in soil. Based on their strong adsorption to soil organic matter and their relative insolubility in water, however, they are expected to be strongly persistent, especially in soils with a high percentage of organic matter. The higher the degree of chlorination is, the more persistent the compound.

### 5.8 POLYBROMINATED BIPHENYLS (PBB's)

#### Structure and Physical Properties



There are 209 possible polybrominated biphenyl isomers. These isomers are usually found in mixtures. The major component isomer of PBB mixtures is 2,2',4,4',5,5'-hexabromobiphenyl (HBB) (WHO 1978, Jacobs et al. 1976). This isomer, in combination with two isomers of pentabromobiphenyl (unspecified), three additional isomers of hexabromobiphenyl (unspecified), and two isomers of heptabromobiphenyl (unspecified) account for 98 percent of the PBB mixtures. The molecular weight of 2,2',4,4',5,5'-hexabromobiphenyl is 627.59. Its melting and boiling points were unavailable.

### Sources

Polybrominated biphenyls are manufactured.

### Metabolites

Certain dibromo-substituted aromatic rings may be subject to attack by biphenyl-oxidizing bacteria that require an adjacent 2-3 position to form the first biphenyl metabolite, cis-2,3-dihydro-2,3-dihydroxybiphenyl (Jacobs et al. 1976). Generally, however, PBB's are considered highly stable chemically although some bromine replacement is possible abiotically.

### Applications

Polybrominated biphenyls have a commercial application as a flame retardant (Jacobs et al. 1976).

### Toxicity

Polybrominated biphenyls are highly suspect as carcinogens (HHS 1983).

### Water Solubility

Polybrominated biphenyls are relatively insoluble in water. Solubility is believed to be in the ppb range and decreases with the addition of bromine. Results of leaching studies on four Michigan soils amended with 100 ppm HBB showed that less than 0.6 percent of the compound was lost when washed with quantities of leachate equivalent to 20 times the average annual rainfall in Michigan (Filonow et al. 1976). Therefore, movement through soil in the water phase can be expected to be negligible.

### Volatilization

No information is available on the vapor pressure of PBB's.

### Microbial Degradation

Evidence has shown microbial metabolism of certain dichloro-substituted aromatic rings of PCB's. Therefore, certain dibromo-substituted aromatic rings of PBB's could be similarly attacked by biphenyl-oxidizing bacteria. These bacteria require an adjacent 2-3 position to form the first biphenyl metabolite, cis-2,3-dihydro-2,3-dihydroxybiphenyl (Jacobs et al. 1976).

### Photodecomposition

Two independent researchers have shown that PBB's are sensitive to light. According to Hill et al. (1982), the observed pattern of PBB degradation indicates a photochemical decomposition mechanism. The work of Jacobs et al. (1978) indicates that photodecomposition of PBB isomers is greater than microbial degradation, but that photodecomposition does not degrade significant amounts of PBB. In addition, the photodecomposition products that do exist appear to be soil-bound and mostly nonextractable.

### Partition Coefficients

The log  $K_{oc}$  for PBB's is 5.34. No measurements of the octanol/water partition coefficient are available.

### Adsorption

A very high direct correlation exists between the organic matter content of soil and amounts of PBB adsorbed (Griffin and Chou 1981). Filonow et al. (1976) showed that 2,2',4,4',5,5'-hexabromobiphenyl adsorption to soils conforms to the Freundlich isotherm,  $r = 0.87$  to  $0.96$ . This team of researchers also showed that neither the percentage of clay nor the pH correlated well with hexabromobiphenyl adsorption.

### Translocation to Plants

Orchard grass grown in PBB-contaminated soil showed no uptake, and carrots showed only minor uptake (Jacobs et al. 1976).

### Experimental Degradation Measurements

In an experiment conducted on Brookston loam, only one isomer of pentabromobiphenyl showed any significant disappearance after a 24-hour incubation period (Jacobs et al. 1976). Other results showed that PBB's were detected in contaminated manure 1 year after their application to soil (Jacobs et al. 1976). Griffin and Chou (1980) found no measurable degradation in PBB-contaminated soils over a 6-month period.

### Detected Levels

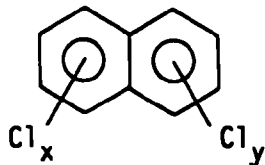
The highest levels of PBB's found in soil, sediment, and water in a survey made near manufacturing and use sites in northeast New Jersey were 4.6 ppm, 60 ppb, and 9.8 µg/liter, respectively (Stratton et al. 1979).

### Half-Life Estimates

No direct estimates of the half-life of PBB's in soil have been made; however, based on their strong adsorption to soil organic matter and relative insolubility in water, PBB's are expected to be strongly persistent, especially in soils with a high percentage of organic matter.

## 5.9 POLYCHLORINATED NAPHTHALENES

### Structure and Physical Properties



The chlorinated naphthalenes are structurally and chemically similar to the polychlorinated biphenyls (PCB's) (Erickson et al. 1978). The molecular weight of naphthalene itself is 128.2, and its melting point and boiling point are 80°C and 218°C, respectively (CRC 1984).

### Sources

Polychlorinated naphthalenes are manufactured.

### Metabolites

A proposed metabolic pathway for naphthalene is hydroxylation, followed by ring cleavage. Naphthalene is oxidized to 1,2-dihydroxynaphthalene through 1,2-dihydro-1,2-dihydroxynaphthalene before ring cleavage (Griffin and Chou 1981).

### Applications

Chlorinated naphthalenes have been used in electric wire insulation and as additives to engine oil (Erickson et al. 1978).

### Toxicity

The penta- and hexachloronaphthalenes are the most highly toxic chlorinated naphthalene isomers (Erickson et al. 1978). They are toxic by ingestion, inhalation, and skin absorption. They also are known to cause chloracne, perhaps because they contain dioxin and/or furan contaminants.

### Water Solubility

The chlorinated naphthalenes are slightly soluble in water. Naphthalene itself is water-soluble at 31.7 ppm (unspecified temperature) (Briggs 1981), and 2-chloronaphthalene is soluble at 6.74 ppm (Callahan et al. 1979).

### Volatilization

No information was available on the vapor pressure or volatility of chlorinated naphthalenes.

### Microbial Degradation

The chlorinated naphthalene 1-chloronaphthalene is metabolized by hydroxylation and ring cleavage of the unchlorinated ring (Verschuere 1983) to form 3-chlorosalicylic acid. No information is available on microbial degradation of the higher chlorinated naphthalenes.

### Photodecomposition

The adsorption band of 1-chloronaphthalene is in the 300-nm region, and this chlorinated naphthalene is susceptible to direct photolysis (Callahan et al. 1979). No information is available for other chlorinated naphthalenes.

### Partition Coefficients

The log  $K_{ow}$  for naphthalene itself has been calculated at 3.36 (Briggs 1981). Partition coefficients are not available for chlorinated naphthalenes, but they will be higher as a function of the degree of chlorination. The log  $K_{ow}$  of 1-chloronaphthalene is 4.12 (Callahan et al. 1979).

### Adsorption

Naphthalene has a high affinity for organic substances. Using Freundlich adsorption isotherms, Rippen et al. (1982) demonstrated that its adsorption to soil is strongly correlated with the organic matter content of the soil.

### Translocation to Plants

No information is available on the uptake of naphthalene by vegetation.

### Experimental Degradation Measurements

No information is available on experimental measurements of chlorinated naphthalene degradation in soil.

### Detected Levels

Soil samples collected in the vicinity of a polychlorinated naphthalenes manufacturing plant contained predominantly tri-, tetra-, and pentachlorinated isomers. Concentrations ranged from 130 to greater than 96,000  $\mu\text{g/kg}$ , with an average of 9400  $\mu\text{g/kg}$  (Erickson et al. 1978). At another site, near a drainage ditch, sediment samples contained 1250 to 5000  $\mu\text{g/kg}$  (Erickson et al. 1978).

### Half-Life Estimates

Low to moderate water solubility, moderate volatility, and strong adsorption to soil organic matter indicate that chlorinated naphthalenes are highly persistent in soil. The octanol/water partition coefficient of naphthalene, however, is significantly lower than those of DDT, hexachlorobenzene, and TCDD. Based on this information, naphthalene is probably less persistent than these compounds and will probably move in the water phase and out of the soil in the vapor phase.

## 5.10 TOXAPHENE

### Structure and Physical Properties

The exact composition of toxaphene is unknown. It is a mixture of chlorinated camphenes that contains more than 170 components having a wide range of gas chromatographic retention times and 4 to 12 carbon atoms per molecule. It is 67 to 69 percent chlorine and has an approximate formula of  $\text{C}_{10}\text{H}_{10}\text{Cl}_8$  (Willis et al. 1983, LaFleur 1974, WHO 1979).

The molecular weight of toxaphene is approximately 413.85, and its melting point ranges from 65° to 90°C (Kirk-Othmer 1984).

### Sources

Toxaphene is manufactured.



### Applications

Toxaphene is an insecticide used primarily on cotton and soybean crops in their early stages of growth (LaFleur 1974).

### Toxicity

Toxaphene is toxic by ingestion, inhalation, and skin absorption. It is also a suspected carcinogen (HHS 1983).

### Water Solubility

The water solubility of toxaphene ranges from 0.4 to 7.0  $\mu\text{g/g}$  (NASH CP File 1985) and 0.4 ppm (Guenzi et al. 1974). Because it is relatively water-insoluble, toxaphene's movement through soil in the water phase will be negligible.

### Volatilization

Toxaphene has a relatively low vapor pressure. Nevertheless, results obtained by Seiber et al. (1979) showed that a decline in toxaphene concentration in the aerated top soil of a cotton field environment occurred primarily by vaporization. According to Willis et al. (1983), vaporization is the major route of toxaphene loss from foliage. The vapor pressure of toxaphene has been variously calculated to be 0.2 to 0.4 mm Hg at 20°C and  $1 \times 10^{-6}$  mm Hg at 25°C (Willis et al. 1983). This great difference is most probably a result of the heterogeneous nature of the mixture of 170 components that comprise toxaphene.

### Microbial Degradation

Parr and Smith (1975) showed that toxaphene degraded rapidly in silt loam soil under anaerobic conditions; the rate of degradation increased with decreasing oxidation-reduction potential. No degradation occurred under aerobic conditions for 6 weeks, and little degradation occurred in soil that had been autoclaved before anaerobic incubation. Table 15 provides the percentage of degradation that occurred after 6 weeks under various conditions.

TABLE 15. TOXAPHENE DEGRADATION UNDER VARIOUS CONDITIONS<sup>a</sup>

Percent degradation	Presence of oxygen		Moisture		Stirred	Unstirred
	Anaerobic	Aerobic	Moist	Flooded		
98	X			X	X	
90	X		X		(unspecified)	
50	X			X		X
0		X	X		(unspecified)	

<sup>a</sup> Parr and Smith (1975).

Similarly, Smith and Willis (1978) noted extensive toxaphene disappearance in both amended and unamended anaerobic environments. Degradation was most complete in flooded, stirred, and anaerobic environments; less complete in flooded, unstirred, and anaerobic environments; and was not detected in aerobic environments (Smith and Willis 1978).

In another experiment, extensive toxaphene degradation was thought to have occurred by anaerobic reduction of the toxaphene components (Seiber et al. 1979).

Williams and Bidleman (1978) showed that toxaphene degraded in anoxic salt marsh sediments to compounds with shorter gas chromatographic retention periods than toxaphene. This degradation occurred in both sterile and nonsterile sediments.

These results indicate that microbial degradation of toxaphene in an anaerobic environment is a likely mechanism of toxaphene loss from soil.

#### Photodecomposition

The limited evidence suggests that toxaphene dehydrochlorinates in prolonged sunlight (WHO 1979). It has a photolysis half life greater than 10 years (Callahan et al. 1979).

#### Partition Coefficients

The  $\log_{10} K_{ow}$  for toxaphene has been measured at 3.23 to 5.43. The  $\log_{10} K_{oc}$  is 4.72 (NASH CP File 1985).

#### Adsorption

Toxaphene has an affinity for hydrophobic solvents and substrates (La Fleur 1974). Measured concentrations have been higher in soils with high

organic matter content than in soils free of organic matter (Gallagher et al. 1979). A linear relation has been determined between toxaphene yield and sediment yield in runoff from silty clay soil (McDowell et al. 1981). These results indicate the strong affinity of toxaphene for soil organic matter, a finding that corroborates the conclusion of the U.S. Department of Health and Human Services (1983) that toxaphene is extremely persistent in soil.

### Translocation to Plants

Gallagher et al. (1979) report the uptake of toxaphene into unspecified plant tissues in both sandy and silty clay loam marshes; concentrations were highest in the roots.

### Experimental Degradation Measurements

In a series of experiments conducted in the top 5 feet of Houston black clay, less than 22 percent of the toxaphene applied over 10 years was recovered. Of the toxaphene that was recovered, 90 to 95 percent was in the top 12 inches of soil (Swoboda et al. 1971). Forty-five percent of the toxaphene applied to a sandy loam soil in 1951 was still there 20 years later (WHO 1979). One-half of the toxaphene applied to a topsoil at a rate of 100 kg/ha remained after approximately 100 days. Toxaphene was then found in the underlying ground water within 2 months (LaFleur et al. 1973).

These results seem to conflict. The varying composition of toxaphene in combination with numerous interacting environmental factors may contribute to the differing behavior of toxaphene under various conditions.

### Detected Levels

In a study conducted in Colorado, toxaphene was discovered in 1 of 50 samples taken from agricultural soils (Mullins et al. 1971). Soil samples taken from three municipal locations in 1969 contained toxaphene concentrations of 0.11, 12, and 15-53 mg/kg. Three of 28 samples taken from one location in 1970 contained concentrations ranging from 7.7 to 33.4 mg/kg, and 1 of 27 samples taken at a second location contained a concentration of 16.1 mg/kg (WHO 1979).

A sediment sample taken at the soil surface 0.2 mile from a toxaphene plant outfall contained 1858 mg/kg, and one taken 1.4 miles away at a depth of 70 to 80 cm contained 5.27 mg/kg (WHO 1979).

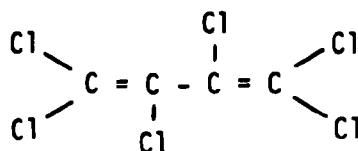
### Half-life Estimates

One estimate of toxaphene half-life in soil is 11 years (Guenzi et al. 1974). Seiber et al. (1979) noted "extensive" toxaphene component degradation after 1 year.

Agreement has not yet been reached on the half-life of toxaphene in soil. Its strong adsorption to soil organic matter, coupled with its relative insolubility in water, indicates strong persistence in soil. Degradation of toxaphene under anaerobic conditions does not indicate biodegradation in the normally aerobic environment of soil pore spaces. These three factors, in combination, increase the likelihood of toxaphene's strong persistence in soil.

### 5.11 HEXACHLOROBUTADIENE

#### Structure and Physical Properties



The molecular weight of hexachlorobutadiene is 260.76, and its melting point and boiling point are -21°C and 215°C, respectively (CRC 1984).

#### Sources

Hexachlorobutadiene is manufactured.

#### Metabolites

No information is available on the breakdown products of hexachlorobutadiene.

#### Applications

Hexachlorobutadiene is used as a heat-transfer liquid and as a transformer and hydraulic fluid (Kirk-Othmer 1984).

### Toxicity

Hexachlorobutadiene is a suspected carcinogen, and it is toxic by inhalation and ingestion (HHS 1983).

### Water Solubility

The water solubility of hexachlorobutadiene is 2 µg/g. Because of this relative insolubility, its movement through the soil in the water phase is probably limited, but slight movement is possible. Results published by Litvinov and Gorenshtein (1982) indicate that rain stimulates the penetration and decreases the volatilization of hexachlorobutadiene.

### Volatilization

Hexachlorobutadiene has a moderate vapor pressure of 22 mm Hg at 100°C. In experiments where measurements in air of 0.08 and 0.03 mg/m<sup>3</sup> were taken one day and one month, respectively, after application of 250 kg/ha, investigators also showed that vaporization of hexachlorobutadiene is quicker from light than from heavy soils, and that increasing the temperature from 13° to 15°C multiplied the vaporization rate fivefold (Litvinov and Gorenshtein 1982).

### Microbial Degradation

No evidence was found to indicate microbial degradation of hexachlorobutadiene. In fact, the evidence indicates that hexachlorobutadiene may be toxic to microflora (Mirzonova and Perov 1968, Drui et al. 1969). Doses of 150 to 250 kg/ha decreased the nitrifying power of the soil slightly; it was restored 2 to 5 months after treatment. Doses of 100 mg/kg did not affect the nitrate content of the soil, whereas doses greater than 100 mg/kg decreased nitrate levels. The actual numbers of microbes were unaffected, even at doses of 1000 mg/kg. Above 1000 mg/kg, the nitrification process was interrupted at the nitrate formation step, possibly as a result of oxygen deficiency in a soil saturated with hexachlorobutadiene vapors (Drui et al. 1969). In another set of experiments, soil nutrient content and hydrolytic enzyme activity decreased and were restored 3 to 4 months later (Mirzonova and Perov 1968).

### Photodecomposition

No information is available on the photodecomposition of hexachlorobutadiene.

### Partition Coefficients

The log  $K_{ow}$  of hexachlorobutadiene is 3.4 (Callahan 1979).

### Adsorption

Investigations show a direct correlation between retention of hexachlorobutadiene and soil organic matter content (Gorenshtein and Litvinov 1983). This is to be expected in view of the relative insolubility of the compound in water. Some movement will occur.

### Translocation to Plants

No information is available on the uptake of hexachlorobutadiene by vegetation.

### Experimental Degradation Measurements

Vorob'eva (1980) discovered that hexachlorobutadiene had disappeared completely 4 years after several aerial applications of 250 kg/ha. The compound was applied 30 cm deep and accumulated to depths of 50 to 75 cm near the plants and 75 to 100 cm in the rows between the plants.

### Detected Levels

In one experiment conducted in Russia, concentrations of 0.08 and 0.03 mg/m<sup>3</sup> were detected one day and one month, respectively, after aerial application of 250 kg/ha; 0.06 and 0.001 mg/ha were detected one day and one month, respectively, after aerial application of 150 kg/ha (Litvinov and Gorenshtein 1982).

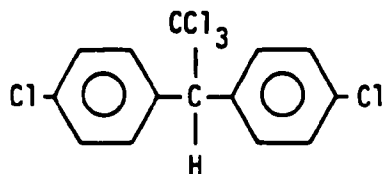
### Half-Life Estimates

No direct estimates have been made of the half-life of hexachlorobutadiene in soil. The results of a few Russian researchers indicate that although hexachlorobutadiene is moderately persistent, it will dissipate from the soil within a few years after aerial application of moderate amounts. This dissipation will occur despite its relative insolubility in water and toxicity to certain soil microbes.

5.12 DDT (DICHLORODIPHENYL TRICHLOROETHANE) AND ITS METABOLITES, DDD (DICHLORODIPHENYLDICHLOROETHANE) AND DDE (DICHLORODIPHENYLDICHLOROETHYLENE)

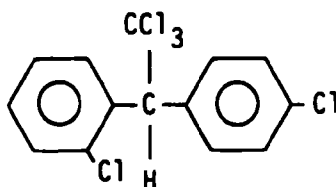
Structure and Physical Properties

p,p'-DDT



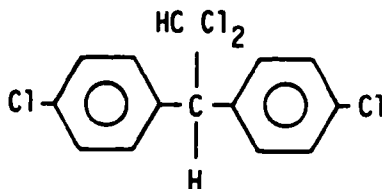
The molecular weight of p,p'-DDT is 354.5. Its melting point and boiling point are 108°C and 260°C, respectively (CRC 1984).

o,p'-DDT



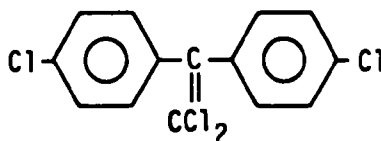
The molecular weight of o,p'-DDT is 354.5. Its melting point is 74°C (CRC 1984).

p,p'-DDD (TDE)



The molecular weight of p,p'-DDD is 320.0. Its melting point is 109°C (CRC 1984).

p,p'-DDE



The molecular weight of p,p'-DDE is 318.0. Its melting point is 88°C (CRC 1984).

### Sources

DDT (Dichlorodiphenyltrichloroethane) is manufactured. Technical DDT is a mixture of p,p'- and o,p'-DDT in a ratio of approximately 3:1. It includes traces of some other isomers and analogs as well (Terriere et al. 1965).

### Metabolites

The primary metabolites of DDT are DDD (TDE) and DDE. Like DDT, they are highly soluble in organic solvents and slightly soluble in water (WHO 1974). Water solubilities range from 0.002 to 0.06 mg/liter.

Dicofol [4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol] is another degradation product of DDT that is sometimes found in trace amounts.

The primary breakdown product of DDT is p,p'-DDE; and the secondary breakdown product is p,p'-DDD (Forsyth et al. 1983, Stewart and Chisholm 1971, Stringer et al. 1974).

### Applications

The pesticide DDT was used primarily on cotton and tobacco. It is no longer in common use because it adversely affects wildlife.

### Toxicity

Toxic by ingestion, inhalation, and skin absorption, DDT is also carcinogenic (WHO 1977).

### Water Solubility

This compound is practically insoluble in water. The water solubility of o,p'-DDT is 0.085 mg/liter at 25°C, and that of DDT (isomer unspecified)



is 0.001 to 0.085 µg/liter (Guenzi et al. 1974, WHO 1974, Fuhremann and Lichtenstein 1980, NASH CP File 1985, Callahan et al. 1979). When water is added to soils that have adsorbed chlorinated hydrocarbons such as DDT, they displace the pesticide and cause an increase in the vapor pressure and subsequent vaporization of the displaced compound (Guenzi et al. 1974). The high persistence and immobility of DDT are attributed, in part, to its very low solubility in water. Amounts adsorbed are inversely related to water solubility.

The extreme hydrophobicity of DDT and its low solubility in water indicate limited leaching. Nevertheless, DDT molecules tend to migrate to the surface and evaporate with water molecules more quickly than the extremely low vapor pressure would predict (Guenzi et al. 1974).

#### Volatilization

The vapor pressures of DDT and its primary metabolites are recorded in Table 16. The vapor pressure of DDT is low, and its metabolite DDE is almost eight times more volatile than DDT itself (Forsyth et al. 1983, Spencer et al. 1974).

TABLE 16. VAPOR PRESSURES OF DDT AND METABOLITES  
(mm Hg)

Compound	Vapor pressure, mm Hg
p,p'-DDT	$1.5 \times 10^{-7}$ at 20°C <sup>a,b</sup>
	$1.9 \times 10^{-7}$ at 20°C <sup>a,c</sup>
	$7.3 \times 10^{-7}$ at 30°C <sup>d</sup>
o,p'-DDT	$5.5 \times 10^{-6}$ at 30°C <sup>d</sup>
p,p'-DDD	$1.0 \times 10^{-6}$ at 30°C <sup>d</sup>
p,p'-DDF	$6.5 \times 10^{-6}$ at 30°C <sup>d</sup>

<sup>a</sup> Willis et al. (1983)

<sup>b</sup> Sleicher and Hopcraft (1984)

<sup>c</sup> Fuhremann and Lichtenstein (1980)

<sup>d</sup> Guenzi et al. (1974)

When the soil moisture is in a certain optimum range, DDT volatilizes. Guenzi and Beard (1970) showed that as soil moisture dropped, DDT was lost at a constant rate until the soil contained less than a monolayer of water on soil surfaces (Guenzi and Beard 1970). Increasing temperature causes an increase in the rate of volatilization (Guenzi and Beard 1970, Baker and Applegate 1970).

Some data suggest that DDT sublimates directly without prior degradation. Test results have shown that sublimation alone can account for the disappearance of low-volatility pesticides, even if they are strongly adsorbed to the soil (Sleicher and Hopcraft 1984). Calculated sublimation rates based on mass transfer through the boundary layer were sufficient to account for the disappearance of DDT.

In other research, DDT losses were attributed primarily to volatilization because the losses in runoff, emigrating insects, and small animals were negligible.

Farmer et al. (1972) obtained maximum volatilization rates, which represented DDT losses of 5 kg/ha per year. Table 17 gives potential volatilization rates of DDT from Gila silt loam at 10 percent soil water content and 100 percent relative humidity.

TABLE 17. POTENTIAL DDT VOLATILIZATION<sup>a</sup>

Soil Concentration, $\mu\text{g/g}$	DDT loss, kg/ha per year
1	0.28
5	1.3
10	2.9
50	4.7

<sup>a</sup> Farmer et al. (1972).

Volatilization rates are partially dependent on the vapor pressure. A comparison of high and low vapor pressure compounds showed that the volatilization rates of DDT from soil were low at first and decreased slowly, whereas compounds of the former group had high initial volatilization rates that decreased rapidly. Both groups were volatilizing at the same rate by the

ninth day, at which point more than half the DDT was still in the soil (Nash 1983). Volatilization may be a significant mechanism for DDT loss from the soil, particularly where soil organic matter content is low.

### Microbial Degradation

Although the results of Forsyth et al. (1983) indicate that DDT is resistant to microbial degradation, other researchers have published contrasting results.

Test results show that DDT degrades much more quickly anaerobically than aerobically, although the path of DDT degradation is not fully understood (Guenzi et al. 1974). The compound DDT degrades anaerobically to DDD, and many microbes can dehydrohalogenate DDT to DDE. Further degradation has been difficult to establish. The compound o,p'-DDT (15% of DDT) converts to o,p'-DDD and o,p'-DDE. Figure 1 illustrates a potential microbial degradation pathway.

A Hydrogenomas sp. degraded DDM by ring cleavage to p-chlorophenylacetic acid. The proposed metabolic pathway included ring hydroxylation followed by ring cleavage (Guenzi et al. 1974). Metabolism of p-chlorophenylacetic acid has been reported, but no metabolic products have been identified. Another possible DDT degradation product is p-Chlorobenzoate.

Sethunathan et al. (1969) noted anaerobic degradation of DDT by Clostridium, possibly by reductive dechlorination (Sethunathan et al. 1969). Some evidence suggests that biodegradation of DDT to DDD is anaerobic and rapid, whereas biodegradation of DDT to DDE is aerobic and slow (Brady 1974). Other work showed that DDT degraded more quickly in flooded, temporarily anaerobic soils than in aerobic soils (Guenzi et al. 1974). This may be due to reductive degradation.

When soil was flooded for 7 weeks, DDT degraded primarily to DDD; there was little effect on DDE isomers. This degradation was observed with and without the addition of organic matter to the soil. Flooding caused a decrease in the quantity of DDE volatilizing from the soil because the DDT that volatilized was degraded to DDD instead of DDE (Spencer et al. 1974).

Alexander (1981), Castro and Yoshida (1974), and Anderson et al. (1970) showed that DDT was modified in nonsterile environmental samples, but not in sterile environmental samples. Degradation rates were increased by adding more organic matter to the soil (Castro and Yoshida 1974). Table 18 shows the important reactions in the transformation of DDT.

Key		
DDE	▪	1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene
DDD	▪	1,1-dichloro-2,2-bis(p-chlorophenyl)ethane
dicofoI	▪	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethanol
DDMU	▪	1-chloro-2,2-bis(p-chlorophenyl)ethylene
DDMS	▪	1-chloro-2,2-bis(p-chlorophenyl)ethane
DDOH	▪	2,2-bis(p-chlorophenyl)ethanol
DDNU	▪	1,1-bis(p-chlorophenyl)ethylene
DDA	▪	2,2-bis(p-chlorophenyl)acetic acid
DBP	▪	4,4'-dichlorobenzaphenone
DDM	▪	bis(p-chlorophenyl)methane
DBH	▪	dichlorobenzhydrol

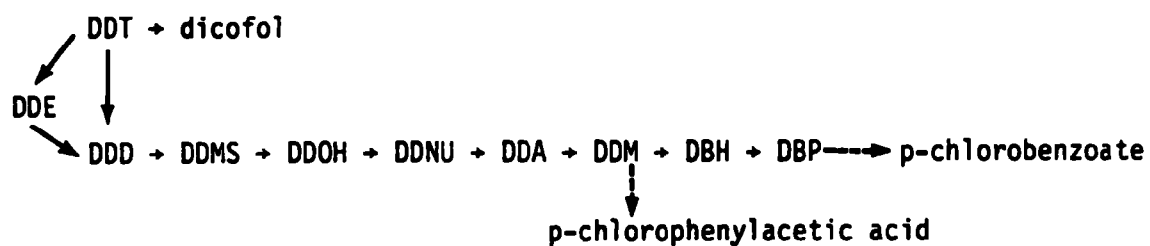


Figure 1. Biodegradation of DDT.

TABLE 18. REACTIONS OF ENVIRONMENTAL IMPORTANCE FOR TRANSFORMATION OF DDT<sup>a</sup>

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Dehalogenation
<sup>b</sup> Ar <sub>2</sub> CHCH <sub>2</sub> Cl → Ar <sub>2</sub> C=CH <sub>2</sub>
Ar <sub>2</sub> CHCHCl <sub>2</sub> → Ar <sub>2</sub> C=CHCl <sub>2</sub>
Ar <sub>2</sub> CHCCl <sub>3</sub> → Ar <sub>2</sub> CHCHCl <sub>2</sub>
Ar <sub>2</sub> CHCCl <sub>3</sub> → Ar <sub>2</sub> C=CCl <sub>2</sub>
Decarboxylation
Ar <sub>2</sub> CHCOOH → Ar <sub>2</sub> CH <sub>2</sub>
Reduction of double bond
Ar <sub>2</sub> C=CH <sub>2</sub> → Ar <sub>2</sub> CHCH <sub>3</sub>
Ar <sub>2</sub> C=CHCl → Ar <sub>2</sub> CHCH <sub>2</sub> Cl
Hydration of double bond
Ar <sub>2</sub> C=CH <sub>2</sub> → Ar <sub>2</sub> CHCH <sub>2</sub> OH

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<sup>a</sup> Alexander (1981).

<sup>b</sup> Ar = Aromatic chlorinated ring.

Evidence shows that the addition of DDT to soil did not adversely affect populations of bacteria or actinomycetes, and the application of DDT at normal rates and 10 times the normal rate did not significantly affect oxygen uptake by soil microbes (Ruffin 1974, Talekar et al. 1978, Hubbell et al. 1973). Harris (1969) noted no significant decrease in biological activity over 48 weeks. Numbers of fungi in soil did increase significantly after soil treatment with a combination of DDT, parathion, and zineb (Hubbell et al. 1973).

Mucor alternans, a fungus isolated from agricultural loam soil, partially degraded DDT in 2 to 4 days into three hexane-soluble and two water-soluble metabolites. None of the metabolites were identified as DDE, DDD, DDA, DBP,

dicofol, or 1,1-bis(p-chlorophenyl) ethane. In the laboratory, DDT degradation was shown with live fungi mycelia only, but dead mycelia did absorb the insecticide. Addition of Mucor alternans spores to soil containing DDT caused no degradation (Anderson et al. 1970).

These results indicate that microbial degradation of DDT is clearly one mechanism by which DDT is lost from the soil. The rate at which biodegradation occurs is not clear.

#### Photodecomposition

The only information available on the photodecomposition of DDT was published by Baker and Applegate (1970). They maintained that ultraviolet radiation catalyzed or accelerated the breakdown of DDT to DDE. Exposure to ultraviolet radiation consistently resulted in additional loss of DDT over the losses obtained without radiation from three different soils, at two different temperatures, and at two different application rates. Table 19 presents these data.

TABLE 19. ADDITIONAL LOSSES OF DDT BY UV RADIATION<sup>a</sup>

Conditions	Percent loss at 30°C	Percent loss at 50°C
5 ppm, 50 days elapsed	4-8	7-9
20 ppm, 60 days elapsed	3-11	29-32

<sup>a</sup> Baker and Applegate (1970).

#### Partition Coefficients

The following log  $K_{ow}$  values have been measured for p,p'-DDT: 5.57, 5.99, 6.19, and 6.36 ln  $K_{ow}$ . Log  $K_{ow}$  values for p,p'-DDD and p,p'-DDE are 5.06 and 5.43, respectively. Log  $K_{oc}$  values for p,p'-DDT, p,p'-DDD, and p,p'-DDE are 5.26, 4.90, and 4.74, respectively (NASH CP File 1985).

#### Adsorption

The extreme hydrophobicity of DDT and its strong affinity for soil organic matter account for its very low leaching rate and relative immobility in soil (Guenzi and Beard 1967, Guenzi et al. 1974, Reed and Preister 1969).

Kiigemagi and Terriere (1972) found that, over a 20-year period, about one-third of the decrease in the amount of DDT and its analogs in the top 6 inches of soil was a result of downward movement. Terriere et al. (1965) found that less than 5 percent of the remaining pesticide was below a depth of 1 foot after 20 years. These results indicate a very slow leaching rate.

Lichtenstein et al. (1971) found that although DDT was applied to a depth of 5 inches, 30 percent of the DDT recovered 10 years later was at a depth of 6 to 9 inches.

A number of researchers have published mobility factors for DDT and its metabolites (Helling 1971, Fuhremann and Lichtenstein 1980). All results indicate the relative immobility of DDT. Table 20 provides relative mobility factors for DDT and some of its metabolites. These factors show that DDE is more mobile than DDT.

TABLE 20. MOBILITY FACTORS FOR DDT AND METABOLITES<sup>a</sup>

Compound	Mobility factor, $R_f$
p,p'-DDE	0.81
o,p'-DDT	0.70
p,p'-DDT	0.62
DBP	0.42
TDE (DDD)	0.24
dicofo1	0.10
DDA	0.00

<sup>a</sup> Fuhremann and Lichtenstein (1980).

Owen et al. (1977) saw little vertical movement of DDT into lower soil horizons over a 10-year period. Sharom et al. (1980) found that DDT was the most highly adsorbed of 12 insecticides tested. A strong correlation was found between adsorption and soil organic matter. Desorption and mobility decreased with decreasing solubility of the insecticide in water. Insecticides were desorbed most easily from sand, less easily from sandy loam, and the least easily from sediment. Almost no DDT was desorbed from soil with four rinses, and results showed 100, 90, 98, and 97 percent adsorption to organic soil, creek sediment, sandy loam, and sand, respectively (Sharom et al. 1980).

Mobility factors were calculated by the following equation:

$$\text{Mobility Factor (MF)} = \frac{\sum_{n=1}^{n=10} (11-n)(x_n/y)}{\quad} \quad (\text{Eq. 5-3})$$

where n = Number of 200-ml fractions

x = Amount of insecticide in fraction

y = Amount of insecticide in treated soil

According to this equation, DDT mobility factors were equal to zero in both sand and organic soil. In spite of different chemical structures, the researchers showed a strong correlation of adsorption and desorption with water solubility (Sharom et al. 1980, Miles et al. 1978).

In other work, adsorption of DDT to four different soils was shown to be directly proportional to the percentage of organic matter in the soil. No DDT was leached from sand or muck with ten 200-ml water rinses (Miles et al. 1978). Using DDD, Mueller-Wegener (1981) also demonstrated a linear relation between soil organic matter content and adsorption.

Lichtenstein et al. (1977) showed that 25 percent of <sup>14</sup>C- labeled DDT became bound to an agricultural soil, which left about 70 percent that was extractable. Stream water and bottom mud contained less than 1 ppm DDT residue, which signified little or no movement of DDT from soils into nearby waterways (Kuhr et al. 1974).

#### Translocation to Plants

Residues of DDT have been detected in oat roots (but not oat tops), in grass roots at concentrations 5 to 15 times higher than those in surrounding soil, and in aerial grass parts at low concentrations (Fuhremann and Lichtenstein 1980, Voerman and Besemer 1975). Residues of DDT have also been found in potatoes (at 0.079 to 0.094 mg/kg), in peanut hulls and forage, and in turnip greens (Uhnak et al. 1979, Young 1969). Tobacco leaves and soybeans took up 0.70 and 0.65 ppm, respectively, from sandy loam soil containing 2, 8, and 16 pounds per acre of DDT (Reed and Preister 1969). Residues of DDT have also been found in sugar beets at 5.5 percent of the soil concentration at planting time (Onsager et al. 1970).



### Experimental Degradation Measurements

Numerous results have been published on measurement of DDT degradation in soil. The amount of DDT converted to DDE ranged from 6.7 percent in Valentine loamy sand to 21.2 percent in Raber silty clay loam (time period unspecified) (Guenzi and Beard 1970).

Over a period of 5 years, 18 percent of the DDT applied to an uncultivated sandy loam and 17 percent of the DDT applied to a cultivated clay was lost (Kiigemagi and Terriere 1972). The decline in total residues was proceeding at a rate of 3.5 percent per year. These investigators referred to another study in which the initial DDT concentration was 2300 ppm; a decline of 30 to 50 percent was noted over a 20-year period.

In a study performed by Lichtenstein et al. (1971), the total amount of DDT recovered 15 years after soil treatment was 10.6 percent of the combined dosage of 10 pounds per acre and 17 percent of the combined dosage of 100 pounds per acre. Soils treated with higher DDT dosages showed higher residue levels, which indicated the relatively higher stability of insecticide in soil treated at a higher dosage. When present in high concentrations, DDT did not metabolize to p,p'-DDE and other residues as quickly as when present at lower concentrations. Fifteen years after application of technical DDT at 10 or 100 pounds per acre, 18 percent and 24 percent, respectively, of the applied dosages were present in the upper 6 inches of soil as p,p'-DDT, o,p'-DDT, and p,p'-DDE. During the 15-year period, only 75.2 percent of the o,p'- isomer was lost, compared with 84.5 percent of the p,p'- isomer, which indicates that the former was more persistent. In other work (Terriere et al. 1965), the ratio of p,p'-DDT to o,p'-DDT ranged from 7 to 14 at different soil levels, which indicates that the o,p'- isomer is less persistent in soil than is the p,p'- isomer.

According to Baker and Applegate (1970), at an application rate of 5 ppm, 21 to 24 percent of DDT was lost from three soils after 50 days at 30°C, and 43 to 50 percent was lost at 50°C. At an application rate of 20 ppm, 22 to 27 percent was lost after 60 days at 30°C and 35 to 44 percent was lost at 50°C. Ultraviolet radiation of the soils increased these DDT losses, as shown earlier in Table 19.

In the fall of 1974, Forsyth et al. (1983) found that the total quantity of DDT residues in the top 12 cm of soil was approximately 38 percent of the total amount applied in 1969. Fifteen years after the last application, 57.1 percent of a total of 585 kg/ha DDT applied remained in the soil (Chisholm and McPhee 1972).

Guenzi et al. (1974) estimated that DDT persisted in the soil for 4 years. The DDT was incorporated into Carrington silt loam at a depth of 13 cm on 5 consecutive days each week for 3 months. Four months after treatment, soil analyses showed that 55.9 percent of the applied DDT remained in disked soil and 74.2 percent remained in undisturbed soil (Guenzi et al. 1974).

Twelve years after application, Owen et al. (1977) showed that soil from areas sprayed with 1.12 kg/ha still showed residues of 4.5 ppm and that 1973 and 1976 levels were not significantly different from 1967 levels. Their conclusions that higher dosages decay more slowly on a percentage basis corroborate the earlier findings of Kiigemagi and Terriere (1972).

Another researcher found that over 7 months (April through October) the ratio of DDE to DDT increased sevenfold, whereas the ratio of DDD to DDT increased fivefold (Miles 1980). In related work, no significant decrease in total amounts of p,p'- and o,p'-DDT was noted 4 years after application to a light sandy soil with 3 percent organic matter; however, over that time the p,p'-DDE concentration more than doubled (Voerman and Besemer 1975).

In a study by Yule et al. (1967), no DDT degradation was noted over a 6-month period. In another study, 25 to 46.3 percent of the p,p'-DDT remained in seven containers of air-dried soil 2 years after application (Saito and Kitayama 1973). In still another study, p,p'-DDT residues exceeded 50 percent of the original dose 3 years after application, and no degradation at all was noted in the winter when the soil temperature was less than 5° to 8°C (Czaplicki 1979). In Norway, roughly 45 percent of DDT sprayed in eight orchards since 1945 remained in 1968 (Stenersen and Friestad 1969). The upper 5 cm was most heavily contaminated; only minor amounts were present in the 15- to 20-cm layer. In another investigation, levels of DDT, DDD, and DDE in orchard soil were unchanged 2 and 4 years after termination of the use of DDT (Kveseth et al. 1977).

Less than 16 percent of the DDT applied to Houston black clay over 10 years was recovered in the top 5 feet of soil, and 60 to 75 percent of the amount recovered was in the top 12 inches (Swoboda et al. 1971). This information indicates that DDT does not leach considerably, as expected from its relative water insolubility. The small amount of downward movement that did occur was thought to be caused by the washing of top soil into large cracks.

In a study by Stewart and Chisholm (1971), 16 percent of the amount of DDT originally applied was recovered from a sandy loam 15 years after its last application, compared with the recovery of less than half that amount (7.5%) of lindane, which is a more water-soluble pesticide.

Application of 10 kg/ha p,p'-DDT to an organic soil in Ontario, Canada, showed a loss of 94.8 percent after 180 days (Miles et al. 1978). Agnihotri et al. (1977) corroborated these findings exactly. In India, Chawla and Chopra (1967) showed p,p'-DDT losses of 36.5 to 38.1 percent and 46.7 to 51.3 percent after 9 months in normal and alkaline soils, respectively. Chisholm and McPhee (1972) showed that 57.1 percent of the applied DDT remained in soil after 16 years, and Stewart and Chisholm (1971) showed that 55 percent of the DDT remained in a sandy loam soil after 15 years.

Over a 7-year period, Ware et al. (1978) found that soil residues of DDT-related degradation products declined an average of 23 percent. Residues in desert soil declined 60 percent.

From 1953 to 1969, Stringer et al. (1974) annually measured DDT levels at an orchard sprayed with technical DDT (77 percent p,p'- and 22 percent o,p'-). After 17 years, 21 percent of the p,p'-DDT and 7 percent of the o,p'-DDT remained. Eighty percent of the recovered DDT was detected in the top 10 cm; none was detected below 50 cm.

In five orchards, DDT residues of 258.8 pounds per acre and 7.3 pounds per acre were detected under trees and between tree rows, respectively, 12 years after application. Concentrations decreased with depth. Seventy to 90 percent of the total residue was DDT (Kuhr et al. 1974).

In a Canadian study, the proportions of p,p'-DDT decreased between 1968 and 1971, whereas the relative content of p,p'-DDE and, to a lesser extent, o,p'-DDT, increased (Yule 1973). In a study by Kuhr et al. (1972) the proportion of DDE in the recovered residue increased from 12 percent after 12 years to 27 percent after 24 years; the percentage of DDT recovered as DDT and DDE

decreased from 50 to 33 to 22 at 6, 12, and 24 years, respectively (Kuhr et al. 1972).

Yeadon and Perfect (1981) found that the final soil residue of plots treated with 70 kg/ha DDT over 4 years in the subhumid tropics was 2 to 3 percent of the amount applied. In Taiwan, 6.6 percent of the DDT applied to silty loam soil at 5 kg/ha remained after 5 years; residues degraded rapidly after spring application (hot and rainy), but accumulated after fall application (cool and dry); and cultivated soil retained more insecticide than did fallow soil (Talekar et al. 1983).

Chapman et al. (1981) showed that DDT degraded more quickly in mineral soil than in organic soil. Reed and Priester (1969) noted a "small" loss of DDT from planting to harvesting time.

These results point toward the strong persistence of DDT in soil. Although some researchers noted relatively rapid dissipation of DDT under certain circumstances, the preponderance of evidence indicates that DDT in soil does not degrade quickly and may last for many decades, or possibly longer.

#### Detected Levels

A World Health Organization report (1974) indicates average soil concentrations of DDT plus DDE were 0.5 ppm in soybean soil, 10.1 ppm in orchard soil, 0.85 ppm in alfalfa soil (including DDD), and 15.10 ppm in onion soil (including DDD). The overall U.S. average equals 0.168 gram DDT per square meter.

On 14 farms, Miles and Harris (1978) found average DDT concentrations of 29 ppm, with a maximum concentration of 60 ppm.

In a study by Stenersen and Friestad (1969), 32 of 55 orchards contained DDT concentrations ranging from 2.3 to 10 mg/kg in the upper 15 cm of soil. Four of the 32 orchards had more than 30 ppm in the upper 15 cm. The average value was 10.1 ppm.

Residues of DDT, DDE, and DDD were detected in Taiwanese asparagus fields at 127.1, 252.2, and 66.9 ppb, respectively (Wang et al. 1981). In Norway, 6.5 ppm DDT was detected in orchard soil (Kveseth et al. 1977). In Finland, 0.02 ppm DDT was detected (Rautapaa et al. 1976).

In a study of soils in five U.S. cities, high DDT levels were found in all samples (Carey et al. 1979). The DDT levels were higher in cultivated areas than in undeveloped areas, and higher in urban soils than in cropland soils. Twenty-seven of 50 samples of Colorado agricultural soils contained DDT (Mullins et al. 1971). In southwest Ontario, DDT levels ranged from less than 0.1 to 29 ppm (Miles and Harris 1978). Apple and peach orchard soils in Ontario had DDT levels of 43.3 and 9.22 ppm, respectively. In West Germany, out of 1035 soil samples from 222 sites with at least one DDT treatment in the preceding 5 years, 4.6 percent had no DDT and 10 percent had more than 2 ppm DDT (Heinisch et al. 1968). In western Oregon, DDT was detected in four different areas, although only one ever received a direct application of DDT (Moore and Loper 1980). Levels in Maryland were measured at 1.5 ppm (Gish 1970). Levels in an estuary in New York were measured at an average of 15 kg/ha and a maximum of 36 kg/ha (Woodwell et al. 1967).

#### Half-life Estimates

According to Edwards (1966), the average time for 95 percent disappearance of DDT is 10 years, and an average of 50 percent remains after 3 years. Chisholm and McPhee (1972) show a half-life estimate of 15 years. Other half-life estimates include 110 days, 2 to 4 years, 10.5 years, 3 years, 1.5 years (for o,p'-DDT only), approximately 12 years (in cultivated soil), 7 years (in desert soils), and 22.9 months (Sleicher and Hopcraft 1984, Stringer et al. 1974, Buck et al. 1983, Onsager et al. 1970, Guenzi et al. 1974).

According to Baker and Applegate (1970), DDT may persist for 10 or more years. Cooke and Stringer (1982) published half-life estimates of 11.7 years, 3.3 years, and 7.1 years for p,p'-DDT, p,p'-DDD, and o,p'-DDT, respectively.

Owen et al. (1977) published a list of half-life estimates for various soils. Table 21 shows these estimates.

TABLE 21. HALF-LIFE ESTIMATES FOR VARIOUS SOILS<sup>a</sup>

Soil	Years
Oregon forest	3
New Brunswick forest	Less than 10
Agricultural	Average 10.5, maximum 35
Light sandy	No loss after 4
Maine forest	Little loss after 9

<sup>a</sup> Owen et al. (1977).

The soils of northern Maine contain many factors that enhance persistence, including high organic content, low temperatures, low microbial populations, slow incorporation of organic matter, and low pH. These factors interact to result in slow decay of DDT. The data indicate that DDT residue decay, especially in forest soils such as those in northern Maine, is slow and may approximate a half-life of up to 35 years.

A summary of properties and resulting half-life estimates is presented in Table 22. The listed values were compiled from throughout this document.

TABLE 22. SUMMARY OF PROPERTIES AND HALF-LIFE  
ESTIMATED FOR TOXIC ORGANIC CHEMICALS

	Water solubility mg/l	Vapor pressure	K <sub>ow</sub> (log)	K <sub>oc</sub> (log)	t <sub>1/2</sub> estimates (in soil)
Hexachlorobenzene	.0062 (23.5°C)	1.91 x 10 <sup>-5</sup> mmHg (25°C)	5.57 <sup>a</sup>	3.59	None (strongly persistent)
1,2-Dichlorobenzene	49-123	1.5 mmHg (25°C)	2.26-3.40	2.23-3.40	None (persistent)
3,3',4,4'-Tetrachloro- azobenzene	Relatively insol.	Moderately low	4 to 5	- <sup>b</sup>	Not persistent
Hexachlorocyclohexane	0.15-17	9.4 x 10 <sup>-6</sup> mmHg (20°C) 1.3 x 10 <sup>-4</sup> mmHg (30°C)	3.80	3.00	Not highly persistent 260 days = t <sub>1/2</sub> estimate 2 years = t <sub>1/2</sub> estimate
2,3,7,8-TCDF	0.0002 (25°C)	2.0 x 10 <sup>-6</sup> mmHg (25°C)	6.95 <sup>a</sup>	-	Strongly persistent
2,3,7,8-TCDD	0.0002 (25°C) 0.006 (30°C)	0.2 mPa	6.15 <sup>a</sup>	5.91	<200 days; 330 days; 190 days; 1 year; 180 days. (indications are a rapid rate for the first 6 mo, then a much longer t <sub>1/2</sub> )
PCB's	0.007-5.9	1 mmHg (89.3°C) 2 chloro- biphenyl 1 mmHg (96.4°C) 4-chloro- biphenyl	6.00 to 6.84 <sup>d</sup>	3.70	Very environmentally persistent Strongly persistent
PBB's	0.0008	-	-	5.34	Strongly persistent
Polychlorinated naphthalenes	1-Cl; 6.74 Slightly soluble	1-Cl; 0.017 (20°C) -	1-Cl; 4.12 -	- -	Highly persistent
Toxaphene	0.4-7.0	0.17-0.40 mmHg (20°C) <sup>a</sup> 1 x 10 <sup>-6</sup> mmHg (20-25°C)	3.3 5.3	4.74 -	11 yr, extensive after 1 yr
Hexachlorobutadiene	2	22 mmHg (100°C)	3.4	-	Moderately persistent
p,p'-DDT	0.002 to 0.085	1.5 to 7.3 x 10 <sup>-7</sup>	3.98 to 6.19	5.26	3 yr, 15 yr, 110 days
o,p'-DDT	0.085	5.5 x 10 <sup>-6</sup>	-	-	-
p,p'-DDD	0.020-0.100	10.2 x 10 <sup>-7</sup>	5.99	4.90	2-4 yr, 10.5 yr, 3 yr
p,p'-DDE	0.01 to 0.12	6.5 x 10 <sup>-6</sup> (20°C)	5.43 to 5.69	4.74	1.5 yr

<sup>a</sup> Estimated.

<sup>b</sup> Information unavailable.

## SECTION 6

### INFORMATION GAPS

During the collection of the information for this report, several data gaps were identified. The behavior of many compounds in soils has not been examined. Among these are the entire classes of biphenylenes and azoxybenzenes. In other cases, the behavior in soils of only one or two representative compounds in a class has been investigated to a significant degree; for example, hexachloro- and 1,2-dichlorobenzene in the chlorinated benzene group, and 3,3',4,4'-tetrachloroazobenzene in the azobenzene group. Compared with the study of chlorinated organic compounds, the brominated, iodinated, and fluorinated species of these compounds have not been studied significantly. Only polybrominated biphenyls (PBB's) were covered sufficiently in the literature for inclusion in this report. The fate of compounds with applications as pesticides or herbicides has been studied extensively, whereas most other toxic organic compounds generally have not. The highly toxic compound TCDD, which has no known applications, is one notable exception.

It may not be necessary, however, to study each compound in depth to draw conclusions about its probable fate in soils. Development of octanol/water partition coefficients ( $K_{ow}$ ) plus the available information on the effects of the degree of halogenation and water solubility may provide sufficient information to predict (by comparison with well-studied compounds) the extent to which a compound will adsorb to soil organic matter. Knowledge of the degree of adsorption of a compound to soil organic matter will give strong clues as to the fate and persistence (and thus the half-life) of a particular compound.

A major difficulty exists in interpretation of half-life estimates. Because experiments are conducted under nonstandard conditions, a comparison of results between different compounds tested in different climates and different soils is not highly meaningful. If several standard sets of conditions were adopted and half-life estimates were developed for a well-studied



compound (e.g., DDT) under each set of conditions, other compounds could also be studied under these standard conditions. In much the same way that specific gravity values for all compounds are related to the density of water at a specified temperature, half-life estimates generated for any test compound could be related to the behavior of the standard compound under the same conditions as the test compound. Relative half-life estimates could be used to generate more meaningful data than currently exist about the similarities and differences among compounds of interest.

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