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Manmade Organic Compounds in the surface waters of the United States; A review of current understanding

James A. Smith, Patrick J. Witkowski
and Thomas V. Fusillo

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CONTENTS

CONTENTS--Continued

ILLUSTRATIONS

Figures 1-10. Plots showing:

ILLUSTRATIONS--Continued

TABLES

TABLES--Continued

TABLES--Continued

ABBREVIATIONS

atm-m^3/mol	atmosphere-cubic meter per mole
^oC	degrees Celsius
cm	centimeters
cm/h	centimeters per hour
hr	hour
kcal/mol	kilocalorie per mole
kg	kilogram
kg/d	kilogram per day
km	kilometer
lb/yr	pounds per year
L-torr/K-mol	liter-torr per degree Kelvin-mole
m^2/h	square meters per hour
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mm	millimeter
mol/L	moles per liter
mol/m^3	moles per cubic meter
ng/L	nanograms per liter
nm	nanometer
pg/L	picograms per liter
ppb	part per billion
ppm	part per million
ppt	part per trillion
rpm	revolutions per minute
torr-L/mol	torr-liter per mole
torr/Molar	torr-liter per mole
µg/g	micrograms per gram
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µmol/L	micromoles per liter

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ABSTRACT

This report reviews the occurrence and distribution of manmade organic compounds in the surface waters of the United States. On the basis of their aqueous solubilities, nonionic organic compounds partition themselves between water, dissolved organic matter, particulate organic matter, and the lipid reservoirs of aquatic organisms. Ionized organic compounds can be adsorbed to sediments, thereby reducing their aqueous concentrations. Transformation processes of photolysis, hydrolysis, biodegradation, and volatilization can attenuate organic compounds, and attenuation rates commonly follow a first-order kinetic process.

Eight groups of manmade organic compounds are discussed:

1. Polychlorinated biphenyls and organochlorine insecticides,
2. Carbamate and organophosphorus insecticides,
3. Herbicides,
4. Phenols,
5. Halogenated aliphatic and monocyclic aromatic hydrocarbons,
6. Phthalate esters,
7. Polychlorinated dibenzo-p-dioxins, and
8. Polycyclic aromatic hydrocarbons.

For each compound group, data pertaining to use, production, and properties are presented and discussed. Processes that influence the environmental fate of each group, as determined primarily through laboratory studies, are reviewed, and important fate processes are identified. Environmental concentrations of compounds from each group in water, biota, and sediment are given to demonstrate representative values for comparison to concentrations determined during ongoing research. Finally, where sufficient data exist, regional and temporal contamination trends in the United States are discussed.

INTRODUCTION

Background

Because of the dramatic increase in the production and use of manmade (anthropogenic) organic compounds in the United States over the past 50 years, the quality of our nation's surface-water systems has gradually deteriorated. Organic contaminants have been detected in the water, sediments, and biota of rivers, estuaries, and lakes throughout the United States. Shackelford and Keith (1976) documented the occurrence of 1,258 organic compounds appearing in 5,720 observations in 33 water types from 1970-76. Gilliom (1985) reported the detection of one or more pesticides in almost 20 percent of sediment samples collected from more than 150 river sites in the United States. Residues of persistent organochlorine compounds have been detected around the world, including Antarctic snow (Peterle, 1969) and fish from depths of 2,500 meters in the Atlantic Ocean (Barber and Warlen, 1979).

Manmade organic compounds enter surface-water systems in point-source discharges, nonpoint-source runoff, atmospheric deposition, and ground-water discharges. The discharge of polychlorinated biphenyls (PCBs) into the Hudson River by two capacitor-manufacturing plants is a notorious example of point-source contamination. Over a 30-year period, these plants combined to discharge PCBs to the Hudson at an average rate of 14 kg/d (Brown and others, 1985). Although the discharge of PCBs to the Hudson by these plants was stopped by 1977, significant residues of the persistent organochlorine contaminants still remain in both the sediment and biota. Nonpoint-source discharges also can contribute to surface-water contamination (Novotny, 1980), particularly with regard to pesticides applied to farmland and forests. In many areas, sediment resulting from eroded soil contains elevated concentrations of sorbed pesticides and is regarded as the primary source of contamination of the surface-water system. Based on land-use data, greater than 97 percent of land area in the U.S. is a potential source of nonpoint contaminant discharges (McElroy and others, 1975). The atmospheric deposition of organic contaminants into surface waters also has been documented. Heit and others (1984) determined that PCB contamination of four remote lakes in Rocky Mountain National Park was attributable to the atmospheric transport and subsequent deposition of the organic contaminants. They found surficial sediments in the lakes had total PCB concentrations as high as 540 μg/kg dry weight. Finally, ground water also can supply a surface-water system with organic contaminants (Frank and others, 1981), but the persistence of soluble ground-water contaminants in surface waters is typically not great because of their volatility (Connor, 1984b).

Purpose and Scope

The increasing production and use of manmade organic compounds coupled with their ease of transport into surface-water systems makes knowledge of their environmental behavior essential to the management of the Nation's freshwater resources. The purpose of this report is to provide an interpretative, critical review of the scientific literature with regard to the occurrence, distribution, and fate of man-made organic compounds in the surface-water systems of the United States. More specifically, the review examines organic-contaminant interactions with bottom and suspended sediment, the water column, and the biota of rivers, estuaries, and lakes. Both laboratory and field studies are reviewed, and where applicable, their results are compared and contrasted. Examples of organic-contaminant concentrations reported in field studies are given to serve as a means of comparison to ongoing research. Special emphasis is given to the environmental variables and the physicochemical properties of the organic compounds that are intrinsic to the distribution and fate of the contaminant. Finally, where sufficient data exist, the regional and temporal distribution patterns of manmade organic compounds in the surface-water systems of the United States are discussed.

PROCESSES AFFECTING THE FATE AND DISTRIBUTION OF ORGANIC COMPOUNDS

The following section is divided into three main parts. The first section reviews sorption interactions between sediments and organic contaminants. The second section discusses bioaccumulation of organic contaminants, and the third section reviews transport and transformation processes affecting organic contaminants in surface-water systems.

Sorption

Water quality has traditionally been assessed by the concentrations of dissolved constituents. However, certain organic contaminants can be sorbed to suspended and bottom sediment and may be present in sediment at concentrations that are orders of magnitude higher than their dissolved concentrations. Sediments can be a reservoir for many persistent organic compounds, causing them to remain in the surface-water system years after input of the contaminant has stopped. Additionally, the sorbed organic contaminant may represent a large fraction of the total mass of contaminant transported downstream. The ability to predict the extent of sorption for a contaminant in a surface-water system may, therefore, be extremely important in assessing water quality.

Definitions

Unlike aqueous concentrations, concentrations of anthropogenic organic compounds sorbed to sediment or soil are expressed as a ratio of the mass of contaminant to the mass of sediment or soil (for example, µg/g, µg/kg, mg/kg). The extent to which an organic contaminant is sorbed to a given sediment at equilibrium is quantified by its distribution (sorption) coefficient, K_d, which is defined as

$$K_d = \frac{C_s}{C_e}$$

where C_s is the concentration of a contaminant sorbed to a specific weight of sediment, and C_e is the concentration of the same contaminant dissolved in an equal weight of water (Olsen and others, 1982).

For a given contaminant-sediment combination, C_s is a function of C_e and commonly is related to C_e by the empirical Freundlich isotherm given by

$$C_s = K\, C_e^{(1/n)}$$

where K and n are empirical constants that are a function of the sorbent and sorbate. If n has a value of unity, a plot of C_s vs. C_e will be linear and K will equal the previously defined sorption coefficient.

The sorption coefficient commonly is expressed on an organic matter basis and is defined as

$$K_{om} = \frac{K_d}{f_{om}} ,$$

where f_{om} is the fractional mass of organic matter in the sediment. Similary, the sorption coefficient expressed on an organic-carbon basis is defined as

$$K_{oc} = \frac{K_d}{f_{oc}} ,$$

where f_{oc} is the fractional mass of organic carbon in the sediment. The values of f_{om} and f_{oc} can be related by the Van Bemmelen factor of 1.724 (Allison, 1965), which assumes that soil or sediment organic matter is composed of 58 percent carbon. This conversion factor is, however, only an approximation, and determinations of f_{oc} and f_{om} typically are obtained by laboratory analyses.

An organic compound's octanol-water partition coefficient, K_{ow}, is defined as the ratio of the compound's concentration in a known volume of n-octanol to its concentration in an identical volume of water after the octanol and water have reached equilibrium.

Adsorption and Partitioning

Sorption of organic compounds by sediments can be accomplished either by an adsorption or partition process. Adsorption is a surface phenomenon that involves either a physical or chemical bond formation between the organic compound and a site on the sediment particle's surface. Physical adsorption is caused by van der Waal's forces, whereas chemical adsorption (chemisorption) is the result of a chemical bond formation between the organic compound and the sediment (Khan, 1978). Ion exchange is an example of chemical adsorption. For a partition process, the organic compound distributes itself between water and the sediment organic matter by molecular forces common to solution, similar to the distribution between water and an organic solvent such as octanol (Chiou and others, 1979; Hassett and others, 1980; Chiou, 1981; Chiou and others, 1982b, 1983b).

Table 1 contrasts the characteristics of partition and adsorption processes (Chiou and others, 1979, 1983b). Adsorption is a surface-condensation process that occurs with high exothermic heat in compensation for losses in entropy. The enthalpy change for adsorption of a solute from water must be greater than the solute's heat of condensation from water (except for cases where adsorption is very weak). For a partition process, the heat of sorption equals the difference between the molar enthalpies of solution of the solute in the organic and water phases and typically is less exothermic than the solute's heat of condensation. Adsorption processes are characterized by nonlinear isotherms, whereas partition processes yield linear isotherms over a wide range of solute solubility. An adsorption process is also characterized by a competitive effect between solutes for a fixed number of surface sites, while a partition process involves independent sorption between individual solutes. Finally, the magnitude of the partition coefficient of an organic solute between an organic phase and water is determined primarily by the solute's solubility in water. The dependence of the octanol-water partition coefficient on solute-water solubility has repeatedly been demonstrated for various organic solutes (Chiou and others, 1977, 1982b; Mackay, 1977; Chiou and Freed, 1977; Miller and others, 1985), in which water solubility was found to be the major factor affecting the partition coefficient. In analogy to the solvent-water system, Chiou and others (1983b) demonstrated that solute solubility also was the primary factor influencing the partitioning of 12 nonionic organic compounds between water and soil organic matter. The relation between aqueous solubility and K_{ow} developed by Chiou and others (1982b) is given in figure 1.

Because of significant differences between the adsorption and partition processes, it is important to determine the mechanism responsible for the sorption of manmade organic compounds to sediments in surface-water systems. Although the issue was considered unsettled by some investigators (Kyle, 1981; Mingelgrin and Gerstl, 1983; MacIntyre and Smith, 1984; Curl and Keoleian, 1984), there is strong evidence to indicate that sorption of nonionic and acidic organic compounds from water by soil or sediment is caused primarily by the partitioning of the solute into the soil/sediment organic matter (Chiou and others, 1979, 1983b, 1985; Witkowski and others, 1987). Sorption of organic bases, on the other hand, appears to occur primarily by adsorption.

Sorption of Nonionic Organic Compounds

The sorptive behavior of nonionic organic compounds characteristic of a partitioning process has been repeatedly observed. Chiou and others (1979) calculated low heats of sorption for 1,2-dichlorobenzene and 1,1,1-trichloroethane sorbed to a Willamette silt loam. Pierce and others (1974) calculated low isosteric heats of sorption for dichlorodiphenyltrichloroethane (DDT) sorbed to several types of particulate matter ranging from -2 to +4 kcal/mol. Because the heat of condensation for DDT is approximately 10 kcal/mol, an

Table 1. Contrasting characteristics of adsorption and partition processes.

Characteristics	
Adsorption	Partition
High heats of sorption	Low heats of sorption
Nonlinear isotherms	Linear isotherms
Competitive sorption	Noncompetitive sorption
	Solubility dependence

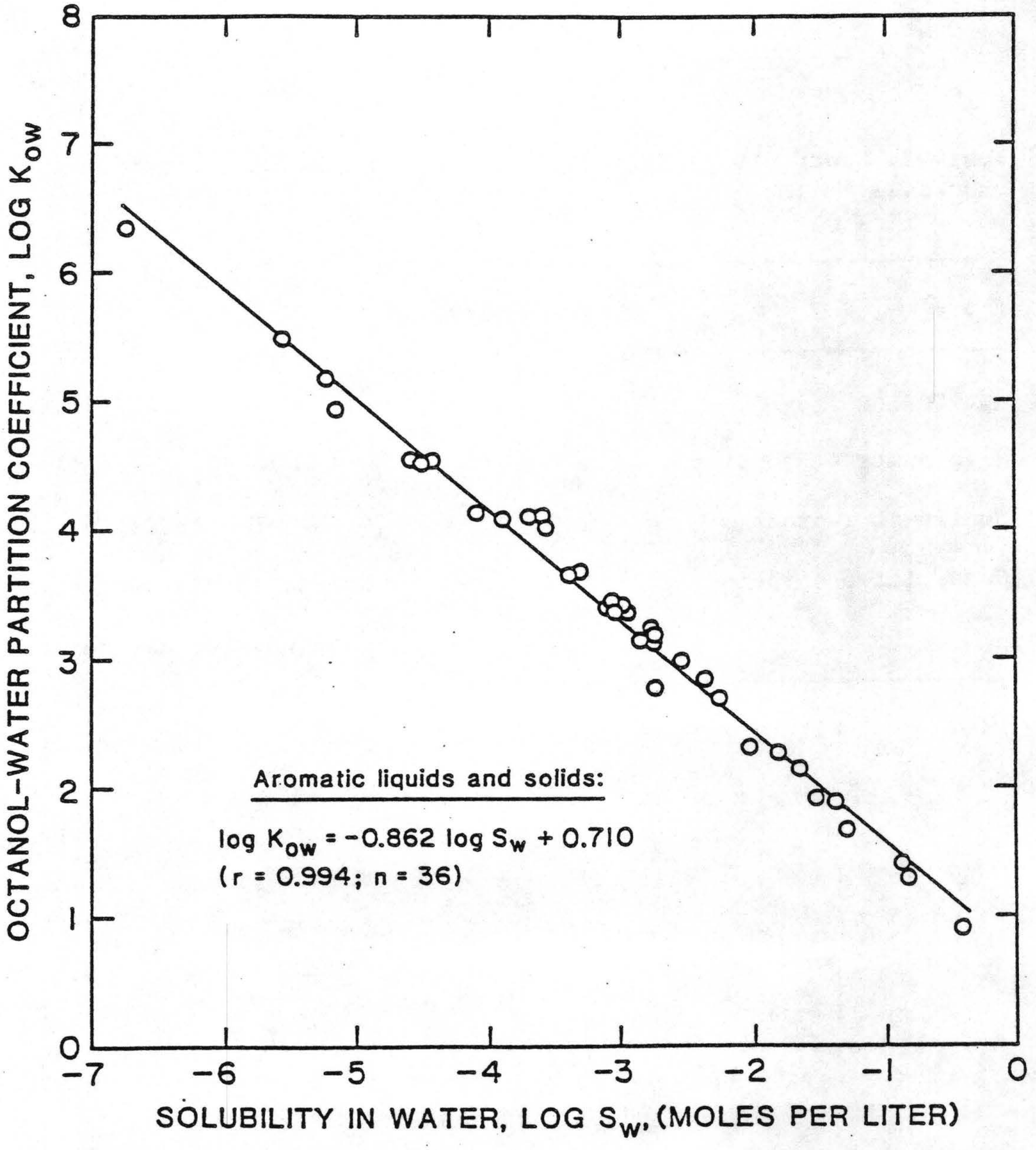

Figure 1. Correlation of octanol-water partition coefficient with water solubility for selected aromatic liquids and solids at 25 °C. The solubilities of solid compounds in the plot are those of their supercooled liquids at 25 °C. [Reprinted with permission from Environmental Science and Technology **16**, 9, (1982). Copyright 1981 by the American Chemical Society.]

adsorption process would require at least 10 kcal/mol (exothermic). The low heats calculated by Pierce and others (1974) are in keeping with a partition process. Khan (1974b) also witnessed low isosteric heats of sorption of the weakly acidic herbicide 2,4-D when sorbed to a fulvic acid-clay complex, again indicating a partition process.

Figure 2 presents sorption isotherms for a variety of nonionic organic compounds partitioned between water and a Willamette silt loam (Chiou and others, 1979). All the isotherms are linear, and, for 1,2-dichloropropane and 1,2-dichloroethane, the isotherms are linear up to equilibrium aqueous concentrations that are 75 and 95 percent of the solute's solubility. This observation, along with the low exothermic heat, cannot be reconciled by an adsorption model. Lotse and others (1968) observed approximately linear sorption isotherms for lindane sorbed to lake sediments. Karickhoff and others (1979) observed isotherm linearity for the sorption of pyrene and methoxychlor to natural sediments. Pierce and others (1974) and Picer and others (1977) witnessed linear Freundlich isotherms for DDT sorption to natural sediments. Hassett and others (1980) reported linear isotherms for dibenzothiophene sorption to a variety of soils and sediments. Finally, Herbes (1977) also observed linear isotherms for anthracene sorption to particulate organic matter. All these examples of linear isotherms are indicative of a partition process rather than an adsorption process.

The noncompetitive effect of binary nonionic solutes on sorption isotherms was demonstrated by Chiou and others (1983b, 1985) and Chiou and Shoup (1985). Figure 3 presents soil/water isotherms for single and binary solutes (Chiou and others, 1983b). No competitive effects are observed. Instead, the data indicate independent sorption that is characteristic of a partition process. Additionally, the isotherms are linear up to 60 and 90 percent of solute saturation.

The solubility dependence of the sorption process also has been observed. Senesi and Testini (1980) noted increased sorption of some nitrogenated herbicides with decreasing solubility. Sharom and others (1980b) noted that the sorption of 12 insecticides by three types of soil was inversely correlated to the insecticides' solubilities. Figure 4 presents data from Chiou and others (1979) showing the linear log-log relation between solubility and the soil organic matter-water distribution coefficient (K_{om}) for a variety of nonionic organic compounds. The data demonstrate that the distribution coefficient decreases with increasing solubility. The observed solubility dependence of the sorption process again lends support to the hypothesis that partitioning between water and the sediment organic matter is primarily responsible for the sorption of nonionic organic compounds by sediments.

Adsorption of nonionic organic compounds does not appear to be a significant mechanism in sediment-water systems due to the ability of polar water molecules to compete successfully with nonionic organic solutes for mineral adsorption sites (Yaron, 1978; Chiou and others, 1981a, 1983b, 1985; Chiou and Shoup, 1985). On the other hand,

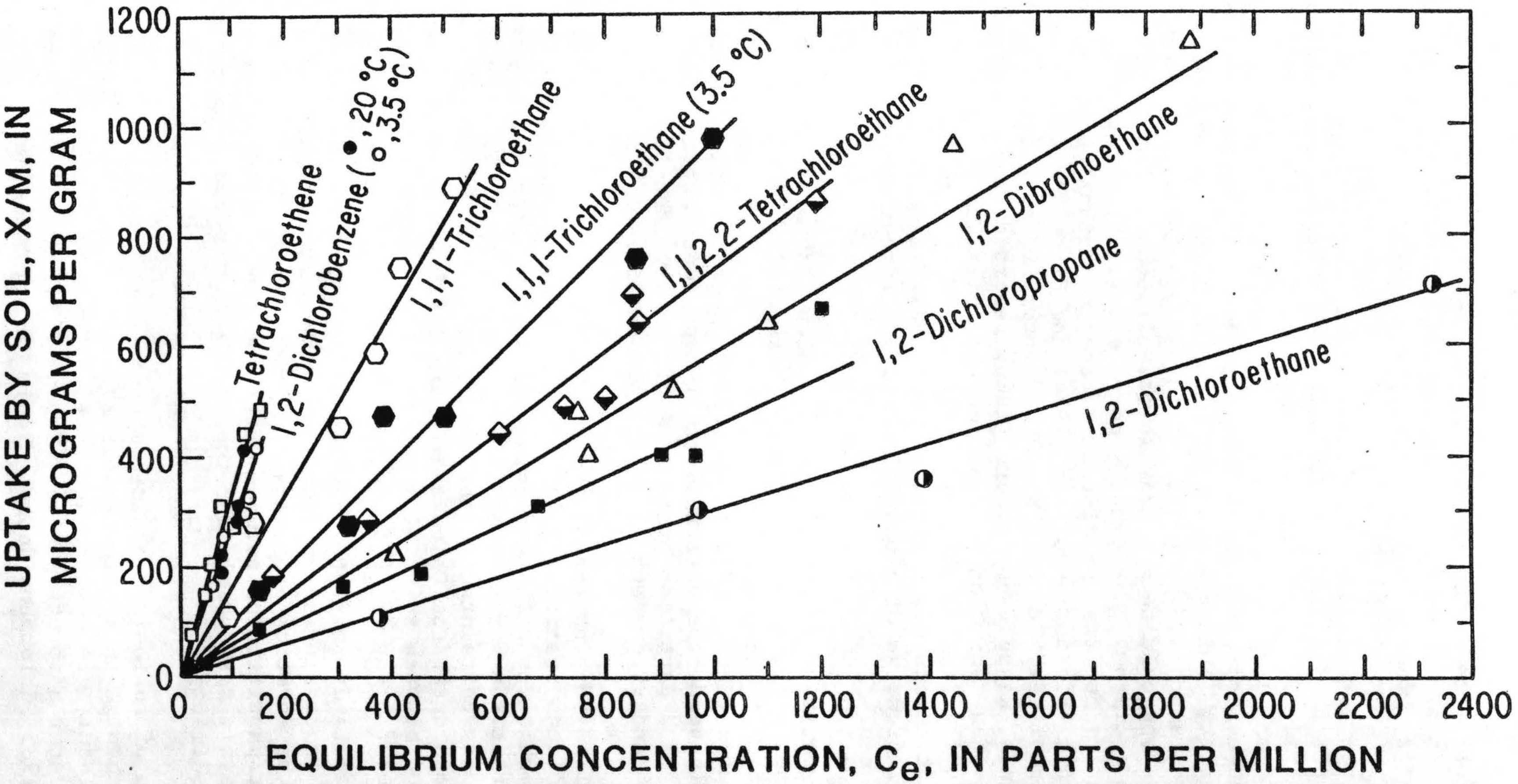

Figure 2. Soil-water equilibrium isotherms of some neutral organic compounds at 20°C. The soil used is a Willamette silt loam with 1.6 percent organic matter, 26 percent clay, 3.3 percent sand, and 69 percent silt. [Reprinted with permission from Science **206**, 831 (1979). Copyright 1979 by the American Association for the Advancement of Science.]

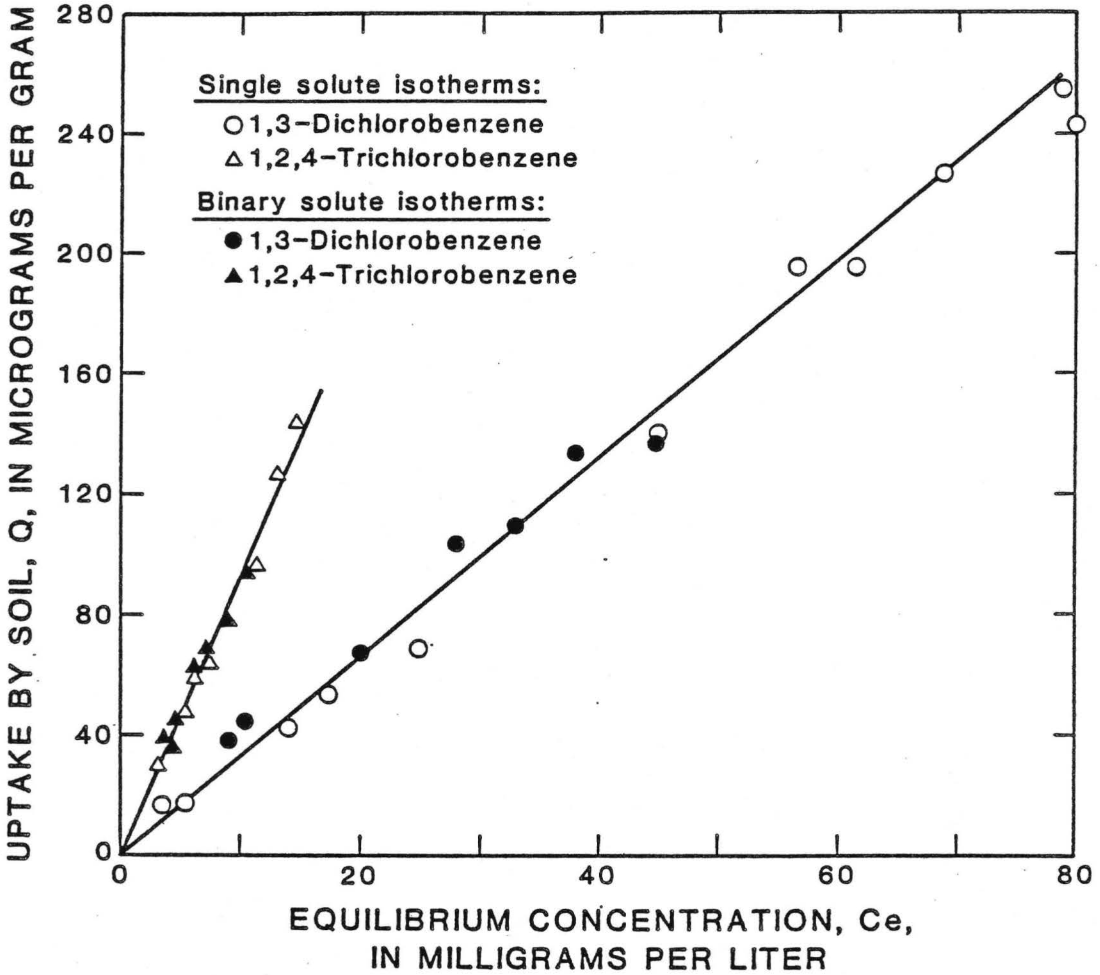

Figure 3. Typical soil-water equilibrium isotherms for 1,3-dichlorobenzene and 1,2,4-trichlorobenzene as single solutes and as binary solutes on a Woodburn silt loam soil at 20°C. [Reprinted with permission from Environmental Science and Technology 17, 229 (1983). Copyright 1983 by the American Chemical Society.]

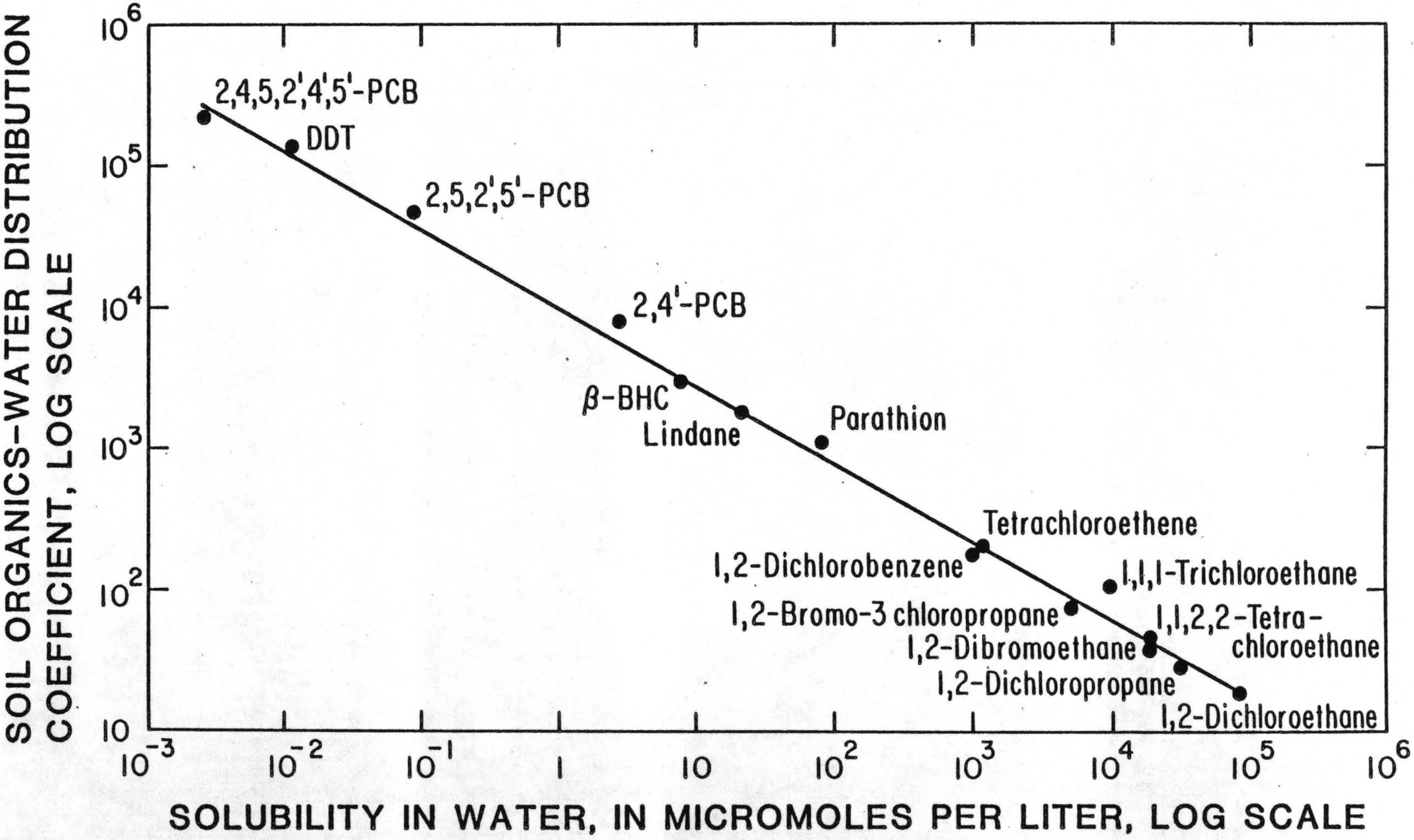

Figure 4. Soil organic-water sorption coefficients plotted as a function of the aqueous solubiliities of selected neutral organic compounds. [Reprinted with permission from Science **206**, 831 (1979). Copyright 1979 by the American Association for the Advancement of Science.]

sorption of nonionic organic compounds in the absence of water may result primarily from an adsorption mechanism. Yaron and Saltzman (1972) found that parathion sorption from a hexane solution decreased with increasing soil moisture content. Chiou and others (1985), when observing parathion and lindane sorption from hexane onto dry and partially hydrated Woodburn soil, observed nonlinear isotherms, strongly exothermic heats of sorption, competitive sorption effects, and dependence on clay content. Additionally, increased soil-moisture content decreased sorption. In the absence of the competitive effects of water for surface adsorption sites, the two nonionic insecticides were apparently adsorbed to the mineral surfaces. In hexane solution, little solute would partition into the soil organic matter because of its high solubility in the organic solvent. A slight increase in the soil-moisture content, however, resulted in a sharp decline in sorption due to adsorptive competition by the water molecules. Similar moisture-content effects have also been observed by Yaron (1978) for the sorption of organophosphorous insecticides to soils. Strong sorption of organic vapors by dry soils has also been attributed to adsorption by minerals since water is not present to compete with the nonionic organic molecules for adsorption sites (Chiou and Shoup, 1985).

The above hypothesis explains the results of Walker and others (1975) who observed greater extraction efficiencies for petroleum hydrocarbons from dry sediment when a more polar solvent was used. Polar solvents, such as methylene chloride, can replace nonionic organic compounds that are weakly adsorbed to the sediment mineral surfaces more effectively than nonpolar solvents such as hexane (Chiou and Shoup, 1985). Likewise, the sorption of a nonionic organic compound from a polar solvent such as methanol or methylene chloride onto dry soil or sediment would likely be insignificant (Chiou and others, 1985). The compound's high solubility in the solvent would greatly limit partitioning into the soil or sediment's organic matter, and the polar solvent would successfully compete with the solute for surface-adsorption sites. This observation is in agreement with the data of Nkedi-Kizza and others (1985), who observed decreased sorption of anthracene, atrazine, and diuron from water onto soil when methanol or acetone was added as a cosolvent. The cosolvent enhanced solute solubility (thus reducing the partition of solute into organic matter) while significant adsorption by minerals was prevented by the polar mixed solvents. In surface-water systems, however, sorption of nonionic organic compounds will always occur from water. Therefore, adsorption processes are likely to be insignificant compared to the partition of the organic compound into the sediment organic matter.

Importance of particulate organic matter

Because sorption of nonionic organic compounds appears to be caused by partition between water and the sediment organic matter, sediments with large organic-matter contents would be expected to sorb greater amounts of solute than sediments with small organic-matter contents. A correlation between organic matter content and sorption has been observed by numerous investigators (Pierce and others, 1974;

Spencer and others, 1974; Choi and Chen, 1976; Herbes, 1977; Rao and Davidson, 1979; Hassett and others 1980; Hassett and Anderson, 1982; Sharom and others 1980b; Abdullah and Ringstad, 1982; Banwart and others, 1982; Nkedi-Kizza and others, 1983; Glotfelty and others, 1984; Oliver and Charlton, 1984; Brown and others, 1985; Stamer and others, 1985), and is an important consideration when comparing sorption data obtained from different sediments. Two sediment samples collected from the same river cross section may have significantly different contaminant concentrations if their organic-matter contents are dissimilar.

To allow comparison of sorption coefficients obtained from different sediments, Karickhoff and others (1979) normalized experimentally determined sediment-water sorption coefficients by dividing by the organic-carbon content of the sediment. The resulting organic-carbon sorption coefficient, K_{oc}, differed little from sediment to sediment. Rao and Davidson (1979) measured soil-water sorption coefficients for several pesticides using three soil types. The sorption coefficients varied greatly with soil type, but, when the coefficients were adjusted to reflect the organic carbon content of the soils used, the resulting K_{oc} values showed much greater independence from the soil type. Similarly, Nkedi-Kizza and others (1983) observed that soil-water sorption coefficients obtained using six particle-size fractions of a Webster soil differed by a factor of 7, while calculated K_{oc} values differed only by a factor of 1.5. In a field study of atrazine and simazine sorption, Glotfelty and others (1984) also observed much less variability in K_{oc} values than in sorption coefficients not normalized for the organic-carbon effect. The results of these studies indicate that sorption coefficients normalized for sediment organic carbon content will best reflect spatial contamination trends by eliminating much of the variability caused by different concentrations of organic matter in sediments.

Because solute solubility in water (S) is the primary factor affecting both the soil organic-matter sorption coefficient (Chiou and others, 1983b) and the octanol-water partition coefficient (Chiou and others, 1982b), a relation can be established between S or K_{ow} and the sediment organic carbon sorption coefficient. Such a relation is depicted in figure 5 for 10 nonionic organic compounds partitioned between water and the coarse-silt fractions of two sediments (Karickhoff and others, 1979). Sorption differences caused by different solute types are accounted for by S or K_{ow}, and differences caused by different sediment types are accounted for by organic-carbon content. Similar relationships have been developed by Banwart and others (1982) and Oliver and Charlton (1984). Chiou and others (1979, 1983b) also have developed such relations, but have normalized the sediment-water sorption coefficient by the organic-matter content rather than the organic-carbon content.

Relations such as the one depicted in figure 5 potentially are very useful because they allow the prediction of the sediment-water

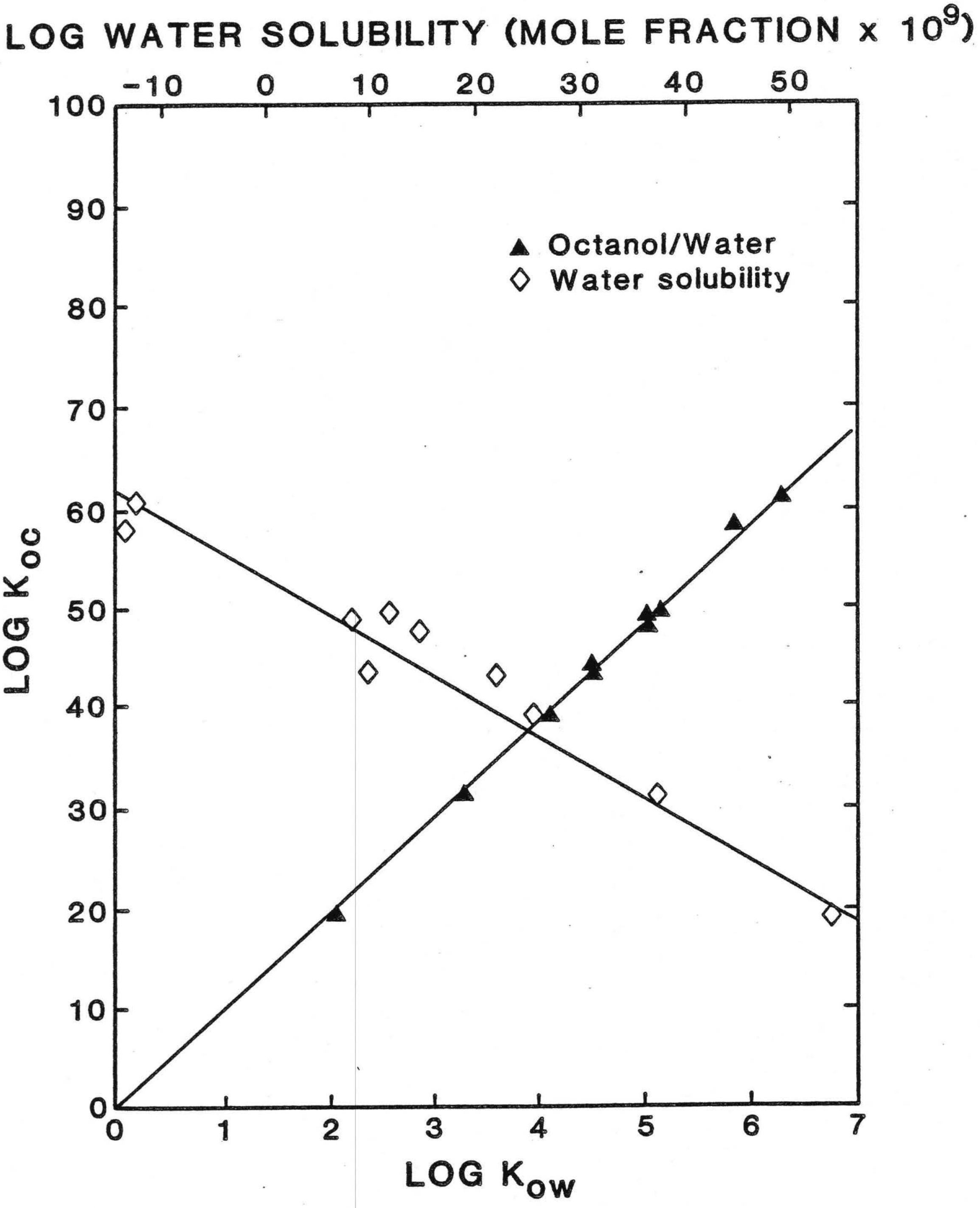

Figure 5. Sorption coefficient normalized for organic carbon content (K_{oc}) as a function of compound water solubility and octanol-water partition coefficient. [Reprinted with permission from Water Research 13, 247 (1979). Copyright 1979 by Pergamon Press Ltd.]

sorption coefficient for a multitude of nonionic organic contaminants with a knowledge of only the sediment organic-matter content and the solute's solubility or octanol-water partition coefficient. The K_{om} (or K_{oc}) value for a given compound will likely show some variation from sediment to sediment due to variations in the composition of the sediment organic matter (Means and others, 1982; Chiou and others, 1983b, 1984). However, this variation is small compared to variations in the sediment-water sorption coefficient prior to normalization for organic-matter content.

In general, sediment organic-matter content has been shown to increase with decreasing particle size (Choi and Chen, 1976; Frank and others, 1979; Scott and others, 1982; Simmons and Kotz, 1982; Ricci and others, 1983; Stamer and others, 1985). Therefore, the highest sorbed contaminant concentrations are commonly found in the silt and clay fractions of surface-water sediments. Bottom sediments with large percentages of silts and clays typically accumulate in areas of low water velocity, such as along the banks of rivers or lakes. Hunter and others (1980), in a study of an Oklahoma stream, observed the highest PCB concentrations in areas of sediment deposition. Routh (1972) likewise detected elevated DDT concentrations in Salinas River sediments in areas of low velocity.

It should be noted that although the highest contaminant concentrations are usually found in the silt- and clay-size fractions of a sediment (because of their usually high organic-carbon content), numerous exceptions have been documented. Stainken and Rollwagen (1979) found no correlation between percent silt/clay and PCB concentrations in sediment samples taken from Raritan Bay. Van Luik (1984) similarly found no correlation between the percentage silt/clay and either PCB or polycyclic aromatic hydrocarbon (PAH) concentrations in sediment samples from the Calumet Sag Channel. In a laboratory study of dibenzothiophene sorption to soils and sediments, Hassett and others (1980) observed no relation between the partition coefficient and either the cation-exchange capacity, the clay minerology, the percentage of clay, or the surface area of the soil/sediment. However, a positive correlation was observed between the partition coefficient and the organic-matter content of the soil/sediment. Organic-matter content, therefore, seems to be the most important indicator of a sediment's sorptive capacity for nonionic organic solutes.

Frank and others (1979, 1980a, 1980b, 1981), after observing the relatively low sorptive capacity of the sand-size fraction of Great Lakes' sediment compared to the silt- and clay-size fractions, corrected their sorption data for the variable content of sand in the different samples. Although this correction was an improvement, the approach depended on the relation between organic-carbon content and particle size and did not consider differences in the organic-carbon contents of the different sediment samples. The studies by Frank and others dealt with nonionic sorbates, such as PCBs and organochlorine insecticides, that will likely sorb by partition into the sediment organic matter. Therefore, a better normalization approach may have been to divide the sorbed contaminant concentration by the organic-matter content of the sediment sample as illustrated by Smith and others (1987). This approach does not depend on the organic-matter content to increase with decreasing particle size. It also accounts for differences in the organic-matter contents of the silt/clay fractions of the different sediment samples.

Importance of dissolved organic matter

Although the sorption coefficient is strongly influenced by the sediment organic-matter content, the presence of dissolved organic matter (DOM) also can influence the sorption coefficient by serving as an additional organic phase into which a solute can partition. In this manner, the DOM increases the apparent solubility of the solute in water while the amount of solute partitioned into the sediment organic matter may remain relatively unchanged because of low concentrations of DOM. The resulting net effect will be a decrease in the sediment-water sorption coefficient. Chiou and others (1986) have demonstrated that the apparent aqueous solubilities of DDT and two PCB isomers increase linearly with DOM content with no indication of competitive effects. They attribute the solubility enhancement of highly water-insoluble organic solutes by DOM to a partitionlike interaction of the compounds with the microscopic organic environment of the high-molecular-weight DOM. The solubility enhancement caused by DOM has also been observed by other researchers for DDT (Wershaw and others, 1969; Carter and Suffet, 1982; Caron and others, 1985); phthalate esters (Matsuda and Schnitzer, 1971); and the alkanes, hexadecane and eicosane (Boehm and Quinn, 1973). For more soluble compounds such as lindane, however, DOM concentrations up to 100 mg/L have been shown to have no significant enhancement effect on solute solubility (Chiou and others, 1986; Caron and others, 1985), which is in agreement with the proposed partition interaction between solute and DOM. Therefore, only relatively insoluble organic compounds, such as DDT or PCBs, are likely to exhibit enhanced solubility and reduced sorption coefficients in the presence of sufficient concentrations of DOM.

The ability of DOM to affect the sorption coefficient helps to explain the phenomenon known as the "solids effect," or the observed decrease in sorption coefficients with increasing sediment concentration. This effect has been studied by numerous researchers (Lotse and others, 1968; Grover and Hance, 1970; Herbes, 1977; O'Connor and Connolly, 1980; Horzempa and DiToro, 1983a; Koskinen and Cheng, 1983; Voice and others, 1983; Curl and Keoleian, 1984; Bowman and Sans, 1985a; Gschwend and Wu, 1985; Voice and Weber, 1985), and in some cases, an order of magnitude increase in the sediment concentration resulted in a decrease of comparable magnitude in the sorption coefficient. Voice and others (1983) and Gschwend and Wu (1985) have found that increased sediment concentrations result in increased DOM concentrations. Because increased DOM can reduce the apparent sorption coefficients of relatively insoluble organic compounds, the relation between the sediment concentration and the sorption coefficient can be at least partially attributed to the solubility-enhancing effect of DOM (Voice and others, 1983; Chiou and others, 1984; Gschwend and Wu, 1985; Voice and Weber, 1985).

DOM, therefore, may be very important in determining the environmental fate of extremely hydrophobic organic pollutants. Sorption coefficients may differ greatly between bottom sediments and suspended sediments because of the large variation in sediment concentration and consequently, the DOM concentration (Voice and Weber, 1985); those organic compounds that partition strongly to DOM may not exhibit the same bioavailability as they would if they existed in a free, solubilized state. Similarly, other fate-influencing processes such as volatilization, hydrolysis, or photolysis also may be substantially affected by the partitioning of organic compounds into DOM. However, available data suggest that under typical environmental conditions, only the least-soluble organic compounds will have their solubilities enhanced by DOM, and that the extent to which these compounds partition into the DOM will depend on the polarity and size of the dissolved organic molecules along with the solute's solubility (Chiou and others, 1986).

Sorption of Ionic Organic Compounds

Herbicides and phenolic compounds represent the majority of environmentally significant ionic organic compounds. Compared to nonionic organic compounds, such as PCBs and chlorinated insecticides, they generally have much higher aqueous solubilities, and as a result, solute partitioning into the sediment organic matter is greatly reduced. Their solubilities are functions of the system pH, so sorption can be expected also to vary with pH. Ionic organic compounds dissociate to either cations or anions, and, based on the surface charge of sediment particles, the ionized organic compound may be able to compete successfully with water molecules for surface adsorption sites. Table 2 lists some of the environmentally important cationic and anionic organic compounds.

Organic acids

The solubility of organic acids increases with pH as a result of increased deprotonation and the resulting anion formation. The organic anion presumably does not displace polar water molecules (or other inorganic cations) bound to surface adsorption sites inasmuch as particle surfaces, like the organic anion, generally are negatively charged (Khan, 1974a, 1980; Hayes and others, 1975; Jackson, 1975; Wang, 1975; Mulholland, 1981; Davis, 1982; Olsen and others, 1982). Therefore, since increased dissociation of the organic acid will not cause increased adsorption and since increased solute solubility will reduce solute partitioning into the sediment organic matter, the sorption of organic acids will be reduced at elevated pH.

Schellenberg and others (1984) noted decreased sorption coefficients for chlorinated phenols when the pH was increased from

Table 2. Selected anionic and cationic organic compounds of environmental significance.

Anionic	Cationic
Dalapon	Ametryn
Dicamba	Atrazine
2,4-D	Cyperquat
2,4,5-T	Difenzoquat
Glyphosate	Diquat
Picloram	Paraquat
Phenol	Benzidine
Chlorophenols	Prometon
Nitrophenols	Prometryn
Cresols	

6.5 to 8.5. The sorption isotherms were linear even at the higher pH values, indicating that solute adsorption was small compared to solute partitioning into the sediment organic matter despite the presence of the phenolate anion. This is consistent with the hypothesis that organic anions are repelled from negatively charged particle surfaces. Linear isotherms for phenolic compounds also have been determined by Scott and others (1982). Khan (1974b) observed nearly linear isotherms and low isosteric heats of sorption for 2,4-D sorption by a fulvic acid-clay complex, despite the fact that more than 50 percent of the 2,4-D was present in its anionic form. Nkedi-Kizza and others (1983) observed approximately linear isotherms for 2,4-D sorption to different soil particle-size fractions and noted the dependence of the sorption coefficient on the soil's organic-matter content. Linear isotherms also have been observed for 2,4,5-T sorption onto soil from water (Koskinen and Cheng, 1983). These results indicate that the organic anions present in solution generally do not exhibit appreciable adsorption due to their negative charge, and any sorption that does occur is primarily attributable to partitioning of the undissociated organic acid into the sediment organic matter (Chiou, 1981). Sorption of organic acids as influenced by partitioning will be reduced at higher pH due to increased solute solubility and decreased undissociated solute concentration in accordance with the results of Schellenberg and others (1984).

Organic bases

Sorption of organic bases to sediment also will be largely controlled by pH, but, in contrast to organic acids, adsorption of the protonated organic cation to particle surfaces (presumably by ion exchange or ion pairing) can be a significant sorption mechanism. Khan (1972a) has noted that sorption of basic herbicides is greatest at pH values close to the herbicides' pK_b values. At pH >> pK_b, the basic herbicides are almost completely in their neutral form and will be unable to compete with water molecules for mineral adsorption sites of the sediment due to their neutral charge. Partitioning into the sediment organic matter may also be low due to the generally high solubility of the basic herbicides. At pH << pK_b, the organic base will be almost completely in its cationic form, but adsorption will be retarded due to the high hydrophilicity of the cations in combination with the increased protonation of many of the acidic functional groups on the sediment organic matter. This counteracting effect makes the efficiency of the adsorption process a maximum at pH around pK_b.

Zierath and others (1980) found that the system pH controlled the sorption of benzidine to soils and sediments by varying the amount of benzidine present in the cationic form. Benzidine sorption increased as the pH was lowered to values approaching the compound's pK_b. Sorption of the ionized species also was correlated to the surface area of the soil/sediment used. Narine and Guy (1982) observed diquat sorption to humic acid to increase as the pH was raised from 2.0 to 9.0. Because diquat is essentially 100 percent in its cationic form within this experimental pH range, the increased diquat sorption at high pH can be attributed to a charge interaction (ion exchange or ion pairing) of diquat with the negatively charged acidic phenolic and carboxylic functional groups (having pK_a values of about 10 and 4, respectively) of the humic acid. The increased protonation of the functional groups at low pH decreases the availability of adsorption sites for the organic cations. The importance of the adsorption process to the sorption of organic bases is demonstrated by the data in figure 6 (Juo and Oginni, 1978), which presents sorption isotherms for paraquat using a variety of soils. The nonlinear isotherms are indicative of an adsorption process. Distinctly nonlinear isotherms also have been reported by Karickhoff and Brown (1978) for the sorption of paraquat by sediment and by Khan (1974c) for the sorption of paraquat and diquat.

Organic cations appear to be adsorbed primarily by an ion exchange mechanism, as is evidenced by the infrared spectroscopic analyses of Khan (1974c) and Senesi and Testini (1980). The adsorption process is, therefore, sensitive to both the charge and atomic radius of the saturating cation associated with the sediment. Khan (1974a) stated that the sediment-associated cations that enhanced adsorption of both diquat and paraquat to a humic acid followed the sequence: $Al^{+3} < Fe^{+3} < Cu^{+2} < Ni^{+2} < Zn^{+2} < Co^{+2} < Mn^{+2} < H^{+} < Ca^{+2} < Mg^{+2}$. The above relation is inversely related to the stability of the element when complexed with humic acid (Khan, 1974a). The stability of an element typically increases both with valence and ionic radius. Strongly bound cations, such as Al^{+3} or Fe^{+3}, are more resistant to displacement by an organic cation than are weakly bound cations, such as Ca^{+2} or Mg^{+2}. The variation in organic-cation sorption as a function of the type of inorganic cation saturating the soil or sediment also has been observed by El-Dib and Aly (1976b) and Hayes and others (1975). Hayes and others (1975) also noted that while different saturating inorganic cations may influence the sorption of bipyridylium herbicides, this influence will also depend on the type of clay mineral present. Karickhoff and Brown (1978) observed sorption coefficients for paraquat to be correlated with the cation-exchange capacity (CEC) of different particle-size fractions of a natural sediment. Zierath and others (1980) similarly noted that benzidine sorption increased directly with particle surface area.

Because sorption of organic bases, such as the bipyridylium herbicides, is primarily due to an adsorption process, solute solubility and sediment organic-matter content may not be sufficient parameters to predict sorption coefficients. As described above, the solute's pK_b and sediment factors, such as cation exchange capacity, surface area, or the charge or atomic radius of the saturating inorganic cation, also may be important to the determination of a sorption coefficient. System parameters, such as pH and ionic strength (Narine and Guy, 1982), may also influence sorption. For these reasons, predictive sorption modeling is more complex for organic bases than for organic acids or nonionic organic compounds. However,

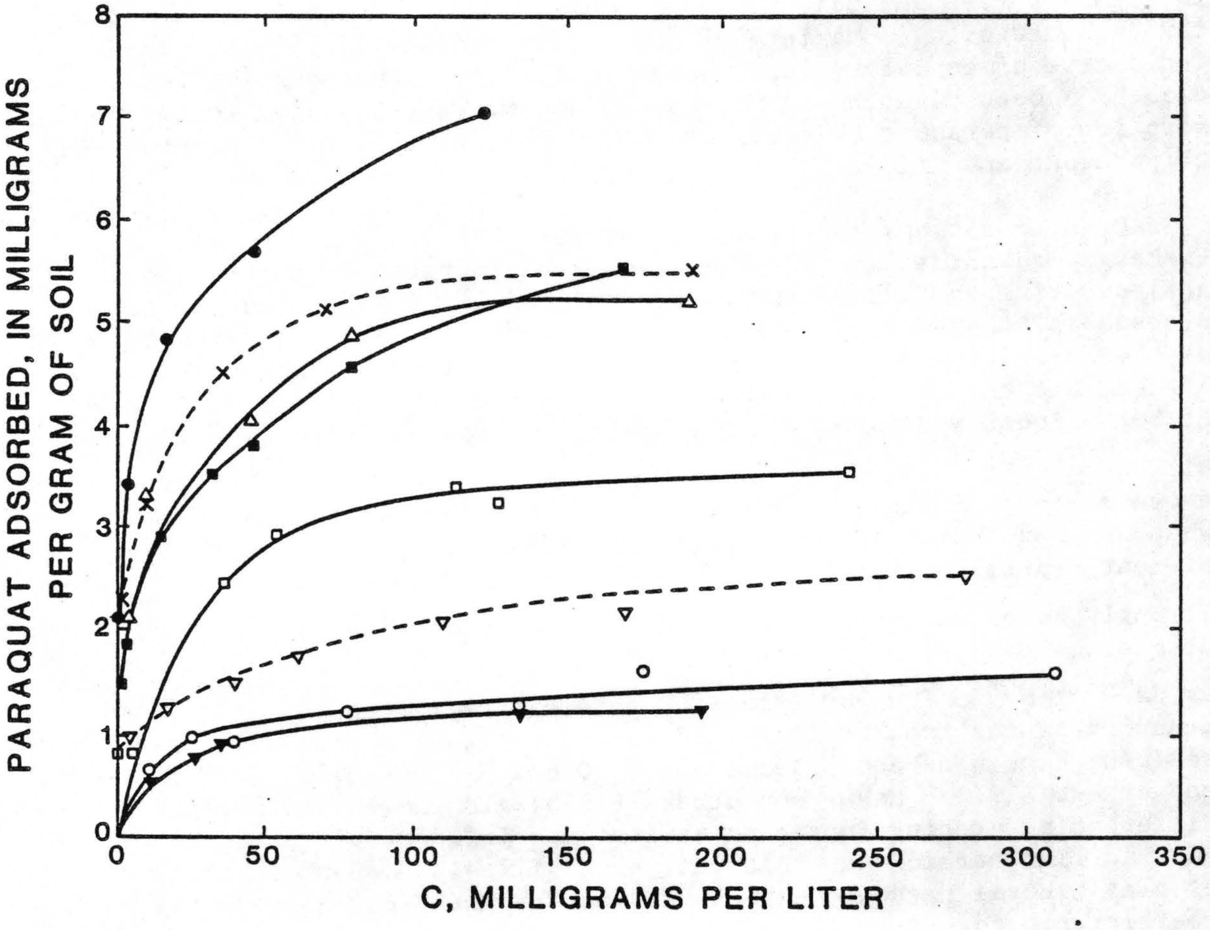

Figure 6. Adsorption isotherms of paraquat in soils. [Reprinted with permission from Journal of Environmental Quality 7, 11 (1978). Copyright 1978 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America.]

the environmentally significant compounds that exhibit the greatest tendency to sorb to surface-water sediments are the hydrophobic, nonionic organic compounds, such as the organochlorine insecticides and PCBs.

Bioaccumulation

Bioaccumulation (or bioconcentration) is the uptake of organic compounds by biota from either water or food. Many toxic organic chemicals attain concentrations in biota several orders of magnitude greater than their aqueous concentrations, and therefore, bioaccumulation poses a serious threat to both the biota of surface waters and to humans that feed on these surface-water species. The extent to which an organic compound tends to accumulate in an aquatic organism is quantified by the bioconcentration factor (BCF). Chiou (1981) defines BCF as the ratio of the concentration of a contaminant in an organism or the tissue of an organism to that in water. BCF also can be defined as the ratio of the accumulation and depuration rates of an organism (Neely and others, 1974). BCFs have been applied to quantify organic-contaminant concentrations in a variety of surface-water organisms. Agarwal and others (1982) documented the accumulation of DDT isomers by the freshwater ciliate Tetrahymena pyriformis. Barker (1984) noted the bioconcentration of organochlorine compounds at four different trophic levels in the Schuylkill River. Belluck and Felsot (1981) observed pesticide bioaccumulation by caddisfly egg masses. Birmingham and Colman (1983) documented diquat accumulation by freshwater plants. Microorganisms also have been shown to accumulate organic compounds (Grimes and Morrison, 1975; Paris and others, 1977; Blair and others, 1982). Additionally, numerous examples of organic compound bioaccumulation have been documented for fish and shellfish (Biddinger and Gloss, 1984).

Importance of Biological Lipid Reservoirs

Hamelink and others (1971) first proposed that the uptake of hydrophobic compounds by fish was primarily accomplished by exchange equilibria between the water and blood followed by storage in the fish's lipid reservoirs. Since then, researchers have investigated the importance of lipid-water partitioning with regard to bioaccumulation.

Hansch and others (1968) implied that the bioaccumulation of organic contaminants from water was comparable to the partitioning of the contaminant between water and an organic solvent such as octanol. In surface-water systems, hydrophobic organic contaminants will partition themselves between water and the lipid reservoirs of biological organisms, with solute solubility in water being a primary factor affecting the magnitude of the BCF for any given organism. However, unlike a solvent-water system, biological lipid-water systems do not attain rapid equilibrium. Slow solute diffusion to the lipid reservoir, combined with metabolic breakdown or aqueous phase transformation processes, can delay or even prevent the attainment of an equilibrium condition (Chiou, 1981). Generally, stable organic compounds with low aqueous solubility exhibit the longest equilibration times. Sanders and Chandler (1972) did not observe an equilibrium condition for PCB uptake from water by crayfish even after 21 days of exposure. Similarly, DDT uptake by goldfish did not result in steady-state concentrations even after 50 days (Rhead and Perkins, 1984). Oliver and Niimi (1983) monitored the bioconcentration of a variety of chlorinated benzenes by rainbow trout and noted that, as compound solubility decreased, the time to reach equilibration generally increased. Dichlorobenzene isomers attained equilibrium after 10 days, while pentachlorobenzene did not reach a steady-state concentration after 119 days. The tri- and tetrachlorobenzenes reached equilibrium after about 15 and 50 days, respectively. For the more soluble organic compounds, such as the herbicides alachlor and dinoseb, bioaccumulation by fathead minnows has been observed to reach equilibrium after only 24 hours (Call and others, 1984).

The time required to reach equilibrium has also been shown to be a function of fish size. Murphy (1971), in a laboratory bioaccumulation study using female mosquito fish, observed that the larger fish accumulated DDT from the water at a slower rate than smaller fish exposed to the same aqueous concentration. Similar results have been observed for the bioaccumulation of dieldrin (Reinert, 1972).

The hypothesis that bioaccumulation is primarily caused by partition into the lipid reservoirs of aquatic organisms is supported by the repeated observation of increased BCFs with increased lipid content. Canton and others (1977) noted that the greatest accumulation of hexachlorocyclohexane occurred in Chlamydomonas cells with the greatest lipid contents. Helwig and Hora (1983) confirmed the lipophilicity of PCBs by quantifying the compound's elevated concentration in fat tissue relative to meat tissue in Minnesota snapping turtles. Niimi (1979) measured the concentrations of hexachlorobenzene (HCB) in lake trout, rainbow trout, and coho salmon from Lake Ontario. The mean fat contents of each species of fish were proportional to their whole-body HCB concentrations. Additionally, HCB concentrations in fish samples within each species increased with fish size. Similar lipid-content effects were observed by Rudling (1970) with pentachlorophenol accumulation, by Ryan and others (1984) for dioxin and PCB accumulation, and by Seguchi and Asaka (1981) for diazinon accumulation. Skea and others (1979) placed fish in submerged cages in the Hudson River to quantify the bioaccumulation of PCBs. Again, the highest PCB concentrations were found in the largest fish (which possessed the highest lipid contents). The results of these studies indicate the importance of lipid content to the bioaccumulation of organic compounds. For a given exposure level, organisms with the highest lipid contents can be expected to accumulate the greatest amount of organic solute on a concentration basis. Similarly, the accumulated contaminant will likely concentrate itself in an organism's lipid reservoirs.

The extent to which an organic compound is bioaccumulated by a given aquatic organism largely depend on its aqueous solubility. As discussed earlier, decreasing solubility correlates with increasing

K_{ow}. Because bioaccumulation appears to be a partitioning process, the BCF can be expected to vary inversely with solubility. Also, the BCF can be expected to vary with K_{ow} such that increasing K_{ow} yields increasing BCF. Examination of the scientific literature reveals that these relations have been demonstrated in the laboratory. Mackay (1982b) compiled data from a variety of sources to develop figure 7, in which the BCFs based on whole-fish mass are used. The majority of the data are from the work of Veith and others (1979), and their plot of log K_{ow} versus log BCF is labeled in the figure along with the plot developed by Neely and others (1974). By selectively disregarding some of the data in figure 7, Mackay (1982b) developed his own relation (labeled "this work" in the figure) having the equation

$$\log \mathrm{BCF} = \log K_{ow} - 1.32$$

with a correlation coefficient of 0.95. The data of Neely and others (1974), not included in the above correlation, resulted in the following relation:

$$\log \mathrm{BCF} = 0.52 \log K_{ow} + 0.124$$

with a correlation coefficient of 0.948. Casserly and others (1983) also correlated K_{ow} with BCF for the green alga, *Selenastrum capricornutum* and established the equation

$$\log \mathrm{BCF} = 0.46 \log K_{ow} + 2.36$$

with a correlation coefficient of 0.83. Similar correlations have been reported by Oliver and Niimi (1983, 1985), Konemann and van Leeuwen (1980), and Southworth and others (1978a, 1978b). Figure 8 presents a plot of BCF as a function of aqueous solubility for a variety of pesticides accumulated by caddisfly egg masses (Belluck and Felsot, 1981). Again, a linear log-log relationship is assumed and defined by the equation

$$\log \mathrm{BCF} = -0.52 \log S + 1.67$$

Other solubility-BCF relations have been demonstrated by Chiou and others (1977), and Metcalf and others (1975). These relations indicate the dependence of the BCF on organic compound solubility and K_{ow}. The BCF tends to increase with decreasing solubility and/or increasing octanol-water partition coefficient.

Although numerous researchers have successfully performed regression analyses for BCFs as a function of either solubility or octanol-water partition coefficient, the predicted BCFs for a given compound by many of the correlation equations are significantly different, sometimes by orders of magnitude. Chiou (1981, 1985) has

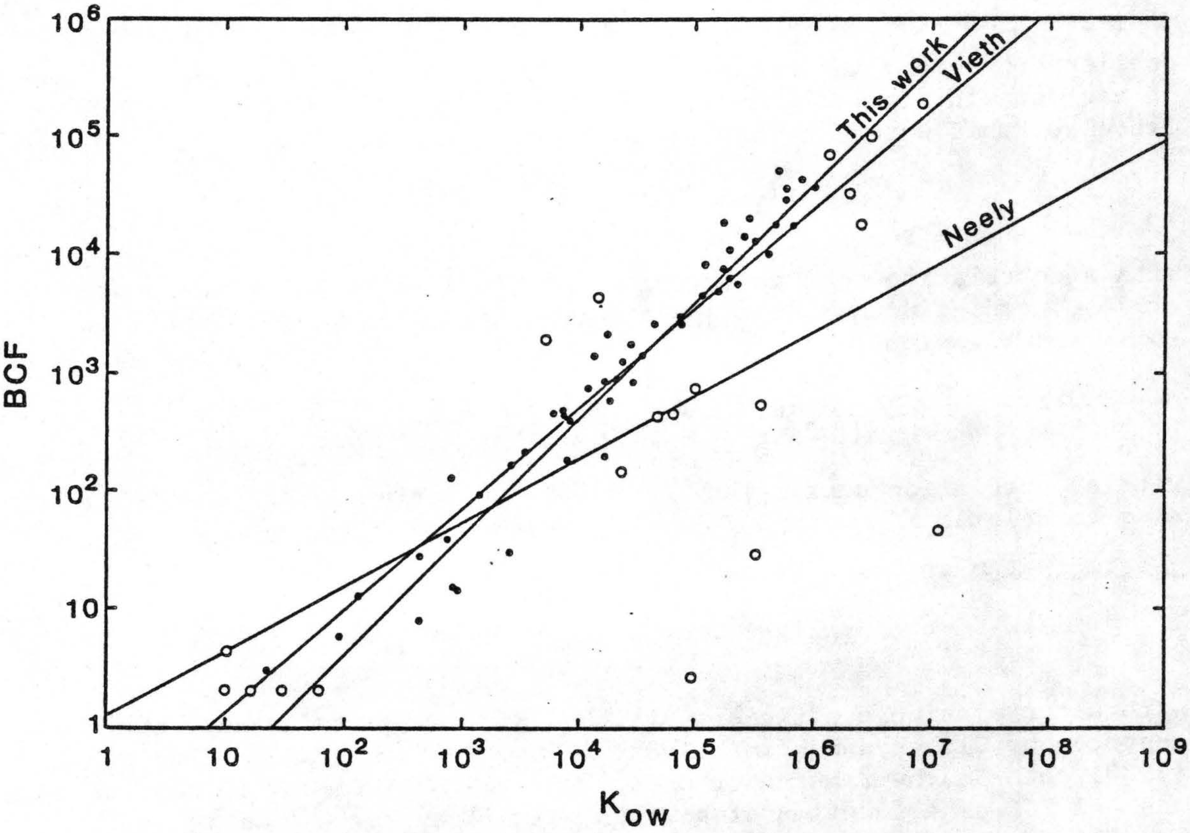

Figure 7. Correlation of bioconcentration factor (BCF) versus octanol-water partition coefficient (K_{ow}) showing the correlations of Veith and others (1979), Neely and others (1974), and Mackay (1982b) (labeled "this work"). Only solid points are included in the regression. [Reprinted with permission from Environmental Science and Technology **16**, 277 (1982). Copyright 1982 by the American Chemical Society.]

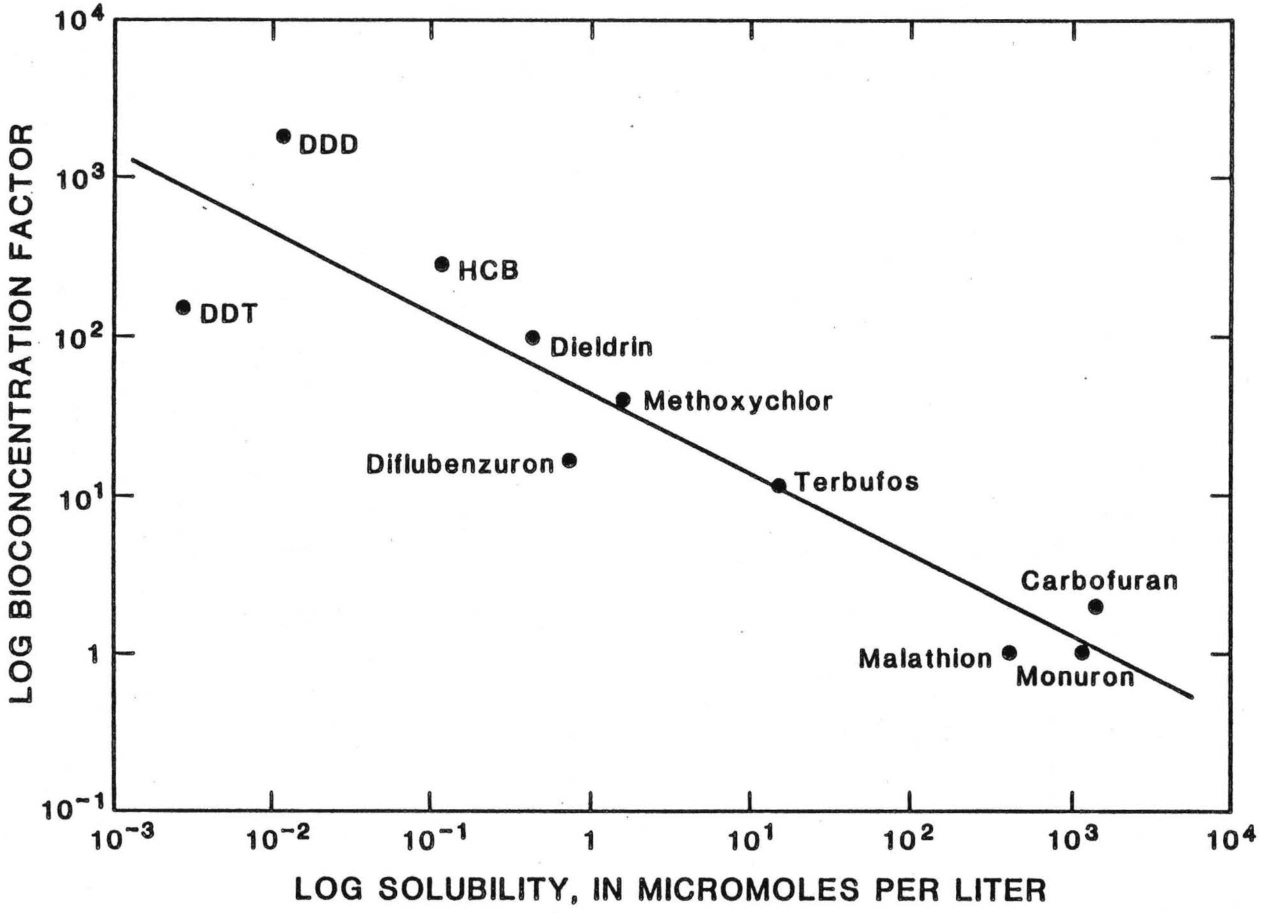

Figure 8. Relation between log water solubility of pesticides and log bioconcentration factor (BCF) for T. tardus egg masses. [Reprinted with permission from Bulletin of Environmental Contamination and Toxicology **26**, 304 (1981). Copyright 1981 by Springer-Verlag New York Inc.]

suggested that these differences are largely accounted for by differences in the lipid contents of the aquatic organisms used to develop the different correlations. To account for this effect, Chiou (1985) normalized BCF values obtained from the work of Konemann and van Leeuwen (1980) and Oliver and Niimi (1983) by dividing them by the fraction of lipid present in the organism. Figure 9 presents a log-log plot of the lipid-normalized BCFs for rainbow trout and guppies versus the triolein-water partition coefficients (K_{tw}) for a variety of organic compounds. The parameter K_{tw} was used instead of K_{ow} because triolein more closely resembles the fish lipid than does octanol. The data are well correlated, and the regression equation takes the form

$$\log BCF = 0.957 \log K_{tw} + 0.245$$

with $n = 18$ and a correlation coefficient = 0.915. Unlike previous regressions, no systematic differences between the two fish species appear evident. Just as sorption coefficients can be estimated from sediment organic-matter content and a compound's solubility or K_{ow}, the above correlation allows the prediction of the BCF only from a knowledge of the organism's lipid content and the compound's K_{tw}. Chiou (1985) also related K_{tw} to K_{ow}, so the BCF can also be determined from the compound's K_{ow} using the following equation:

$$\log BCF = 0.893 \log K_{ow} + 0.607$$

with $n = 18$ and a correlation coefficient = 0.904.

Differences between predicted and actual BCFs can arise due to a variety of factors (Chiou, 1985). The BCFs determined in figure 9 are assumed to be at an equilibrium condition. If a compound is unstable in water or is metabolized at a rate greater than the rate of equilibration with the organism's lipid reservoir, actual BCFs will be lower than predicted values. Also, partitioning of an organic compound into the non-lipid phases of an organism may be significant for compounds of high aqueous solubility. Thirdly, dissolved organic matter may enhance the solubility of organic compounds which in turn would result in lower apparent BCFs than predicted by a compound's K_{ow}. Finally, Niimi and McFadden (1982) and Oliver and Niimi (1983) have observed that BCFs increase slightly with increasing solute concentration (although Isensee and Jones (1975) and Canton and others (1977) did not observe variance of BCFs with the solute's aqueous concentration). Despite these possible sources of variation in the prediction of BCFs, consideration of the lipid contents of different aquatic organisms will likely result in better comparability of BCFs.

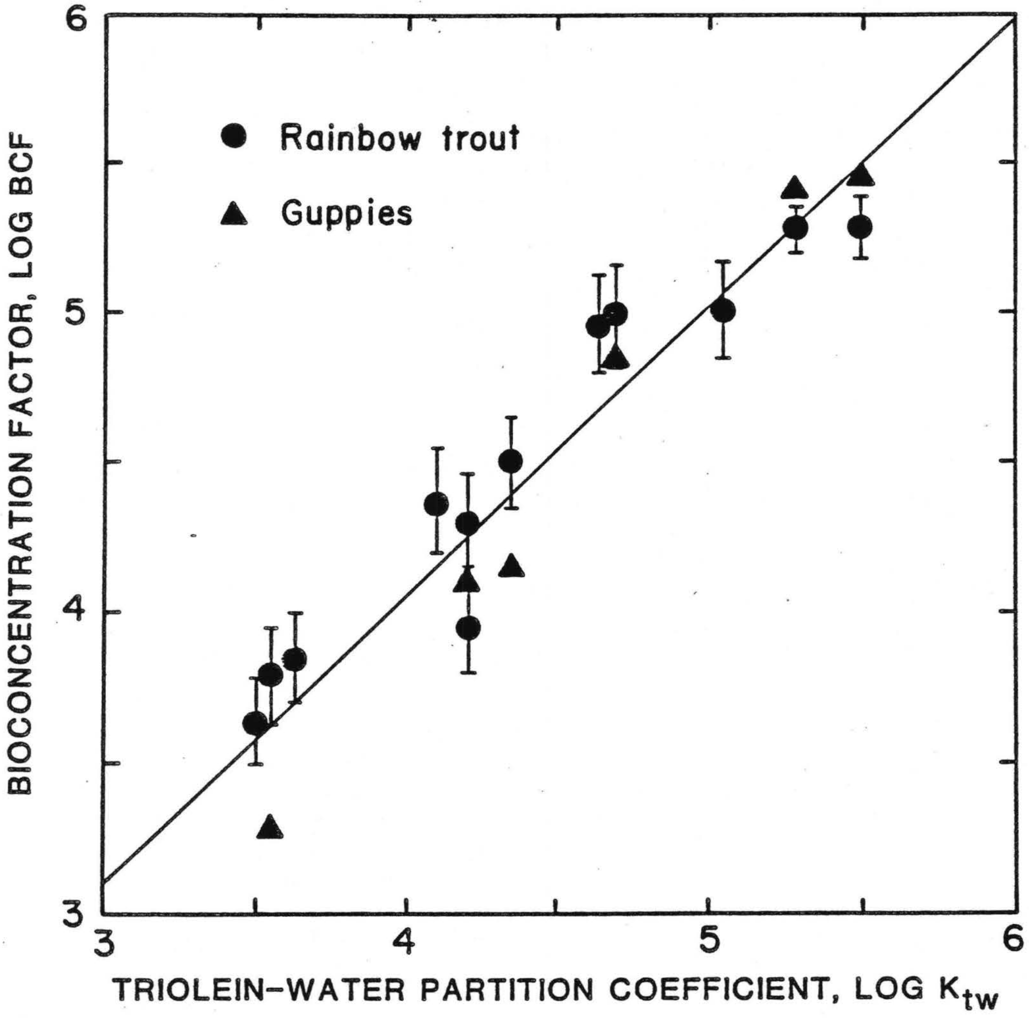

Figure 9. Correlation of log bioconcentration factor (BCF) on the basis of fish lipid content with log triolein-water partition coefficient (K_{tw}) for a variety of nonionic organic compounds.

Vertical limits of bars for rainbow trout are the minimum and maximum BCFs reported. [Reprinted with permission from Environmental Science and Technology **19**, 61 (1985). Copyright 1984 by the American Chemical Society.]

Biomagnification

There has been considerable debate as to whether bioaccumulation of organic compounds in aqueous systems is based on the physicochemical properties of the compound acting in combination with the physiology of the aquatic organism, or if it is attributable to the trophic transfer of these compounds through the food chain (Biddinger and Gloss, 1984). The latter concept of aqueous-system biomagnification, or the accumulation of organic compounds through trophic transfer, is not well substantiated by the scientific literature.

Previous assumptions of biomagnification have been based on data that neglected to account for physiological differences between organisms. In most cases, reports of aqueous system biomagnification were confused with the concept of bioaccumulation resulting from the uptake of organic chemicals directly from water. To determine if biomagnification is an important process in aqueous systems, recent studies have been conducted to isolate the relative importance of food and water to the uptake of organic compounds by aquatic organisms. The results of these studies have indicated that the uptake of contaminants through food has only a small effect on the accumulation of organic contaminants by aquatic organisms relative to uptake resulting from exchange equilibria with water.

Canton and others (1975) studied the bioaccumulation of hexachlorocyclohexane (HCH) using the following food chain combinations: algae-daphnia, daphnia-guppy, and guppy-trout. When compared with contamination by water alone, the transfer of HCH through the food chain was minimal, and the authors concluded that the uptake of HCH from water was much more important than uptake through food. In a study of atrazine uptake by freshwater molluscs and fish, Gunkel and Streit (1980) illustrated that the feeding of contaminated food to the organisms did not increase their equilibrium whole-body atrazine concentration above the level obtained by exposure to contaminated water only. Additionally, by noting that the highest BCFs were occurring in the organs of the fish with high blood circulation, they postulated that atrazine is taken in by the gills and transported in the blood to the organs. They went on to use tritiated-water-balance calculations to determine that the swallowing of water and the exchange of water through the skin are of little importance to either the fish's water balance or its accumulation of atrazine. Niimi and Cho (1983) analyzed fish from Lake Ontario representing two trophic levels and noted that pentachlorophenol (PCP) levels in the fish from the different trophic levels were not significantly different. In an earlier study, Niimi and McFadden (1982) illustrated that rainbow trout exposed to aqueous PCP concentrations of 35 ng/L and 660 ng/L accumulated 9 μg and 115 μg of PCP, respectively, after an exposure period of 115 days. Although the fish's diet had a PCP concentration of 3 μg/kg, the authors estimated that no more than 2 μg of PCP were accumulated through diet. Southworth and others (1979) also confirmed the importance of the uptake of organic contaminants from water. They showed that the uptake rates of acridine by freshwater fish via ingestion of contaminated invertebrates (0.02

μg/g/h) or by ingestion of contaminated sediment (0.01 μg/g/h) were insignificant relative to the rate of direct uptake from water (1.40 μg/g/h).

In further support of the hypothesis that aqueous solute concentrations control the extent of bioaccumulation are the data of Canton and others (1977) and Paris and others (1977). The former study determined that the accumulation of HCH by the marine algae *Chlamydomonas* was the same for both living and dead cells. The study of Paris and others (1977) reported the same results for the bioaccumulation of toxaphene by a variety of aquatic microorganisms. The metabolic processes of the aquatic organisms, therefore, had no measurable effect on the equilibria established between the water and the lipid reservoirs of the microbes.

Some laboratory studies have noted that the uptake of organic contaminants from food has significantly contributed to the bioaccumulation of the compound in the aquatic organism. However, many of these studies did not allow an equilibrium condition (essentially zero change of contaminant concentration in the aquatic organism with time) to be established. Rhead and Perkins (1984) found that either dietary exposure or solution exposure of DDT to goldfish could be the dominant source of accumulation, depending on their relative concentrations. However, equilibrium conditions were apparently not obtained in any of their experiments. Therefore, their experiments only demonstrated that dietary exposure to DDT can significantly enhance the rate of DDT bioaccumulation. It did not demonstrate that dietary exposure could increase the magnitude of an equilibrium BCF determined from water exposure only. In a similar study, Shannon (1977) observed the relative importance of food versus water uptake to the bioaccumulation of dieldrin by channel catfish. Catfish exposed to 2 mg/kg of dieldrin through their diets combined with exposure to 75 ng/L of aqueous dieldrin accumulated significantly more of the compound than catfish exposed only to aqueous dieldrin. Here again, however, an equilibrium condition was not attained in either of the exposure experiments. Skea and others (1981) fed brook trout a mirex-contaminated diet for 100 days and noted a substantial accumulation of the compound in the fish. Equilibrium conditions were not attained and no comparison was made with mirex exposure through water only. These studies indicate that prior to equilibrium, uptake of organic contaminants by aquatic organisms can occur both through dietary and aqueous exposures, but they do not support the concept of biomagnification.

In some cases, increases in BCFs are mistakenly attributed to biomagnification when, in fact, they are caused by differences in lipid contents. In a study of four different trophic levels in the Schuylkill River, Barker (1984) reported PCB levels of 56 μg/kg in the primary producers, 125 μg/kg in the primary consumers, and 650 to 700 μg/kg in the secondary and tertiary consumers. Although data such as these commonly are attributed to biomagnification, Barker attributes the variations primarily to differences in the lipid contents of the trophic levels along with other physiological factors such as age, sex, sex cycle, and diet. Of the aquatic organisms examined by Barker, the highest organochlorine residues were detected in the American eels, which typically have very high lipid contents relative to other aquatic organisms.

The studies discussed above indicate that the popular concept of biomagnification in aquatic systems is not well supported by the scientific literature. Future studies need to take into account physiological differences between aquatic species (and even different specimens) and BCFs should be compared only if the values are obtained at an equilibrium condition. The available data suggest that accumulation of organic contaminants by aquatic organisms is primarily caused by solute partitioning between water and the lipid reservoirs of the organism.

Transformation Processes

This section reviews the following four transformation processes that remove organic contaminants from aqueous solution:

1. Photolysis
2. Hydrolysis
3. Biodegradation
4. Volatilization

Each process attenuates the concentration of an organic compound in solution by a different chemical, physical, or biological mechanism. The magnitude of the attenuation depends upon the combination of physicochemical properties of the compound and the environmental conditions of the water body where the compound is present. The removal mechanism, as well as the environmental and compound-specific properties influencing the rate of removal, are reviewed for each of the four processes.

In addition to detailing the environmental and physicochemical factors influencing the removal of contaminants by the above four processes, this section also examines the kinetics of the removal processes. Each transformation process can be represented, mathematically, by a first-order rate law. Other representations, such as higher-order rate laws, also are reviewed where appropriate. The first-order rate law is emphasized because it is the simplest kinetic description and is applicable to all four processes. The rate law for each process is described by a constant whose magnitude reflects the influence both of environmental factors and physicochemical properties. Consequently, the rate constant is useful as a relative measure for determining which of the four competing processes dominates the organic contaminant removal under a specific set of environmental conditions.

Photolysis

The study of photochemistry in natural waters is still a relatively new and emerging field. Only in the last decade has the knowledge obtained about atmospheric photochemistry during the last century been extended to the photochemical processes in marine and freshwaters (Miller, 1983; Zafiriou and others, 1984). The environmental photolysis of organic compounds is a complicated series of processes that depends on:

1. Properties of the particular organic molecule,
2. The characteristics of the water body, and
3. The input of sunlight.

This section reviews the component factors from the above three categories that appear to have the greatest influence on the process of photolysis in surface-water systems.

Photolysis is the degradation of compounds by the action of light. The aqueous photochemical reactions collectively referred to as photolysis can be further categorized as direct and indirect (or "sensitized") photolysis (Zepp and Cline, 1977). Direct photolysis is defined as the absorption of light by a compound causing a chemical reaction involving the energized molecule. The absorbed radiation transforms the molecule into an excited state with a greater tendency to react in order to return back to a more stable ground-state configuration. The possible resulting reaction mechanisms can include, but are not limited to, molecular rearrangement, dissociation, and oxidation.

Indirect photolysis refers to those photochemical reactions in which an organic compound interacts with other previously energized molecules rather than directly with solar radiation. Natural waters provide an abundance of potential reactive species which can absorb radiation and then react with organic contaminants by indirect photolytic mechanisms. These light absorbing species (called chromophores) include humic substances, transition-metal ions, organic-free radicals, and oxidizing species, such as peroxides, singlet oxygen, and ozone (Miller, 1983). Because it is difficult to separate and isolate the dominant photochemical mechanisms in natural waters, most studies do not attempt to differentiate between the different types of photolytic reactions (Callahan and others, 1979). Much of the available laboratory data and the remainder of the current discussion focuses on the physicochemical properties and environmental variables that influence the direct photolysis of organic contaminants.

The importance of photolysis to the degradation of organic compounds in surface-water systems is measured by the photolysis-rate constant, which is a measure of an organic compound's photodecomposition over time. The magnitude of the photolysis-rate constant depends on the amount and wavelength of the solar radiation that reaches a particular compound and on the ability of the compound to absorb that energy source. Environmental variables determine the intensity and spectral distribution of wavelengths of light available to a compound. Physicochemical properties, such as the light-absorption coefficient, determine the efficiency of the conversion of the energy into the photochemical transformation of the compound.

The intensity and spectral distribution of solar radiation is attenuated in the atmosphere through absorption by gases--for example, ozone--and scattering by molecules and aerosols. The degree of attenuation varies with the time-of-day, season, geographic location, and the thickness of the ozone layer. At the air-water interface, the two sources of radiation originating from the atmosphere are direct radiation and sky radiation. The latter type of radiation is derived from the scattering of direct radiation into the water body. The radiation reaching the air-water interface either is reflected back into the atmosphere (generally less than 10 percent) or is refracted into the water body at an angle different from the angle of incidence. Once in the bulk solution, light is further attenuated by absorption and scattering. Light is absorbed by water molecules, dissolved solids, and suspended sediment. Absorption of light also occurs as a result of the biological activity of photosynthetic organisms. Attenuation by scattering in the water column has a smaller impact than absorption on the penetration of light, and is generally ignored in obtaining first-order approximations of light intensity (Zepp and Cline, 1977).

In addition to the environmental variables, the photolysis rate also depends on certain characteristics of the organic contaminant. Of the light that reaches the compound, only light absorbed by the chemical can cause photolytic degradation. The percentage of available light absorbed by the contaminant depends on its molar extinction coefficient and its concentration. In other words, the presence of the solute changes the value of the absorption coefficient of the solution from the value attributable solely to pure water. Based on the fundamental law of photochemistry, the average photolysis rate, at a specific wavelength in a completely mixed water body, is directly proportional to the rate of light absorption by the solute per unit volume (Zepp and Cline, 1977). To obtain the actual, average photolysis rate, this relation is summed over all the wavelengths in the ultraviolet- and visible-light range and multiplied by a constant. The constant, called the quantum yield of the reaction, represents the efficiency of usage of the absorbed radiation by the solute for the particular photochemical reaction. From the intensity of radiation at a particular depth in a water body, the average photolysis rate is estimated from the properties of the solute; namely the molar extinction coefficient, the concentration, and the quantum yield for the photochemical reaction.

The most commonly used representation for a direct photolytic process is a first-order kinetic expression,

$$d[C]/dt = -k_p[C].$$

In this expression, the rate of change of a compound's concentration (resulting from photolysis) is directly proportional to the concentration of the compound multiplied by a first-order rate constant, k_p, with units of reciprocal time.

The first-order rate constant is the product of the rate constant for the absorption of light by the chemical, k_a, multiplied by the quantum yield (0) (the efficiency of energy conversion for the photochemical reaction), or

$$k_p = (k_a) (0).$$

The determination of the absorption-rate constant takes into account the environmental variables for a specific system, such as time-of-day, season, latitude, ozone thickness, and depth in the water body, as well as the absorption characteristics, such as the molar extinction coefficient, of the particular compound.

The influence of the compound's absorption properties on the rate of direct photolysis is illustrated by the following example. Zepp and Cline (1977) calculated the direct photolysis rates for carbaryl (a carbamate insecticide) and trifluralin (a dinitroaniline herbicide). Both compounds have similar quantum yields for reactions in air-saturated water, but their peak absorption of radiation occurs in different parts of the ultraviolet- and visible-light ranges. Consequently, for the same set of environmental conditions (midday, midsummer, latitude 40°N), the absorption rate for trifluralin is 400 times larger than that for carbaryl, and the direct photolysis of trifluralin is two orders of magnitude more rapid than that of carbaryl (Zepp and Cline, 1977).

The intensity and spectral distribution of light are as important as the absorption properties of the compound in determining the photolysis rate. The data of Zepp and Cline (1977) illustrate the difference that chemical properties can have on the photolysis rate. This difference is not constant, but varies with environmental conditions. Different combinations of time-of-day, season, latitude, and ozone thickness will selectively filter out different wavelengths of light. Because the two compounds absorb radiation of different wavelengths, this filtering process may serve to alter the intensity of usable radiation available to the compounds. Thus, for the same set of environmental conditions, two compounds can photolyze at different rates because of differences in the energy content of the range of solar radiation (the specific set of wavelengths) they absorb.

Using the first-order rate equation for direct photolysis, an expression can be derived for a compound's half life. The half life (originally devised to measure the decay of radioactive material) refers to the time required for one half of the initial concentration of a compound to be removed solely by direct photolysis. The half-life expression for a first-order, direct photolysis process is,

$$t_{1/2} = 0.693/k_p$$

and it is dependent on only the quantum yield and the absorption coefficient for a particular compound. Compounds with high absorption coefficients and high quantum yields will have low half-life values indicating a rapid removal of the compound by photochemical processes. Because the half-life concept provides an indication of the rate of reaction in units of time (as opposed to rate constants in units of reciprocal time), it is a tangible measure for comparing photolysis with other first-order rate processes, such as hydrolysis, volatilization, and biodegradation.

Although estimates of the photolytic half lives of certain organic chemicals account for many environmental and compound-specific properties, additional factors should be considered to improve the approximation of the photolytic degradation of an organic contaminant. For example, cloud cover can reduce the intensity of ultraviolet radiation by as much as 50 percent and thereby alter the degradation kinetics of an organic compound. In contrast, variations in the elevation of a stream within a geographical area can increase light intensity by 15-20 percent for every kilometer increase in elevation. Also, daily changes in the thickness of the ozone layer can vary as much as 30 percent, causing changes in atmospheric scattering and absorption.

The influence of other factors on the photolysis process have not been well quantified. For example, it has yet to be determined how varying concentrations of chromophores, such as dissolved and particulate organic matter, affect the rate and extent of indirect photolysis reactions. In many studies, the effect of light scattering in the water column is ignored, but it may be significant in turbid lakes and rivers. Finally, the mixing of water continually changes the temporal and spatial distribution of available sunlight and chemical concentrations. Current photolysis models are still at a stage of development where they assume a spatially homogeneous distribution of the contaminant throughout the depth of the water column.

Although the laboratory protocols and the kinetic representations for direct photolysis have been fairly well established, similar procedures for indirect photolysis are only beginning to be understood. Indirect photolysis is a much more complicated phenomenon and it is mediated by any one of a variety of natural compounds. The chemical kinetics are represented by a second-order process where the rate of removal depends on both the compound's concentration and on the concentration of the reactive intermediate (U.S. Environmental Protection Agency, 1979a). The difficulty encountered in applying this kinetic approach is in experimentally measuring the concentrations of the reactive intermediates which frequently have half lives on the order of microseconds or less (Zafiriou and others, 1984). Nevertheless, Miller (1983) states that the contribution of indirect photolytic processes to the overall photolysis rated may be significant. The increasing ability of researchers to isolate, monitor, and measure the chromophores present in natural waters (for example, humic substances, transition metal ions, free radical and other oxidizing species) will likely result in the increased understanding of both indirect and direct photolysis of anthropogenic organic compounds in surface-water systems.

Hydrolysis

Hydrolysis is a transformation process that changes the chemical speciation of an organic contaminant. Like photolysis, biodegradation, and volatilization, the extent of contaminant removal by hydrolysis depends both on the chemical properties of the organic compound and aqueous medium. Also, like other transformation processes, the hydrolysis of organic contaminants is mathematically represented by a first-order kinetic process. This section summarizes some of the equations and physicochemical factors influencing the rate and extent of the hydrolysis reaction for different classes of organic compounds.

Hydrolysis is the reaction of a compound with water resulting in an exchange of some functional group, X^-, of the organic molecule with a hydroxyl group, OH^-, from the aqueous medium. The overall mechanism can be represented by the following reaction sequence

$$RX + H_2O \dashrightarrow ROH + HX ,$$

where RX is the organic molecule and X is a particular functional group. The individual reaction steps involve the formation of one or more intermediates which combine to transform the compound by the above, simplified mechanism. On the basis of this mechanism, the hydrolysis rate is expressed by a first-order rate law such that

$$-d[RX]/dt = K_h[RX] ,$$

where $-d/dt[RX]$ = rate of hydrolysis of compound RX, mass $\text{volume}^{-1}\,\text{time}^{-1}$

K_h = hydrolysis rate, time^{-1}

$[RX]$ = concentration of compound RX, mass volume^{-1}.

In a manner similar to other transformation processes, the rate of contaminant removal by hydrolysis depends on the chemical structure of the compound and the influence of pH, temperature, ionic strength, and the presence of other compounds, such as humic substances. The contribution of each factor to the overall rate of hydrolysis is accommodated by modification of the above first-order rate law to explicitly account for the additional variable. For example, the rate of hydrolysis depends on the pH of the aqueous solution. Depending on the particular organic compound, the hydrolysis rate is increased by the addition of acid or base to the system. In this case, the rate expression is rewritten to reflect the explicit dependence of the reaction rate on the concentration of acid, $[H^+]$, and base, $[OH^-]$:

$$-d[RX]/dt = K_a[H^+][RX] + K_b[OH^-][RX] + K_n[RX] = K_h[RX] ,$$

where K_a and K_b are second-order rate constants (mass volume^{-1} time^{-1}). This relation shows that the rate of hydrolysis depends on the product of the acid or base concentration multiplied by the contaminant concentration. K_n is the first-order rate constant for the pH-independent reaction.

Incorporation of the effects of acid- or base-promoted catalysis increases the order of the overall hydrolysis expression from first to second order. The rate now depends, explicitly, on the concentration of two components, [RX] and $[OH^-]$ or $[H^+]$. Rearranging the rate equation to express it solely in terms of $[H^+]$ is done using the expression for the dissociation of water, $K_w = [OH^-][H^+]$, and by cancelling the [RX] in each term. From the above equation, this gives,

$$K_h = K_b K_w/[H^+] + K_a[H^+] + K_n \ .$$

From this expression, it is apparent that at elevated pH, the overall rate constant is controlled by the first term on the right side of the equation (assuming $K_b K_w$ is sufficiently large). Under acidic conditions, the elevated H^+ concentration makes the second term on the right side dominate in the determination of the overall rate constant (assuming K_a is sufficiently large). At neutral pH, the last term on the right side controls the rate of reaction. Thus, for a particular reaction, the rate depends on the pH of the aqueous medium as well as on the relative magnitude of the three rate constants, K_a, K_b, and K_n. Because the order of the reaction varies with pH (second order for acid or base conditions and first order at neutral pH) the overall hydrolysis rate constant, K_h, is sometimes termed a pseudo-first-order constant (Mabey and Mill, 1978). It is the observed or estimated rate constant for hydrolysis at a constant pH.

In addition to pH, other factors influence the rate of hydrolysis of organic contaminants; these include temperature, ionic strength of the solution, and the presence of other natural organic compounds, such as humic substances. In general, the rate of hydrolysis increases with temperature, and this observation follows the commonly cited Arrhenius equation. This equation relates the rate constant of a chemical reaction to the absolute temperature of the system and, for a specific reaction, takes the form

$$k = A \exp [-E/RT],$$

where k is the rate constant, E is the activation energy, R is the universal gas constant, T is the absolute temperature, and A is a constant.

The presence of dissolved ions in solution also can increase or decrease the rate of hydrolysis. The extent of this effect depends on the organic contaminant and specific ions and their concentrations. In some natural waters, the total concentrations of dissolved anions and cations is low (less than 0.01 molar) and the influence of ionic strength on the rate of reaction is small (Mabey and Mill, 1978). In other types of waters, such as brackish, estuarine, and marine, the significance of the effect increases with dissolved-ion concentration.

Many of the recent investigations of dissolved organic matter, including humic substances, show that these substances collectively play an important role in the kinetics of contaminant hydrolysis. Humic substances can increase or decrease the rate of hydrolysis depending on the concentration of organic matter and the pH of the solution (Purdue, 1983). In general, the humic substances will inhibit base-catalyzed hydrolysis reactions (for example, 2,4-D ester; Purdue, 1983) and accelerate acid-catalyzed hydrolysis reactions (for example, atrazine; Li and Felbeck, 1972). The ability of humic substances to partition certain organic contaminants affects the rate of hydrolysis, because the reactivity of the humic-contaminant mixture differs from that of the free dissolved contaminant in solution (Purdue, 1983). Consequently, whether the contaminant is free or partitioned influences the overall rate of hydrolysis as well as the extent of catalysis of the reaction based on changes in pH.

Biodegradation

Microorganisms decompose organic compounds through enzymatically mediated reactions. The driving force behind these reactions is the microorganisms' need for energy, carbon, and other essential nutrients. Some manmade organic compounds can serve as organic substrates which are degraded by enzymes and used for cellular growth. Consequently, the degradation of an organic contaminant can be monitored by examining the growth of a microbial population that utilizes the compound as a substrate. In addition to the chemical structure of the organic compound and the type of microbial population, certain environmental factors influence the biodegradation process. Among the most important are temperature, pH, and the amount of oxygen present in the system. These factors are discussed in this section, along with the kinetics of the biodegradation process.

The rate of biodegradation is a function of the size of the microbial population and the concentration of the organic contaminant. To achieve a noticeable amount of contaminant degradation, a sufficiently large microbial population must be present. In addition, for a single substrate system, sufficient contaminant must be present to result in enough cell growth to sustain the microbial population. Under ideal conditions (a large resident population and ample substrate for growth), the rate of growth is limited by the rate of its cellular metabolic and reproductive systems.

The rate of biodegradation of an organic contaminant is examined in terms of the rate of microbial growth, assuming all of the consumed contaminant is converted into mass for biological growth and no other competing substrates are available. The relation between growth rate and substrate concentration is represented by the Monod equation for microbial growth:

$$\mu = \mu_{max} \frac{[C]}{K_s + [C]}$$

where, μ = the specific growth rate, which represents the rate of growth per unit amount of biomass, time^{-1};

μ_{max} = the maximum specific growth rate, time^{-1}

[C] = the contaminant or substrate concentration, mass volume^{-1}; and

K_s = concentration of contaminant corresponding to a growth rate, μ, equal to $\mu_{max}/2$, mass volume^{-1}.

Figure 10 graphically depicts the relation between substrate concentration and specific growth rate (Benefield and Randall, 1980). At low substrate concentrations, the specific growth rate increases linearly with an increase in the substrate concentration. At high substrate concentration, the growth rate approaches and maintains a limiting growth rate that is independent of substrate concentration. Because the rate of biodegradation and consequently the rate of microbial growth is the result of many enzyme-catalyzed processes, the Monod equation is sometimes replaced by the analagous Michaelis-Menten equation for enzymatic reactions (Banerjee and others, 1984a). The mathematical forms of the Monod and Michaelis-Menten equations are the same. The difference lies in the scale of observation used to interpret the equation parameters and variables. The Monod equation applies specifically to microbial growth, whereas the more general Michaelis-Menten equation applies to any biochemical process whose rate of substrate reaction is catalyzed by enzymes.

Using the Monod equation for microbial growth, an expression for the rate of contaminant removal is formulated in terms of the contaminant concentration and the size of the microbial population. This expression is written as

$$-d[C]/dt = \mu \frac{X}{Y} = \mu_{max} \frac{[C]}{K_s + [C]} \quad \frac{X}{Y} = K_b \frac{[C]\ X}{K_s + [C]}$$

where, [C] = contaminant or substrate concentration, mass volume^{-1};

K_b = biodegradation rate constant, time^{-1};

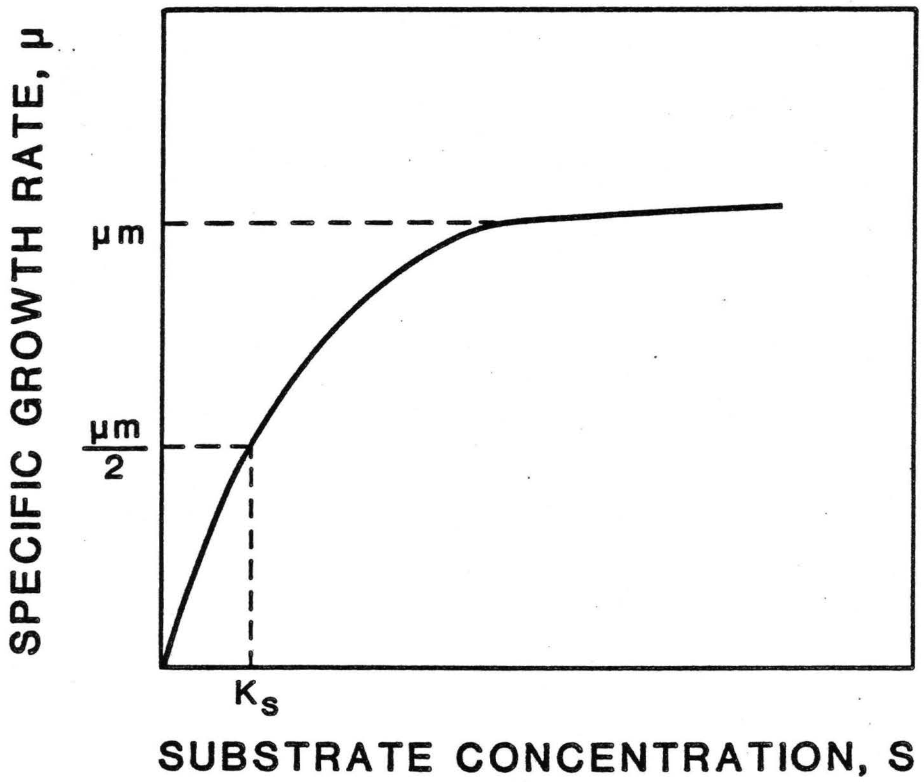

Figure 10. Relation between microbial growth rate and substrate concentration.

Y = the growth yield, equal to the biomass produced per unit amount of chemical consumed; and

X = biomass per unit volume, mass volume^{-1}.

The constants μ_{max}, K_s, and Y depend on the characteristics of the microbes, pH, temperature, and the presence of other nutrients. For example, the amount of biomass produced for a unit amount of contaminant consumed, Y, depends on the ease of assimilation and conversion of that substrate into cellular components. Values of Y vary with the species of microbes, the chemical structure of the contaminant, and the environmental conditions of the system.

The above kinetic equation for the rate of contaminant removal simplifies under a number of specific environmental conditions. For example, at high contaminant concentration, $[C] \gg K_s$, the equation reduces to the following form:

$$-d[C]/dt = K_b X .$$

In this case, the rate of degradation is first-order and only depends on the biomass concentration. Another possible and more likely case, is that the contaminant concentration is very low, $[C] \ll K_s$. In this case the equation becomes;

$$-d[C]/dt = K_b [C] X/K_s = K_{b2} [C] X ,$$

where K_{b2} is the second-order rate constant. The rate of degradation depends both on the contaminant concentration and the biomass population size. A third possibly is common to many surface waters and occurs when the biomass population is relatively large and constant. In addition, the contaminant concentration is relatively low, so that the consumption of contaminant will not radically alter the population concentration. These conditions represent the specific case where microbes are acclimated to the chemical and actively utilize the compound. In this case, the degradation rate is termed pseudo-first order and it is represented mathematically as:

$$-d[C]/dt = K_b' [C],$$

where $K_b' = K_{b2} X$.

The above equations show that the two primary factors influencing the rate of biodegradation of an organic contaminant are the microbial-population density and the concentration of the contaminant (substrate). Different combinations of substrate concentration and population density can significantly alter the shapes of substrate-disappearance curves that are functions of time (Simkins and Alexander, 1984; Alexander, 1985). Additional factors are embedded within the biodegradation rate constant. These include the differences in assimilability between contaminants, as well as the differences between various species of microbes responsible for converting the contaminants into biomass. Microbial populations are sensitive to variations in environmental conditions, and different combinations of temperature, pH, and oxygen content of the water may provide an advantage to one species competing with another species for the same substrate. The contributions of these environmental variables to determine the rate of biodegradation commonly are significant.

A change in temperature can alter the balance of competition between microbial species using a contaminant as substrate. Each class of bacteria has an optimum temperature range within which a maximum growth rate is attainable assuming a sufficient supply of all other essential nutrients. Bacteria are commonly classified on the basis of the temperature range where their optimum growth occurs. Psychrophilic bacteria grow best at temperatures ranging from -5 to 30° C. Mesophiles grow best at temperatures between 15 and 45° C. Thermophilic (heat-loving) bacteria grow best at temperatures ranging from 45 to 75° C (Benefield and Randall, 1980). Within the temperature range of each group of bacteria, the rate of biochemical reaction approximately doubles for every increase of 10° C. However, this relation, known as the van't Hoff rule, is valid only over a limited range for bacteria, because further increases in temperature eventually breakdown the cellular growth and reproductive mechanisms (Benefield and Randall, 1980). Other more-complicated relations describing the influence of temperature on the rate of reaction are based on the Arrhenius equation. These relations include correction factors that show how temperature affects the microbial-growth and decay rate, the dominant organism groups, and the availability of nutrients--factors that contribute to alteration of the rate of contaminant removal (Novak, 1974).

Like temperature, the oxygen content of a water system contributes to the determination of which class of microbes can best degrade a particular organic contaminant. Depending on the mechanism by which microorganisms obtain their energy, different classes of organisms can exist under aerobic, anaerobic, or anoxic conditions. Thus, the oxygen content of the water/sediment system determines which group of microorganisms competes for the contaminant as a substrate, and ultimately, the rate of the contaminant's degradation.

In summary, the biodegradation of an organic compound is primarily determined by two components of the system: the microorganisms and their substrate--the organic contaminant. The microorganisms are sensitive and responsive to the condition of their immediate environment, including temperature and oxygen content, as well as to the chemical nature of the organic substrate. For rapid removal and conversion into biomass, the substrate must be readily decomposable and more assimilable than other available organic compounds. For this system, the rate of biodegradation depends largely on the density of the microbial population and the concentration of the contaminant. The reaction dynamics are approximated by a kinetic relation that is limited by the maximum growth rate of the microbial population. The order of the reaction rate for the degradation of the contaminant depends on the abundance of the microorganisms and the organic substrate. For many environmental cases, characterized by a stable microbial population and a small contaminant concentration, the equation simplifies to a pseudo-first-order expression. Only one parameter--the biodegradation rate constant--is needed to parameterize this kinetic representation. In this approach, the rate constant is specific for a single organic compound, a particular population of microorganisms, and the temperature and oxygen content characterizing the aqueous system.

Volatilization

Volatilization and condensation are two complementary processes contributing to the exchange of organic compounds across the air-water interface. Both processes involve phase changes of the organic compound, either from gas to liquid or liquid to gas, and are driven by concentration gradients between the respective bulk phases. Volatilization, in the present context, refers to the evaporation and vapor-phase transport of an organic compound from aqueous solution into the atmosphere. This section examines only volatilization, even though condensation and volatilization of organic compounds are controlled by many of the same chemical properties and environmental variables.

A number of compound properties and system variables combine to determine the extent of volatilization of an organic chemical. The most important chemical properties are vapor pressure and water solubility. Commonly, the ratio of these two properties is expressed as the Henry's law constant, where the constant, H, is equal to vapor pressure divided by water solubility. The Henry's law constant represents the equilibrium distribution of concentrations of the organic chemical between the air and water phases at equilibrium. Air and water temperatures are important environmental variables controlling volatilization. In addition, the degree of air turbulence caused by the wind and the amount of subsurface mixing generated by velocity gradients in the water have a significant influence on the rate of volatilization. This section discusses the relative contributions of these chemical and environmental factors and examines some models currently used to represent the volatilization process.

From a physical standpoint, the potential volatility of an organic compound in a pure solution is related to its vapor pressure. In a natural water body, the actual rate of volatilization depends on the extent to which the environmental conditions attenuate the potential volatility of the compound. Competing processes, such as sorption with water-column particulates, act to suppress the vapor pressure attainable if all of the compound remained in a dissolved and unassociated state. In general, however, the greater the vapor pressure of a compound the greater its mass loss rate (flux). Other factors also influence the volatilization rate, but most do so through their effect on vapor pressure or on the movement of the compound away from the air-water interface. Vapor pressure, for example, increases with temperature and thereby increases the rate of volatilization. In addition, increasing the temperature also increases the rate of diffusion, which serves to enhance the movement of organic molecules away from the interfacial boundaries.

Volatilization is a transformation process that acts to establish an equilibrium between the concentrations of a compound in the bulk phases of air and water. The driving force behind this process is the difference in concentrations (more precisely, the chemical potentials) of the compound in the two bulk phases. The retarding forces that prevent the instantaneous attainment of an equilibrium state are those that reduce the chemical potential difference of the compound between the two bulk phases. The overall resistance can be considered to be the sum of the resistance experienced in a different part of the entire physical system. The greatest of the component resistances serves to control the rate for the overall movement of a compound from the water to the air.

If the physical system is assumed to consist of two bulk phases--air and water--separated by a stagnant near-surface water layer and a stagnant near-surface air layer, the component resistances in the system can be examined. These include the resistance to diffusion in the (1) water column, (2) near-surface water layer, (3) surface-film layer (if any), (4) near-surface air layer, and (5) the air column. Neglecting the presence of surface films (such as oil spills) for now, the majority of the resistance occurs in the near-surface gas and liquid layers (Smith and others, 1980). The magnitude of the resistance in these two layers varies with the thickness of these interfacial layers; this, in turn, depends on factors, such as temperature, wind and water turbulence, and the specific properties of the compound of interest--for example, diffusivity and/or molecular weight.

Many investigators use a first-order process as a mathematical representation of volatilization (Mackay and Leinonen, 1975; Mackay and others, 1979, 1983; Dilling, 1977; Southworth, 1979; Chiou and others, 1980, 1983a; Smith and others, 1980, 1981, 1983; Rathbun and Tai 1982, 1984). For this representation, the rate of removal of a compound from the water phase by volatilization depends on the concentration of the compound in solution and on the volatilization rate constant. An expression for this relation is

$$d[C]/dt = K_v [C] ,$$

where [C] is the dissolved concentration of the compound in solution and K_v is the volatilization rate constant. The usefulness of this approach depends on the ability to obtain an accurate estimate of the volatilization rate constant for a particular compound and a given set of environmental conditions.

Initial attempts to estimate volatilization rates were based on the belief that organic compounds codistill with water into the atmosphere (Acree and others, 1963; Mackay and Wolkoff, 1973). The codistillation hypothesis implies that the simultaneous evaporation of water and organic compounds somehow enhances the volatility of the organic compound to rates not normally expected solely on the basis of the chemical's physical properties. From a theoretical standpoint, it has been shown that the volatilization of organic compounds and water are mechanistically independent processes and no evidence for a thermodynamic coupling has yet to be presented (Chiou and Manes, 1980; Spencer and others, 1973). In addition, Chiou and Manes (1980) have reported experimental results demonstrating that, under certain conditions, organic solutes evaporate while water vapor condenses. The use of the term "codistillation" should be avoided because it incorrectly implies that water loss enhances volatilization of organics by codistillation and that water loss is necessary for volatilization of significant quantities of organic compounds (Spencer and others, 1973).

The estimation of the volatilization-rate constant is based on a two-film-layer model, because, for many compounds, the resistance to volatilization occurs in either the gas or liquid near-surface layers. This approach is based on the two-film, mass-transfer model originally proposed by Whitman (1923). This model assumes uniformly mixed air and water phases separated by thin films of air and water in which transport is by molecular diffusion. The model's volatilization-rate constant is expressed in terms of the mass-transfer rates of the organic compound across the liquid and gas-phase boundary layers. The general expression for the volatilization rate constant is

$$K_v = \frac{1}{L}\left(\frac{1}{k_1} + \frac{RT}{H k_g}\right)^{-1},$$

where K_v is the volatilization rate constant (hr^{-1}); L is the depth (cm) which equals the interfacial area divided by the liquid volume; k_1 is the liquid-film mass transfer coefficient (cm/h); R is the gas constant (L-torr/K-mol); T is the absolute temperature (K); H is the Henry's law constant (torr-L/mol); and k_g is the gas-film mass transfer coefficient (cm/h). The first term within parentheses represents the liquid-film resistance, whereas the second term represents the gas-film resistance. An important assumption behind the two-film layer model is that the organic solute is at equilibrium between the water and air phases at the interface (Smith and others, 1983). This equilibrium is described by the Henry's law constant, which is the organic-solute concentration in the air (mol/m^3) divided by the organic-solute concentration in water. Because atmospheric concentrations are frequently expressed in partial pressures, P (Pascals), they can be converted to mol/m^3 by using the ideal-gas law ($n/V=P/RT$).

From the above expression, it is seen that the volatilization-rate constant depends on the Henry's law constant for the organic compound as well as the liquid and gas mass-transfer coefficients. The Henry's law constant is a function of the compound properties, whereas the mass-transfer coefficients are a function of both the compound properties and environmental variables. The liquid-film, mass-transfer coefficient is expressed as the diffusion coefficient (D, in m^2/h) for the given organic solute divided by the thickness of the stagnant liquid film. The diffusion coefficient in a particular phase is related to the molecular weight of the organic solute. Transport in the boundary layer is by molecular diffusion, because the air and liquid films are considered stagnant. The thickness of the liquid film depends on the level of water turbulence in the system. In other words, the thickness of the stagnant water layer decreases with increasing water velocities (turbulence). The same relations hold true for the gas-film, mass-transfer coefficient except that they apply to the gas phase, and air turbulence imparts the wind-shearing force. Consequently, the rate of volatilization depends on the diffusion properties of the organic compound in the respective stagnant film phases. Diffusion, in turn, is related to the molecular weight of the organic molecule, the concentration or vapor density of the organic compound, and temperature which influences both the vapor density and the diffusion process.

The difficulty in applying the two-film model is trying to measure or estimate the liquid and gas mass-transfer coefficients accurately in actual water bodies. The overall mass-transport rate of a substance may depend on liquid-phase and/or gas-phase resistance, based on the relative magnitude of k_1 and Hk_g. A simplifying approach is to determine, from the two-film equation, which film-phase resistance dominates for particular values of the Henry's law constant (Dilling, 1977; Mackay, 1979; Mackay and others, 1979; Smith and others, 1980, 1981, 1983). Smith and others (1980) found that, for compounds having Henry's law constants greater than 3,500 torr/Molar (4.4×10^{-3} atm-m^3/mol), the liquid-phase resistance controlled approximately 95 percent of the mass transfer for alkanes and benzene. The compounds with constants falling above the 3,500 torr/Molar demarcation are considered high to be highly volatile. For compounds with constants falling below 10 torr/Molar (1.2×10^{-5} atm-m^3/mol) the gas-phase resistance controls mass transfer, and these compounds are considered to be of low volatility. For compounds with Henry's law constants falling within the range of 10 to 3,500 torr/Molar, the liquid and gas phase resistances are significant, and both terms in the two-film equation must be included in the calculation of the volatilization-rate constant. These compounds are considered to have intermediate volatility--for example, DDT (Mackay, 1979). These three groupings, based on Henry's law constants, provide a convenient way to categorize the potential volatility of organic substances so that experimental methods can be devised to measure mass-transfer coefficients for the phase (air, water, or both) imparting the dominant resistance to volatilization.

Smith and others (1980) have proposed a method to predict the volatilization rate of highly volatile organic compounds in streams on the basis of laboratory measurements. Highly volatile compounds experience resistance to mass transport, primarily in the liquid-film phase, whereas resistance in the gas film is considered negligible. Consequently, estimation of the volatilization-rate constant simplifies to estimation of only the liquid-phase, mass-transfer coefficient. Using oxygen as a high volatility reference compound, Smith and others (1980) used results of previous studies to show that the ratio of the liquid-film, mass-transfer coefficient of an organic compound to the reaeration coefficient for oxygen is constant over a wide range of turbulence levels. If this ratio is measured in the laboratory, and if the oxygen reaeration constant is measured in an actual water body, the corresponding field liquid mass-transfer coefficient can then be calculated for the organic compound. Theoretical justification for the constancy of the mass-transfer coefficient ratio for the organic compound and oxygen as well as a test of the method to predict volatilization of benzene and six other chlorinated hydrocarbons is reported in Smith and others (1980).

The rate of mass transfer of low volatility compounds is controlled by resistance in the gas film, whereas resistance in the liquid-film is relatively small. Smith and others (1981, 1983) suggest the use of water as a reference compound, because its rate of evaporation is controlled entirely by gas-phase, mass-transfer resistance. The ratio of the mass-transfer coefficients for water and the organic compound is constant, and any effect of gas-phase turbulence is equal (and thereby cancels) for the two compounds. Based on the ratio, the gas-film, mass-transfer coefficient is estimated from field measurements of the water evaporation flux, relative humidity, and air temperature. Smith and others (1981, 1983) demonstrated this approach for two organic compounds with low volatility and two organic compounds with intermediate volatility. For compounds with intermediate volatility, estimates are required for both the gas-film and liquid-film, mass-transfer coefficients. These can not be estimated by a single experiment but require independent measurements of each coefficient. Methods to obtain these estimates are described by Southworth (1979), and Smith and others (1981, 1983).

Despite the fact that the two-film theory is commonly used to model volatilization, it has several important limitations. One of the basic assumptions of the two-film theory is that the surface layer of the solvent (water) is stationary and not evaporating, so that a solute has to move to the liquid surface by diffusion to evaporate. This assumption only applies to solutes that are evaporating much faster than the solvent; it breaks down when the loss rate of the solvent is comparable to or greater than the loss rate of the solute. For the latter case, the solute is not required to diffuse to the liquid surface to evaporate, inasmuch as the solvent at the old surface is gone. Therefore, even if no diffusion occurred, the solute would then be at the newly generated surface and will evaporate. The failure of the two-film theory to account for solvent evaporation may make the model somewhat inaccurate for describing the evaporative behavior of solutes that are relatively nonvolatile. Another possible weakness of the two-film theory is its strong emphasis on the diffusion of the solute, without considering that the solvent also is diffusing. Because the solvent is the dominant component of the mixture, its diffusive motion may cause additional movement of the solute to the surface. Therefore, the size of the solute molecule may not have a strong influence on solute diffusion in water; in other words, the solute may be 'pushed' by the solvent's diffusive motion. Finally, the two-film theory treats the concentration gradient of the solute in the liquid film as the driving force for evaporation. In fact, the concentration gradient is merely the result of uneven evaporative loss rates between solute and solvent and should not be treated as the driving force for evaporation of the solute.

Chiou and others (1980, 1983a) have presented an alternative first-order model for volatilization that explicitly accounts for the effects of solute concentration and system turbulence. The model differs from the previously described two-film approach, because it explicitly treats the influence of air turbulence and subsurface mixing on the evaporative behavior of organic solutes of different volatility. In addition, although the two-film model only gives relative resistances, the model proposed by Chiou and others (1980, 1983a) gives relative as well as absolute resistances. The absolute liquid-phase and air-phase resistances are based on pure liquid and vacuum as the reference states.

Chiou and others (1980, 1983a) report that for compounds with small Henry's law constants (low volatility and gas-phase-controlled diffusion), the rate of volatilization is enhanced by air turbulence but not by subsurface mixing. On the other hand, the volatilization rate of volatile solutes increases with air turbulence and subsurface mixing. The degree of enhancement by liquid mixing is a function of the magnitude of the Henry's law constant. In addition, Chiou and others (1983a) examined the influence of system conditions on the ratio of mass-transfer coefficients for different organic-solute combinations in water. They found the ratios of mass transfer coefficients for organic solutes are constant with respect to changes in air turbulence and water mixing if the organic compounds have similar or low Henry's law constants. The ratios are not constant for compounds with vastly different or high Henry's law constants. These results show that a careful examination of compound properties and system conditions is necessary before reference compounds, such as oxygen, can be used to estimate volatilization rates for organic compounds in natural waters.

A number of statistical approaches have been proposed to estimate mass-transfer coefficients (either liquid, gas, or both) of organic compounds from field properties that characterize the degree of air and water turbulence. For example, Rathbun and Tai (1982) measured liquid-film, mass-transfer coefficients for ethylene and propane and correlated their magnitudes with a number of hydraulic and geometric properties of streams (stream energy, depth of flow, average velocity, and stream slope). The regression equations derived for ethylene and propane are then used to estimate mass-transfer coefficients for other highly volatile organic compounds after the proper adjustment is made on the basis of molecular diffusivity, molecular weight, or molecular diameter. Mackay and Yeun (1983) used a similar statistical approach but chose different stream and compound properties than those of Rathbun and Tai for their correlation studies. Mackay and Yeun (1983) developed separate regression equations for the gas- and liquid-film, mass-transfer coefficients. They used friction velocity as the hydrodynamic parameter and the Schmidt number to characterize differences between organic solutes. The Schmidt number (viscosity divided by density multiplied by diffusivity) incorporates the solute-diffusion properties as well as a temperature dependence, whereas the friction velocity is related to the windspeed. The correlations were tested and found to yield reasonable results for 11 organic compounds under a number of windspeed conditions. Although these correlations do allow estimates of mass-transfer coefficients necessary to apply the two-film model to the process of volatilization, they also show that more research needs to be conducted to increase understanding of factors that control the mass-transfer coefficients in the gas and liquid films.

In summary, the current approach to representing the volatilization of organic compounds from surface-water bodies is through the use of a first-order-rate expression. In this form, the rate of volatilization depends on the concentration of the compound in solution and on the volatilization-rate constant. The most common way to represent the volatilization-rate constant is by the two-film resistance model. This model is parameterized by the Henry's law constant and a gas-film and a liquid-film, mass-transfer coefficient. In some cases, depending on the magnitude of the Henry's law constant of the compound of interest, the resistance of volatilization can be approximated by the gas-film resistance and/or the liquid-film resistance. Generally, the Henry's law constant is obtainable from independent measurements of the organic compound's water solubility and vapor pressure. Vapor pressures can be estimated from correlation equations based on boiling or melting points (Mackay and others, 1982) or by experimental procedures. Burkhard and others (1985) review and assess the predictive ability of 11 methods as they are applied to 15 chlorinated biphenyl isomers. Because of the number of existing approaches to estimate the Henry's law constant, the usefulness of the two-film model depends on obtaining values for the gas- and liquid-film, mass-transfer coefficients.

The difficulty in estimating the gas- and liquid-film, mass-transfer coefficients stems from their dependence on system conditions (such as temperature, wind turbulence, and water mixing) and compound properties (such as diffusivity or molecular weight). Statistical approaches have tried to correlate mass-transfer coefficients with system variables for organic compounds for which some experimental data are available. These correlation equations are extrapolated to other organic solutes of similar volatility by making corrections on the basis of diffusivity, molecular weight, or molecular diameter. Experimental approaches derive estimates by the use of reference compounds--for example, oxygen, carbon dioxide, radon, or other organic solutes--whose variation in parameter values is constant relative to the organic compound of interest over a particular range of conditions. These studies indicate that no entirely satisfactory method has been developed to estimate the different mass-transfer resistances (gas or liquid) over the full range of volatilities exhibited by the organic solutes.

Although the two-film model is a promising approach to quantifying the volatilization rate of organic compounds, a number of other factors still need to be incorporated in this model. The presence of natural or manmade organic films (or surface-active agents) creates another layer that acts to further retard volatilization. This surface film possesses a characteristic thickness and a resistance to diffusion that has to be considered in addition to the air- and water-boundary layers already treated in the two-film model (Smith and others, 1980; Mackay, 1982a). The two-film model gives the theoretical maximum volatilization rate for a given set of environmental conditions. Other water and atmospheric phenomena (such as stratification and aerosol formation) as well as competing processes (such as sorption, photolysis, hydrolysis, and biodegradation) reduce the amount of organic solute available for volatilization. For some of these processes, relative comparisons of first-order-rate constants can be used to determine the transformations that control the aquatic fate of an organic compound.

POLYCHLORINATED BIPHENYLS AND CHLORINATED INSECTICIDES

Uses, Production, Properties, and Regulatory Limits

Polychlorinated biphenyls (PCBs) and chlorinated insecticides have been grouped together in this section because of their similar behavior in surface-water systems. As a group, they are the most persistent anthropogenic organic compounds introduced into the environment since the lead and arsenic pesticides of the early 1900's. Although the use of many of these contaminants has been banned in the U.S. for more than a decade, significant residues contaminate the sediment, water, and biota of the country's surface waters. Figure 11 shows the structural diagrams of 2,2',4,4',5,5'-PCB and some of the more common chlorinated insecticides.

PCBs are synthetically produced by the catalyzed chlorination of biphenyl. Because of their chemical and thermal stability, inertness, and dielectric nature, they have been used as plasticizers, as hydraulic lubricants in gas turbines and vacuum pumps, in heat-transfer systems, and as dielectric fluids in electrical capacitors and transformers. Aroclor[1] is the trade name for one manufacturer's PCBs. Aroclors are mixtures of a variety of polychlorinated bi- and terphenyls that are identified by a four-digit number. The first two numbers refer to the type of molecule primarily used in the mixture (12- refers to biphenyl, 54- refers to terphenyl), and the second two numbers specify the percent chlorine (by weight) in the mixture. Aroclor 1016 was marketed more recently in response to the environmental problems associated with the persistence of the other Aroclor mixtures. This product contains predominantly mono-, di-, and trichlorobiphenyl isomers. The approximate molecular compositions of Aroclor mixtures are given in table 3. Additionally, some uses of PCBs suggested by the manufacturer are detailed in table 4.

PCBs were first synthesized in 1929, with production escalating in the U.S. during the 1960's. Production reached its peak in 1970, when 38,600 metric tons were produced (Moore and Ramamoorthy, 1984). The manufacturer voluntarily decreased and eventually ceased production of PCBs during the 1970s. Because of the environmental persistence and toxicity of PCBs, their production, sale, distribution, and disposal were first regulated under the provisions of the Toxic Substances Control Act of 1976. In the same year, the U.S. Environmental Protection Agency (USEPA) set 0.001 μg/L as the water-quality criterion for PCBs to protect freshwater and marine aquatic life (U.S. Environmental Protection Agency, 1976). In 1977, PCB use was restricted by USEPA, and in 1979, all manufacture, sale, and distribution of PCBs in the U.S. was prohibited (Haley, 1984). Despite the cessation of production, PCBs are estimated to be present in 2 million transformers and 2.8 million capacitors currently in use in the U.S. (Moore and Ramamoorthy, 1984).

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[1] Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

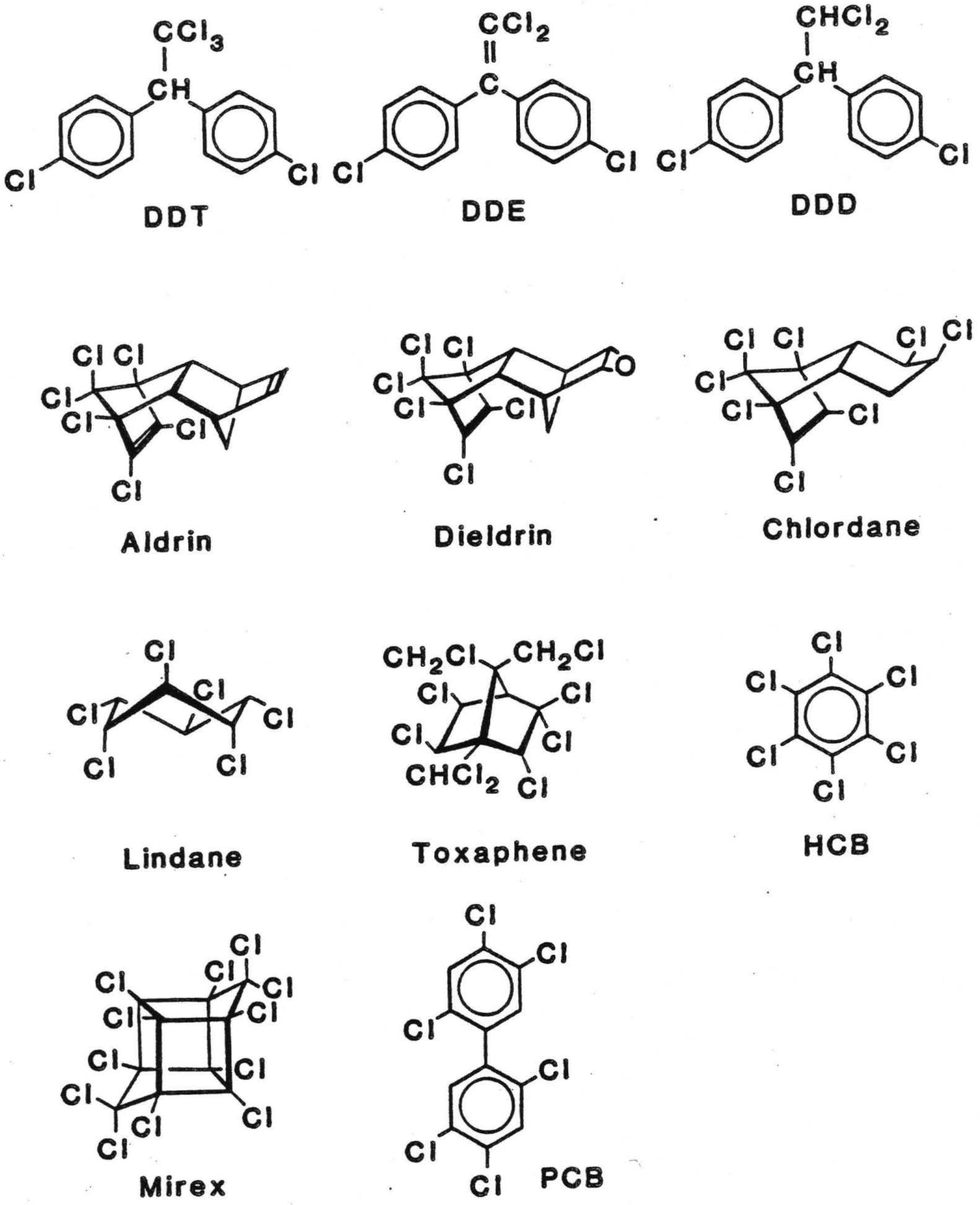


Figure 11. Structural diagrams of selected chlorinated insecticides and a polychlorinated biphenyl.

Table 3. Approximate molecular composition of some Aroclor mixtures.
[From Hutzinger and others, 1974]

Empirical formula	Molecular weight	Percent chlorine	Percentage in each Aroclor mixture						
			1016	1221	1232	1242	1248	1254	1260
$C_{12}H_{10}$	154.21	0	<0.1	11	<0.1	<0.1	nd	<0.1	nd
$C_{12}H_9Cl$	188.65	18.79	1	51	31	1	nd	< .1	nd
$C_{12}H_8Cl_2$	223.10	31.77	20	32	24	16	2	.5	nd
$C_{12}H_7Cl_3$	257.54	41.30	57	4	28	49	18	1	nd
$C_{12}H_6Cl_4$	291.99	48.56	21	2	12	25	40	21	1
$C_{12}H_5Cl_5$	326.43	54.30	1	< .5	4	8	36	48	12
$C_{12}H_4Cl_6$	360.88	58.93	< .1	nd	< .1	1	4	23	38
$C_{12}H_3Cl_7$	395.32	62.77	nd	nd	nd	< .1	nd	6	41
Average molecular weight			257.9	200.7	232.2	266.5	299.5	328.4	375.7

nd - not detected

Table 4. Some uses of polychlorinated biphenyls suggested by the manufacturer. [From Moore and Ramamoorthy, 1984]

Base material	Type of Aroclor used and its percent content in final product	Purpose of Aroclor use and beneficial result
Polyvinyl chloride	1248, 1254, 1260 (7-8%)	Secondary plasticizers to increase flame retardance and chemical resistance
Polyvinyl acetate	1221, 1232, 1242 (11%)	Improved quick-track and fiber-tear properties
Polyester resins	1260 (10-20%)	Stronger fiberglass; reinforced resins and economical fire retardants
Polystyrene	1221 (2%)	Plasticizer
Epoxy resins	1221, 1248 (20%)	Increased resistance to oxidation and chemical attack; better adhesive properties
Styrene-butadiene co-polymer	1254 (8%)	Better chemical resistance
Neoprene	1268 (40%) (1.5%)	Fire retardant injection moldings
Crepe rubber	1262 (5-50%)	Plasticizer in paints
Nitrocellulose lacquers	1262 (7%)	Co-plasticizer
Ethylene vinyl acetates	1254 (41%)	Pressure-sensitive adhesives
Chlorinated rubber	1254 (5-10%)	Enhances resistance, flame retardance, electrical insulation properties
Varnish	1260 (25% of oil)	Improved water and alkali resistance
Wax	1262 (5%)	Improved moisture and flame resistance

The use of organochlorine insectides began with the discovery of the insecticidal properties of DDT by Paul Müller in 1939. In that year, DDT was chosen as the most promising new synthetic organic insecticide. Müller was awarded the Nobel Prize for his discovery 9 years later (Reutergardh, 1980). Technical-grade DDT contains approximately 80 percent p,p'-DDT and 15-20 percent o,p'-DDT (Verschueren, 1983). The metabolic-degradation products of p,p'-DDT are p,p'-DDE and p,p'-DDD, and their residues are commonly found in the environment.

Following the discovery of DDT, numerous other organochlorine insecticides were developed and used. Lindane, the gamma isomer of hexachlorocyclohexane (HCH), was found to be an effective insecticide in 1942, followed by chlordane in 1945, and heptachlor, aldrin, dieldrin, and toxaphene in 1948. Toxaphene is produced by the chlorination of terpene derivatives and is a mixture of more than 170 components. Endrin and endosulfan were first introduced in the 1950's. Mirex was first prepared in 1946 but not used extensively until 1969 when it was used to control fire ants in the southern U.S. The degradation product of mirex is kepone. Methoxychlor also became widely used in 1969 in response to the ban of DDT in the U.S. In the past 10 years, it has been estimated that the quantities of insecticides applied has decreased due to the use of more potent insecticides, such as the pyrethroids permethrin and fenvalerate, which require much lower application rates than older organochlorine insecticides, such as toxaphene (Gilliom, 1985).

The production of organochlorine insecticides in the U.S. has been greatly curtailed over the last 15 years owing to their environmental persistence, toxic effects, and lipophilic nature. DDT and aldrin/dieldrin use peaked in the mid-1960's at annual values of 70,000 and 9,000 metric tons, respectively. By 1970, these values had decreased to 36,000 and 5,000 metric tons, respectively. Currently (1987), production of these compounds in the U.S. is negligible. Other organochlorine insecticides currently applied to crops (such as toxaphene) are having their uses restricted (Moore and Ramamoorthy, 1984). Additional use data for these and other chlorinated insecticides, along with detection limits and water-quality criteria, are presented in table 5.

Environmental Fate

Organochlorine insecticides and PCBs are characterized by relatively low aqueous solubilities and high octanol-water partition coefficients (table 6). Because low solute solubility correlates with high sediment-water sorption coefficients for nonionic organic compounds, it is expected that PCBs and organochlorine insecticides would strongly partition into sediment organic matter and dissolved organic matter. Laboratory and field studies have corroborated this hypothesis.

Table 7 presents some partition coefficients that have been determined for PCBs and chlorinated insecticides in laboratory

Table 5. Detection limits, water quality criteria, and use data for selected organochlorine insecticides. [µg/L is micrograms per liter; lb/yr is pounds per year; from Gilliom (1985)]

Chemical	Detection limit (µg/L)[1]	Water Quality Criteria (µg/L)		Principal uses and sources	National use on farms (million lb/yr)				Total use, 1981 (million lb/yr)
		Human health[2]	Aquatic life		1966	1971	1976	1982[3]	
Aldrin	0.01	0.0007	0.002	Corn	15	7.9	0.9	nr	0.8
Chlordane	.15	.005	.004	Corn, termites, general purpose	0.5 (Most farm uses cancelled in 1974)	1.9	nr	nr	9.6
DDD	.05	.0002	.001	Fruits and vegetables, degradation product of DDT.	2.9 (Cancelled in 1972)	0.2	nr	nr	0
DDE	.03	.0002	.001	Degradation product of DDT and DDD.	nr	nr	nr	nr	0
DDT	.05	.0002	.001	Cotton, fruits, vegetables, general purpose.	27 (Cancelled in 1972)	0.1	nr	nr	0
Dieldrin	.03	.0007	.002	Termite control, degradation product of aldrin.	0.7 (Most farm uses cancelled in 1974)	0.3	nr	nr	0
Endrin	.05	.1*	.002	Cotton, wheat	0.6	1.4	0.8	nr	0.3
Heptachlor epoxide	.01	.003	.004	Degradation product of heptachlor; used on corn and termites.	1.5	1.2	0.6	nr	2.0
Lindane	.01	.4*	0.08	Livestock, seed treatment, general purpose.	0.7	0.7	0.2	nr	0.8
Methoxychlor	.10	100*	.03*	Livestock, alfalfa, general purpose.	2.6	3.0	3.8	0.6	5.0
Toxaphene	.25	.007	.013	Cotton, livestock	35	37	33	5.9	16

nr = none reported

1. Detection limits are for water samples. Bed-sediment detection limits are 10 times greater and in units of micrograms per kilogram (Lucas and others, 1980).
2. Except for values marked with an asterisk, which are from U.S. Environmental Protection Agency (1977), all criteria are from U.S. Environmental Protection Agency (1980a). The human health criteria from the 1980 publication represent the average concentrations associated with an incremental increase in cancer risk of 10^{-5} (one additional cancer per 100,000 people) over a lifetime of exposure. The aquatic life criteria are for freshwater environments and represent 24-hour average concentrations.
3. Data for 1966, Eichers and others (1970); for 1971, Andrilenas (1974); for 1976, Eichers and others (1978); for 1982, U.S. Department of Agriculture (1983). Data for 1982 do not include use on livestock or use in California, Colorado, Connecticut, Maine, Massachusetts, Nevada, New Hampshire, New Jersey, New Mexico, Oregon, Rhode Island, Utah, Vermont, West Virginia, and Wyoming.

Table 6. Experimentally determined octanol-water partition coefficients (K_{ow}), solubilities, and vapor pressures of selected polychlorinated biphenyls (PCBs) and organochlorine insecticides. [mg/L is milligram per liter; mm is millimeter]

Compound	Log K_{ow}	Solubility (mg/L)	Vapor pressure (mm of Hg)	Reference
Biphenyl	4.09	7.5	1.8	1,2,3
2,4'-PCB	5.10	-	0.28	4,3
4,4'-PCB	5.58	0.062	8.99×10^{-3}	5,2,3
2,5,2',5'-PCB	5.81	0.016	4.27×10^{-3}	5,2,3
2,4,5,2'5'-PCB	6.11	0.010	-	5,2
2,4,5,2',4',5'-PCB	6.72	0.00095	4.57×10^{-4}	5,2,3
p,p'-DDT	6.36	0.0031	1.9×10^{-7}	1,2,6
o,p'-DDT	-	0.026	5.5×10^{-6}	6
p,p'-DDD	5.99	0.020	10.2×10^{-7}	6
o,p'-DDD	6.08	-	18.9×10^{-7}	6
p,p'-DDE	5.69	0.040	6.5×10^{-6}	6
o,p'-DDE	5.78	-	6.2×10^{-6}	6
Lindane	3.70	7.87	1.6×10^{-4}	7,7,6
Aldrin	-	0.017	6.0×10^{-6}	6
Dieldrin	-	0.195	1.8×10^{-7}	6,2
Chlordane	5.48*	0.056	1.0×10^{-5}	8,6,6
Toxaphene	-	0.74	0.2 - 0.4	6
Endrin	-	0.26	2×10^{-7}	6
Heptachlor	-	0.056	3×10^{-4}	6
α-Endosulfan	-	0.53	1×10^{-5}	6

* - Value calculated from structural parameters according to Mabey and others (1982)

1. Chiou and others (1982b)
2. Verschueren (1983)
3. Burkhard and others (1985)
4. Chiou and others (1983b)
5. Chiou and others (1985)
6. Callahan and others (1979)
7. Chiou and others (1986)
8. Mabey and others (1982)

Table 7. Experimentally determined sorption coefficients for some polychlorinated biphenyls (PCBs) and organochlorine insecticides. [Dash indicates no data available]

Compound	Soil/sediment	OC or OM (%)	K_d	K_{oc} or K_{om}	Reference
2,4,4'-PCB	Silt loam	1.9 (om)	460	24,000	1
2,5,2'-PCB	Suspended river sediment	4.1 (oc)	10,000	250,000	2
Hexachloro-biphenyl	Lake Michigan sediment	2.9 (oc)	9,000	310,000	3
Hexachloro-biphenyl	Suspended river sediment	4.1 (oc)	13,000	300,000	2
Aroclor 1254	Lake Michigan sediment	1.7 (oc)	7,000	410,000	4
DDT	Marine sediment	2.7 (oc)	48,000	1,800,000	5
DDT	Soil samples	-(om)	-	140,000	6
p,p'-DDE	Suspended river sediment	4.1 (oc)	41,000	1,000,000	2
Lindane	Silt loam	1.9 (om)	14	740	7
Lindane	Creek sediment	2.8 (om)	24	860	8
α-chlordane	Suspended river sediment	4.1 (oc)	13,000	300,000	2
β-chlordane	Suspended river sediment	4.1 (oc)	10,000	250,000	2
Endrin	Sand	0.7 (om)	58	8,300	8
Kepone	Estuarine sediment	-	1,700	-	9
Methoxychlor	Clay	1.2 (oc)	1,100	90,000	10

OC - organic carbon; OM - organic matter

1. Chiou and others (1983b)
2. Oliver and Charlton (1984)
3. Voice and others (1983)
4. Voice and Weber (1985)
5. Pierce and others (1974)
6. Chiou and others (1979)
7. Chiou and others (1985)
8. Sharom and others (1980b)
9. Huggett and others (1980)
10. Karickhoff and others (1979)

and field studies. The values for the distribution coefficients, K_d, and the distribution coefficients normalized for organic carbon, K_{oc}, or organic matter, K_{om}, are very high, especially for DDT, DDE, and the PCBs. These high sorption coefficients indicate the strong tendency of these compounds to partition into the sediment organic matter. Even lindane, one of the more soluble of the organochlorine insecticides, has been documented as having K_{om} values greater than 800 (Sharom and others, 1980b).

As a result of their high sorption coefficients, insecticides and PCBs having low dissolved concentrations in water (in the parts-per-trillion range) can still have very high concentrations in sediment (up to the parts-per-million range). In an Oklahoma stream, Hunter and others (1980) determined that PCB concentrations in sediment ranged from 0.23 to 7.2 ppm, yet the concentration of PCBs in the water was undetectable. Likewise, at one location in the Hudson River, Nadeau and Davis (1976) detected PCB concentrations in sediment of almost 3,000 ppm, even though the aqueous concentration in the overlying water was only 3.0 ppb. These studies indicate the importance of sorption to the transport, fate, and distribution of organochlorine insecticides and PCBs in surface-water systems.

In addition to their affinity for sediment organic matter, these chlorinated organic compounds also tend to partition strongly into the lipid reservoirs of aquatic organisms. The resulting concentration of the compound in the biota can be as much as one million times greater than the compound's aqueous concentration. Table 8 presents bioconcentration factors (BCFs) for a variety of chlorinated insecticides and PCBs and for a variety of aquatic organisms ranging from microorganisms to fish. Differences in the values of BCFs among different compounds result largely from differences in each compound's solubility in water. For a given compound, the BCF can be expected to vary with the lipid contents of the different organisms. BCFs greater than 10,000 have been observed, and even the more soluble insecticides such as lindane have been bioconcentrated to values hundreds of times greater than the compound's aqueous concentration. Therefore, even low aqueous concentrations of organochlorine insecticides and PCBs can produce environmentally significant concentrations of these compounds in aquatic organisms.

In addition to their typically low solubilities and high octanol-water partition coefficients, PCBs and chlorinated insecticides also are characterized by relatively low vapor pressures (table 6). Compounds with low vapor pressures typically have low mass-loss rates (fluxes) from solution. However, PCBs and some of the chlorinated insecticides in water are relatively volatile, because their low water solubilities cause relatively high loss rates from water. The rate of volatilization for a given compound depends on factors such as the suspended sediment concentration and its organic-matter content, the concentration of dissolved organic matter, temperature, and the water's turbulence. Increased concentrations of organic matter result

Table 8. Experimentally determined bioconcentration factors for some polychlorinated biphenyls (PCBs) and organochlorine insecticides.

Compound	Aquatic organism	Bioconcentration factor	Reference
PCB	Fish	12,000	Metcalf and others (1975)
PCB	Largemouth bass	2,800	Martell and others (1975)
Aroclor 1254	Guppies	200	Gooch and Hamdy (1983)
4-PCB	Brown trout	4,025	Sugiura and others (1979)
DDE	Fish	12,000	Metcalf and others (1975)
trans-chlordane	*B. Subtilis*	2,300	Grimes and Morrison (1975)
cis-chlordane	*B. Subtilis*	2,000	Grimes and Morrison (1975)
α-HCH	*Chlamydomonas*	310	Canton and others (1977)
β-HCH	Brown trout	658	Sugiura and others (1979)
Lindane	*B. Subtilis*	100	Grimes and Morrison (1975)
Lindane	Brown Trout	442	Sugiura and others (1979)
Toxaphene	*B. Subtilis*	3,400	Paris and others (1977)
Endrin	Algae	140-222	Grant (1976)
Dieldrin	*B. Subtilis*	1,200	Grimes and Morrison (1975)
Heptachlor Epoxide	*B. Subtilis*	800	Grimes and Morrison (1975)

in increased sorption and, consequently, decreased volatilization (Haque and others, 1974; Callahan and others, 1979). Increases in temperature or turbulence, however, will increase the rate of volatilization.

Volatilization from solution and other atmospheric discharges (such as incineration) combine with atmospheric transport to contribute to the widespread distribution of PCBs and some of the chlorinated pesticides. Munson (1976) detected both toxaphene and PCBs in rainwater collected at Sollers Point, Maryland. Heit and others (1984) have determined PCB concentrations up to 194 μg/kg in the sediments of remote Rocky Mountain Lakes that had not been directly affected by point source discharges of PCBs. They concluded that PCBs were present in the lakes due to the atmospheric deposition of the contaminants. Similarly, atmospheric deposition has been attributed to be the primary source of PCB contamination to the Great Lakes (Murphy and Rzeszutko, 1977; Eisenreich and others, 1979). Haines (1983) found residues of a variety of organochlorine insecticides in brook trout taken from six remote lakes in New England. Because the lakes had been surrounded with forested land that was untreated with pesticides for at least 80 years, it was concluded that the contaminant residues were atmospherically deposited. Volatilization, atmospheric transport, and subsequent deposition, therefore, partly explain the numerous detections of PCBs and organochlorine insecticides around the globe.

In addition to their ability to partition into organic matter and biological lipid reservoirs and their tendency to volatilize and be transported atmospherically, the chlorinated insecticides and PCBs are, in general, highly resistant to chemical or biological transformation. As a result, they are extremely persistent environmental contaminants, whose residues commonly remain years after the source of contamination has stopped.

The biodegradability of PCBs decreases with increased chlorination of the molecule, with the more highly chlorinated biphenyls being extremely resistant to biodegradation (Sayler and others, 1977). The biotransformation of PCBs is enhanced by an increase in the number of C-H bonds available for hydroxylation by microbial enzymes (Haley, 1984). Increased chlorination decreases the number of C-H bonds and, therefore, inhibits biodegradation. PCBs also are extremely resistant to oxidation and both acidic and basic hydrolysis (Callahan and others, 1979). Neither oxidation nor hydrolysis are likely to transform PCBs significantly in the environment. There is some evidence to indicate that PCBs can be partially dechlorinated by photolysis, particulary when exposed to short-wave ultraviolet light. Bunce and Kumar (1978) calculated that highly chlorinated biphenyl molecules would lose one chlorine molecule per year in shallow waters. In the same 1-year period, however, they predicted that only 5 percent of the lesser chlorinated biphenyls would lose a chlorine molecule photolytically. Although both biodegradation and photolysis transform PCBs at a very slow rate, they may be the most significant long-term transformation processes due to the negligible degradative affects of hydrolysis and oxidation.

The chlorinated insecticides also are relatively resistant to biodegradation. Aldrin has been shown to be biotransformed to dieldrin, but this product is strongly resistant to further degradation (Callahan and others, 1979). Likewise, DDT has been biotransformed to both DDD and DDE in natural systems, with the latter compound being highly resistant to continued biodegradation. Microbial decomposition of DDT occurs primarily through DDD formation by reductive dechlorination under anaerobic conditions (Johnsen, 1976). Other chlorinated insecticides such as chlordane, endosulfan, heptachlor, toxaphene, and mirex do not appear to biodegrade at significant rates in natural surface-water systems (Callahan and others, 1979; Aslanzadeh and Hedrick, 1985). Lindane is one of the few chlorinated insecticides that has been shown to biodegrade at significant rates in natural systems, with documented degradation products being penta- and tetrachloro-1-cyclohexanes and penta- and tetrachlorobenzenes (Moore and Ramamoorthy, 1984).

Oxidation of the organochlorine insecticides is not an important factor affecting their fate, with the possible exception of the oxidation of aldrin to dieldrin in the presence of oxygen or ozone (Callahan and others, 1979). Hydrolytic half-lives for the chlorinated insecticides typically are greater than 1 year, with the exception of heptachlor, which is rapidly hydrolyzed to 1-hydroxychlordene. Photolytic reactions degrade the chlorinated insecticides in laboratory experiments, and this process may be important to the long-term fate of these compounds. Moore and Ramamoorthy (1984) state that sunlight reaching the earth potentially will have enough energy to cleave aromatic C-Cl bonds or an aliphatic alcohol's C-H bonds but not aromatic C-C and H-OH bonds.

Environmental Distribution

Because of the tendency of PCBs and chlorinated insecticides to partition into sediment organic matter and biological lipid reservoirs, elevated concentrations of these contaminants have been reported in soils, sediments, and aquatic organisms throughout the U.S. and other parts of the world. Tables 9 and 10 present some of the documented residues of PCBs and organochlorine insecticides in sediments and biota, respectively. The highest sediment PCB residues have been observed in the Hudson River near the former discharges of two capacitor-manufacturing plants. It has been estimated that over 150,000 kg of PCBs were discharged to the Hudson River from these two plants over a 30-year period ending in 1976 (Brown and others, 1985). Sediment residues have been reported to be greater than 2,000 mg/kg (Nadeau and Davis, 1976). The sediments of Los Angeles Harbor have also been grossly contaminated with high concentrations of organochlorine compounds, including dieldrin (1800 μg/kg), total DDT (770 μg/kg), and PCBs (140 μg/kg) (Choi and Chen, 1976).

Biota from diverse locations across the U.S. also have been contaminated with organochlorine residues (table 10). Again, the Hudson River serves as an example of the 'worst-case' PCB

Table 9. Means and ranges of detectable sediment residues of polychlorinated biphenyls (PCBs) and organochlorine insecticides. [μg/kg is micrograms per kilogram]

Compound	Locality	Mean (μg/kg)	Range (μg/kg)	Sampling method	Ref.
PCB	Delaware River	123	2-830	core	1
PCB	Los Angeles Harbor	140	900-4500	grab	2
PCB	Lake Ontario shoreline marsh	0.02	0.002-0.038	grab	3
PCB	Rocky Mountain National Park	277	98-540	grab	4
PCB	Southern Puget Sound, WA	25.8	0.7-330	no data	5
PCB	Niagara River, Lake Ontario	65.7	47.7-121.5	suspended sediment	6
PCB	Rock Reservoir, IA	13	5.7-28.5	core	7
PCB	Bay of Quinte, Lake Ontario	385	200-620	dredge	8
PCB	Raritan Bay, NY	212	3-2035	grab	9
Aroclor 1016	Hudson River, NY	2047*	6.6-6700	grab	10
t-DDT**	Los Angeles Harbor	768	115-3212	grab	2
t-DDT	Salinas River, CA	no data	1-190	grab	11
DDT	Trinity River, TX	16.3	0.25-53.6	grab	12
DDE	Rock Reservoir, IA	2.4	1.1-7.4	core	7
DDD	Rock Reservoir, IA	2.4	0.6-7.3	core	7
Chlordane	Belmont Lake, NY	171	20-580	core	13
Chlordane	Trinity River, TX	13.7	0.15-64.0	grab	12
Mirex	Lake Ontario shoreline marsh	0.01	no data	grab	3
Mirex	Niagara River, Lake Ontario	7.1	3.9-18	suspended sediment	6
Dieldrin	Los Angeles Harbor	1800	900-4500	grab	2
Dieldrin	Rock Reservoir, IA	2.9	0.3-6.4	core	7
Endrin	Trinity River, TX	9.4	0.15-20	grab	12
Heptachlor	Trinity River, TX	5.28	0.7-9.3	grab	12
Heptachlor Epoxide	Rockaway River, NJ	4.5	0.7-10	grab	14
Lindane	Trinity River, TX	0.32	0.1-0.7	grab	12
α- and β-HCH	Niagara River, Lake Ontario	14.3	6.9-33	suspended sediment	6

* Concentrations for mean and range in units of milligrams per kilogram
** Denotes total DDT (includes all DDT, DDE, and DDD isomers)

1. Hochreiter (1982)
2. Choi and Chen (1976)
3. Glooschenko and others (1981)
4. Heit and others (1984)
5. Mowrer and others (1977)
6. Oliver and Charlton (1984)
7. Ricci and others (1983)
8. Scott (1980)
9. Stainken and Rollwagen (1979)
10. Nadeau and Davis (1976)
11. Routh (1972)
12. Qasim and others (1980)
13. Wood and others (1986)
14. Smith and others (1987)

Table 10. Detectable residues of polychlorinated biphenyls (PCBs) and organochlorine insecticides in biota.

Compound	Locality	Aquatic organism	Mean (µg/kg)	Maximum (µg/kg)	Reference
PCB	Schuylkill River Reading, PA	American eel	3,700	8,100	1
PCB	Milwaukee River, WI	Red horse sucker	6,630	-	2
PCB	New Bedford Harbor	Mussel	-	17,000	3
PCB	Hudson River	Atlantic tomcod liver	37,500	98,200	4
PCB	New York Harbor	Lobster	230	410	5
PCB	Utah Lake	Carp	115	-	6
PCB	Long Island Sound	Windowpane flounder liver	1,500	2,300	7
t-DDT*	Atlantic Ocean	Deep sea fish	7,100	27,000	8
t-DDT	Milwaukee River, WI	Red horse sucker	150	-	2
t-DDT	Lake Superior	Lake trout	3,250	9,780	9
p,p'-DDE	New England lakes	Brook trout	18	34	10
Dieldrin	Atlantic Ocean	Deep sea fish	20	30	8
Dieldrin	New England lakes	Brook trout	4	7	10
α-HCH	New England lakes	Brook trout	11	19	10
β-HCH	Milwaukee River, WI	Red horse sucker	60	-	2
Lindane	Lake Superior	Lake trout	190	-	9
Heptachlor	Lake Superior	Lake trout	1,630	2,770	9
Heptachlor epoxide	Milwaukee River, WI	Red horse sucker	20	-	2
Chlordane	Schuylkill River, Reading, PA	American eel	180	270	1
Endrin	Schuylkill River, Reading, PA	American eel	9	19	1
Aldrin	Lake Superior	Lake trout	120	220	9
Endosulfan	Milwaukee River, WI	Red horse sucker	20	-	2
Toxaphene	Louisiana lakes	Spotted gar	410	800	11

* Denotes total DDT (includes all DDT, DDE, and DDD isomers)

1. Barker (1984)
2. DeVault (1985)
3. Farrington and others (1983)
4. Klauda and others (1981)
5. Roberts and others (1982)
6. Smith and others (1974)
7. Greig and others (1983)
8. Barber and Warlen (1979)
9. Parejko and others (1975)
10. Haines (1983)
11. Winger and Andreasen (1985)

contamination, with concentrations found in the livers of Atlantic tomcods approaching 100 mg/kg (Klauda and others, 1981). Brown and others (1985) have documented lipid-based PCB concentrations in the fillets of whole yearling pumpkinseeds in the Hudson River greater than 1000 mg/kg. The 8-year discharge of kepone into the James River estuary in Virginia also caused extreme contamination of biota, with concentrations in the muscle of white perch being as high as 10 mg/kg (Huggett and others, 1980). Concentrations of organochlorine insecticides and PCBs commonly are highest in American eels, inasmuch as this species has a relatively high lipid content (Barker, 1984; Zitko, 1971).

In contrast to sediment and biological residues, aqueous concentrations of PCBs and chlorinated insecticides are typically low, with values typically in the parts-per-trillion range. In a study of a Tennessee river, Jaffe and others (1982) detected the insecticides hexachlorobenzene, heptachlor, aldrin, chlordane, dieldrin, and endrin in water samples at mean concentrations of 5.3, 3.2, 5.1, 16.7, 0.8, and 1.2 ppt, respectively. Rihan and others (1978) similarly detected aqueous concentrations of aldrin (0.01 to 0.49 ppt), lindane (0.02 to 0.16 ppt), p,p'-DDT (2.73 to 12.31 ppt), and heptachlor (undetectable to 0.18 ppt) in the surface waters of northern Mississippi. These concentrations are typical of contaminated surface waters, and their low magnitudes are consistent with the low solubilities of the contaminants.

PCBs and chlorinated insecticides have been shown in field studies to be extremely persistent and ubiquitous environmental contaminants. Nevertheless, increased restrictions on the use and production of these compounds generally have resulted in a slow but steady decline of their environmental residues over the last 10 to 15 years.

Several researchers have noted decreases in biological residues of PCBs and chlorinated insecticides over time. Wszolek and others (1979) determined that DDE concentrations in 12-year old fish taken from Cayuga Lake in central New York had decreased from 11.7 ppm to 3 to 4 ppm over an 8-year period. Over the same time span, PCB residues exhibited less of a decline, with concentrations decreasing only from 15.7 ppm to 13 ppm. As a result of an accidental discharge of PCBs to Escambia Bay, Florida in 1969, Wilson and Forester (1978) monitored PCB concentrations in the bay's oysters from 1969 to 1976. Despite the fact that no known point-source discharges of PCBs contaminated the bay after 1969, residues in the oysters showed only a slight decline over the study period, with an apparent equilibrium PCB concentration of about 0.5 ppm recorded in 1976. Sullivan and others (1983) reported that PCB concentrations in fish of the lower Fox River, Wisconsin had declined steadily from 1976 to 1981. Figure 12 presents some of the temporal trends of PCB contamination in water and fish of the Hudson River at a site approximately 50 km below the former discharges of the two capacitor-manufacturing plants (Brown and others, 1985). The data demonstrate a distinct decline in aqueous and lipid concentrations of PCBs with time.

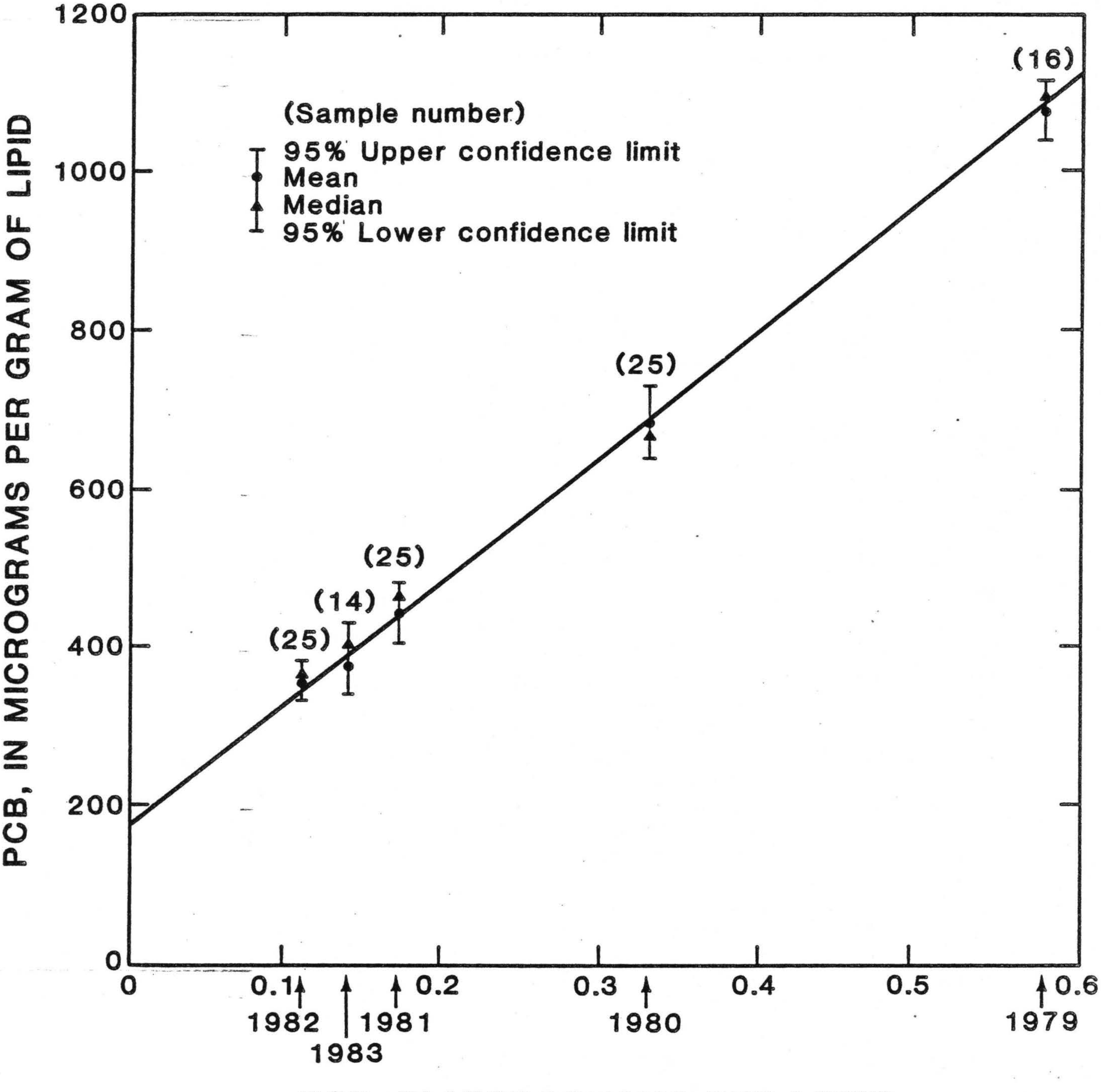


Figure 12. Relation of summer mean polychlorinated biphenyl (PCB) concentrations in water and lipid-based PCB concentrations in fillets of whole yearling pumpkinseed collected September 1977-83 at Stillwater, New York. [Reprinted with permission of Environmental Science and Technology 19, 659 (1985). Copyright 1985 by the American Chemical Society.]

Organochlorine residues in sediments have also shown a general decline over time. Gilliom (1985) reported the results of the U.S. Geological Survey-U.S. Environmental Protection Agency Pesticide Monitoring Network, which monitored selected pesticides in the water and bottom sediments of more than 150 river sites across the U.S. The number of detections of chlorinated insecticides in bed sediment decreased steadily from 1976 to 1978, except for a slight increase occurring in 1979 (figure 13). In the monitoring network, 36 station-chemical combinations exhibited statistically significant trends in pesticide concentration, 29 trends decreased with time. Five of the seven increasing trends occurred in the Black River in Kingstree, South Carolina, and most of these trends involved either DDD, DDE, DDT, chlordane, or dieldrin.

PCB contamination trends in sediment generally have been constant or have slowly declined over the last 10 years. Ricci and others (1983) collected sediment cores from an Iowa reservoir and determined that PCB residues were greatest in the deepest sections of the core, indicating that the more recently deposited sediments were less contaminated with PCBs. They observed similar trends for DDE and DDD. Van Luik (1984) on the other hand, found no correlation between PCB concentration and core depth for sediment cores collected from the Calumet-Sag channel. Sediment PCB concentrations in the Hudson River have gradually decreased since the mid-1970's, but much of this decrease can be attributed to substantial dredging operations that have removed an estimated 500,000 m^3 of sediment over a 25-year period (Brown and others, 1985). Also, some of the Hudson River's contaminated sediment has been transported into the Raritan Bay and is believed to be accumulating (Stainken and Rollwagen, 1979). Sullivan and others (1983), although observing a decline in the PCB concentrations of fish from the Fox River, Wisconsin, observed no significant decline in the sediment PCB concentrations of the river from 1976 to 1981. These studies indicate the extreme persistence of PCBs and also may indicate that, depite the cessation of their production, PCB residues present in capacitors and transformers throughout the U.S. may still be contaminating surface waters.

Regionally, the highest PCB concentrations typically are found near industrial areas. Martel and others (1975), in a study of a northern Virginia watershed, observed that the highest sediment PCB concentrations in the watershed were near the most industrialized areas. Similarly, Mowrer and others (1977) found the highest PCB residues in sediments and mussels of Puget Sound, Washington, in industrialized and heavily populated areas, and the lowest concentrations observed in scarcely populated areas surrounding the bay. Farrington and others (1983) analyzed mussels taken from 62 locations from the eastern and western coastal waters of the U.S. from 1976 to 1978. In all 3 years of the study, mussels taken from water near urbanized areas had PCB concentrations at least an order of magnitude greater than mussels taken from water near rural areas. Nationally, PCB concentrations were generally highest along the northeastern coast from the Chesapeake Bay to Cape Ann, Maine.

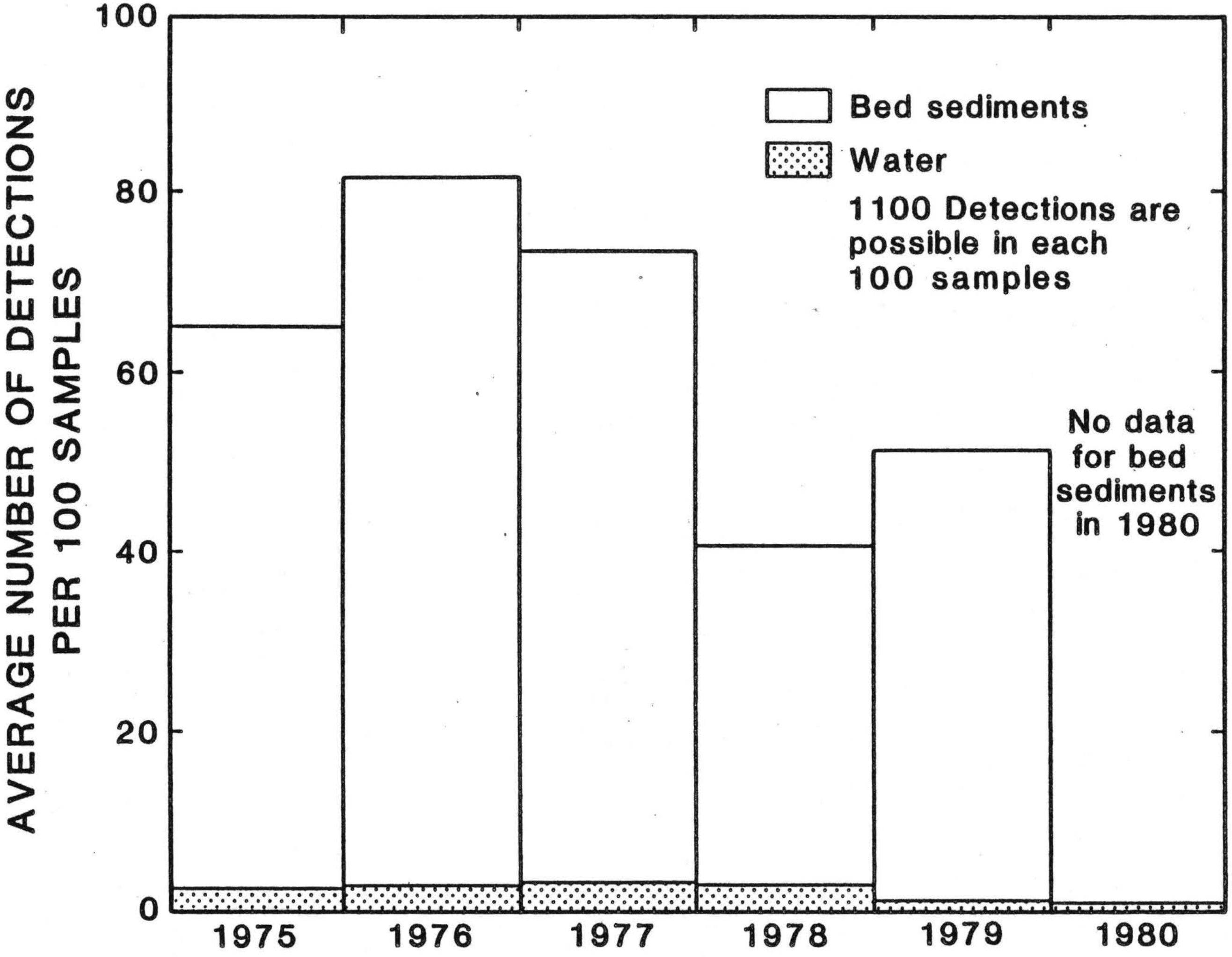


Figure 13. Frequency of detection of organochlorine insecticides in water and bed-material samples from stations in the U.S. Geological Survey-U.S. Environmental Protection Agency Pesticide Monitoring Network, 1975-1980 (reprinted from Gilliom, 1985).

Residues of chlorinated insecticides are not necessarily highest in industrialized regions. Gilliom (1985) described pesticide use as being "strongly regional, with most use of each chemical occurring in only one or two regions of the country." Because compounds such as DDT and toxaphene are applied primarily in cotton-growing areas, their residues are likely to be highest in these areas. Compounds such as aldrin and chlordane are applied principally to corn and, therefore, are expected to be found in corn-producing areas. However, residues in industrial areas also can be high, as evidenced by the data of Qasim and others (1980), who determined that aqueous pesticide concentrations in the Trinity River, Texas, were highest in the central reach of the river which drained crop land, pasture, and forest. However, sediment pesticide concentrations were highest in the upper reaches of the river, which drains the metropolitan areas of Dallas and Fort Worth. The authors attribute this contamination to numerous point-source discharges of wastewater-treatment plants. When surface-water contamination can be attributed to runoff from crop land, the highest concentrations are likely to be observed after a heavy rain (Pfaender and others, 1977).

PCBs and chlorinated insecticides have severely impacted our environment, and, despite their drastically declining use over the last 10 to 20 years, their residues are likely to persist in the sediment, water, and biota of the nation's surface-water systems for many years to come. At present, these compounds are being replaced with less-persistent organic compounds. New insecticides, such as the carbamate and organophosphorus insecticides discussed in the next section, have found increasing use. PCBs have similarly been replaced with such compounds as phenylxylylethanes, di-isopropylnaphthalenes, and isopropylbiphenyls (Addison and others, 1983).

CARBAMATE AND ORGANOPHOSPHORUS INSECTICIDES

Uses, Production, Properties, and Regulatory Limits

In response to the environmental concern over the persistence of the chlorinated insecticides, the carbamate and organophosphorus (OP) insecticides have seen increasing use over the last 20 years because of their relatively short half lives in the environment. In addition, they have been increasingly recommended for the control of pests that are not specifically controlled by the organochlorine insecticides. Figure 14 presents the structural diagrams of some of the more common carbamate and OP insecticides. The octanol-water partition coefficients, solubilities, and vapor pressures of some of these compounds are given in table 11.

Table 12 presents usage data for some of the OP insecticides (Gilliom, 1985). Of the group, malathion and parathion have probably seen the most widespread use. The use of parathion, although it is relatively nonpersistent in the environment, has decreased considerably in recent years because of its high toxicity to mammals. The compound inhibits the activation of the acetylcholinesterase enzyme in the nervous systems of animals (Baum, 1982), and its use has resulted in numerous deaths of humans involved in its manufacture and application. Decline in the use of parathion is evidenced by its production decrease from 50.6 million lb (pounds) in 1969 to 15 million lb in 1971 (Mulla and others, 1981). In contrast, malathion is the least toxic of the organophosphorus insecticides and has been used to protect livestock, to control fleas in kennels, and to control other household and garden pests (Baum, 1982). Its low toxicity to animals is attributed to carboxyesterases that degrade malathion to nontoxic metabolites in birds, mammals, and resistant insects (Mulla and others, 1981). The production of malathion in the U.S. reached a high in 1971 of 30 million lb (Mulla and others, 1981).

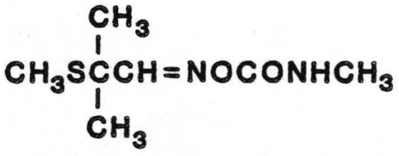
Table 13 presents some usage data for the carbamate insecticides. Carbaryl, first synthesized in 1953 and introduced in 1958, is the most widely used of the carbamate insecticides and has been shown to control over 150 major pests (Rajagopal and others, 1984).

Environmental Fate

As is evidenced from the half lives in table 14, the carbamate and OP insecticides are among the least environmentally persistent pesticides. This is primarily attributable to their relatively rapid chemical and biological degradation both in soil and surface-water systems.

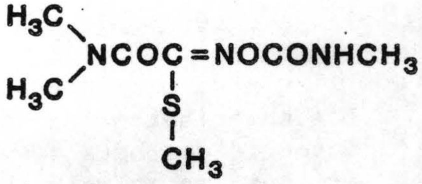
Several researchers have documented the chemical and biological attenuation of the OP insecticides. Walker (1976) determined that 97 percent of malathion added to sterile and nonsterile river water was degraded after 18 days incubation in the dark. Parathion was more

CARBAMATE INSECTICIDES

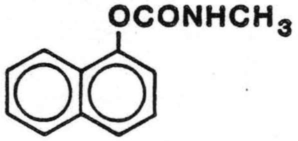


$$CH_3S\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH=NOCONHCH_3$$

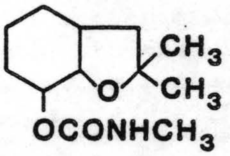
Aldicarb



Oxamyl

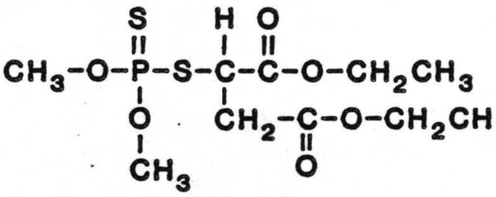


Carbaryl



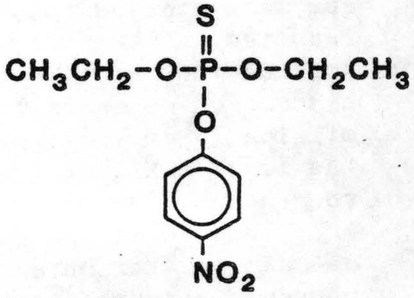
Carbofuran

ORGANOPHOSPHORUS INSECTICIDES

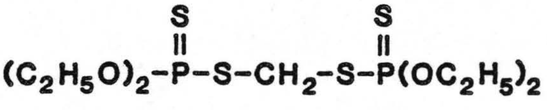


$$CH_3-O-\overset{S}{\overset{\|}{\underset{\underset{\underset{CH_3}{|}}{O}}{\underset{|}{P}}}}-S-\overset{H}{\overset{|}{\underset{\underset{CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2CH}{|}}{C}}}-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$$

Malathion

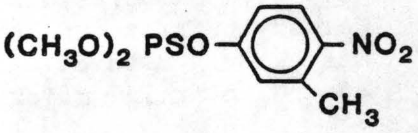


Parathion

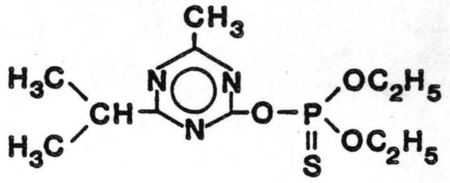


$$(C_2H_5O)_2-\overset{S}{\overset{\|}{P}}-S-CH_2-S-\overset{S}{\overset{\|}{P}}(OC_2H_5)_2$$

Ethion



Fenitrothion



Diazinon

Figure 14. Structural diagrams of selected carbamate and organophosphorus insecticides.

Table 11. Experimentally determined octanol-water partition coefficients, solubilities, and vapor pressures of selected organophosphorus and carbamate insecticides.
[Numbers in parentheses indicate references; dash indicates no data available]

Compound	Log K_{ow}	Solubility (mg/L)	Vapor pressure (mm of Hg)
Malathion	2.89 (1)	145 (1)	1.25×10^{-4} (1)
Parathion	3.81 (1)	24 (1)	0.57×10^{-5} (1)
Dimethylparathion	2.04 (2)	55-60 (2)	-
Diazinon	-	40 (3)	-
Ethion	-	2 (3)	1.5×10^{-6} (2)
Fenitrothion	3.38 (2)	30 (2)	5.4×10^{-5} (2)
Chlorpyrifos	5.11 (2)	0.4 (2)	-
Aldicarb	-	-	1.0×10^{-4} (2)
Carbaryl	-	40 (2)	<0.005 (2)
Carbofuran	-	320 (2)	2.0×10^{-5} (2)

1. Mulla and others (1981)
2. Verschueren (1983)
3. Gilliom (1985)
4. Belluck and Felsot (1981)

Table 12. Detection limits, water-quality criteria, and use data for selected organophosphorus insecticides. [µg/L is micrograms per liter; lb/yr is pounds per year; from Gilliom (1985)]

Chemical	Detection limit (µg/L)[1]	Water quality criteria (µg/L)		Principal uses and sources	National use on farms[3] (million lb/yr)				Total use, 1981 (million lb/yr)
		Human health[2]	Aquatic life		1966	1971	1976	1982	
Diazinon	0.10	nd	nd	Corn, general purpose	5.6	3.2	1.6	0.3	9.0
Ethion	0.25	nd	nd	Citrus fruits	2.0	2.3	nr	nr	2.0
Malathion	0.25	nd	0.1	General purpose	5.2	3.6	2.8	1.6	28
Dimethyl parathion	0.25	nd	nd	Cotton, wheat	8.0	28.	23.	11.	20
Methyl trithion	0.50	nd	nd	Not identified	nr	nr	nr	nr	0.1
Parathion	0.25	nd	0.04	Wheat, corn, sorghum	8.5	9.5	6.6	4.0	5.0
Trithion	0.50	nd	nd	General purpose	nr	nr	nr	nr	0.1

nr = none reported; nd = no data available.

1. Detection limits are for water samples. Bed-sediment detection limits are 10 times greater and in units of micrograms per kilogram (Lucas and others, 1980).
2. U.S. Environmental Protection Agency (1977).
3. Data for 1966, Eichers and others (1970); for 1971, Andrilenas (1974); for 1976, Eichers and others (1978); for 1982, U.S. Department of Agriculture (1983). Data for 1982 do not include use on livestock.

Table 13. Characteristics of selected carbamate insecticides.

Compound	Type	Uses	Trade name(s)
Aldicarb	Oxime carbamate	Insects, mice, nematodes	Temik
Oxamyl	Oxime carbamate	Insects, nematodes	Vydate
Arprocarb (propoxur)	N-methylcarbamate	Insects	Baygon, Unden, Sendran, Suncide, Blatanex
Carbaryl	N-methylcarbamate	Insects	Sevin
Carbofuran	N-methylcarbamate	Soil insects	Furadan

Table 14. Approximate persistence of pesticides in soils. [From Metcalf, 1972]

Pesticide	Approximate half-life, years
Lead, arsenic, copper, mercury	10-30
Chlorinated insecticides	2-4
Triazine herbicides	1-2
Benzoic acid herbicides	0.2-1
Urea herbicides	0.3-0.8
Chlorinated herbicides	0.1-0.4
Organophosphorus insecticides	0.02-0.2
Carbamate insecticides	0.02-0.1

persistent, with only a 16 to 23 percent loss occurring after 40 days. Microorganisms capable of degrading both compounds were isolated. Sudhakar-Barik and Sethunathan (1978) noted the biological hydrolysis of parathion in soils, water, and sediments, and the formation of a degradation product, p-nitrophenol, within 6 hours after the second or third additions of the insecticide. Sharom and others (1980a) found that 40 percent of the ethion and leptophos and essentially 100 percent of the diazinon and mevinphos added to natural water samples was degraded within 16 weeks. In a study of malathion degradation in soil, Gibson and Burns (1977) observed malathion half lives of about 1 day. When the soil's organic matter was removed, however, degradation was three to six times slower. The authors hypothesized that the organic matter has a catalytic effect (by acting as a stable enzyme) on the degradation of malathion. Wolfe and others (1977) modeled the chemical degradation of malathion as a function of pH and temperature. Acid degradation was slow (malathion half life of 4 years at pH = 4), but alkaline degradation was fast enough to be a competitive degradation pathway in the environment (malathion half life of 22 hours at pH = 8.2). Weinberger and others (1982) documented both hydrolytic and photolytic decomposition of fenitrothion in aquatic microcosms. Eidt and others (1986) applied fenitrothion formulations to two Canadian streams and observed that the compound's aqueous concentration was rapidly attenuated in both streams. These studies indicate that the OP insecticides are generally susceptible to rapid chemical and microbial degradation in natural systems.

Numerous studies also have documented the chemical and biological degradation of the carbamate insecticides. Carbaryl is rapidly hydrolyzed at alkaline pH (Wolfe and others, 1978), and it has been biologically degraded to 1-naphthol in the laboratory (Rajagopal and others, 1984). Aldicarb has similarly been observed to have hydrolytic half lives of 55 and 6 days at pH values of 8.85 and 9.95, respectively (Given and Dierberg, 1985). Sharom and others (1980a) determined that essentially 100 percent of the carbofuran added to sterile and nonsterile natural water was degraded after 16 weeks incubation. Carbaryl was degraded even more rapidly, with almost 100 percent removal occurring after only 4 weeks. Comparison of the sterile-water and nonsterile-water degradation data revealed that, for both compounds, chemical degradation appeared to be of primary importance to the attenuation, with biological processes playing only a secondary role. Figure 15 compares the $^{14}CO_2$ evolved from three ring-labeled ^{14}C-insecticides (parathion, carbaryl, and carbofuran) applied to flooded and nonflooded soils (Rajagopal and others, 1984). These data in combination with the results of Sharom and others (1980a) indicate that while the initial chemical or biological transformation step of carbaryl or carbofuran may be rapid, ring cleavage of the molecules may be slow (less than 3 percent of ring-labelled ^{14}C evolved as $^{14}CO_2$ for either carbaryl or carbofuran after 30 days).

Sorption to sediments and bioaccumulation generally are not

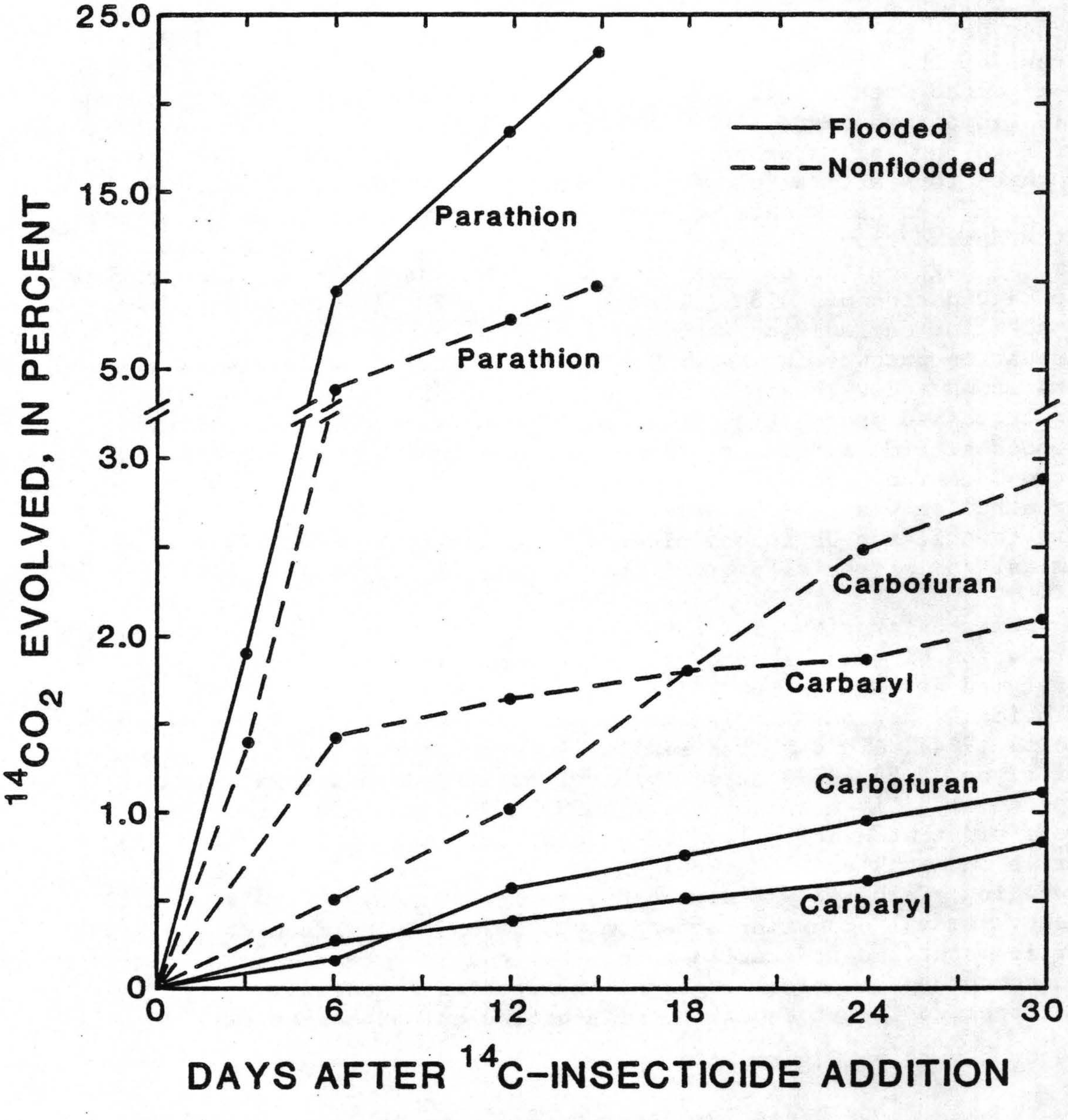


Figure 15. Cumulative $^{14}CO_2$ (percentage of added ring-labeled ^{14}C-insecticide) evolved in a soil planted to rice under flooded and nonflooded conditions. [Reprinted with permission of Residue Reviews 93, 113 (1984). Copyright 1984 by Springer-Verlag New York, Inc.].

significant fate processes for most of the carbamate and OP insecticides because of their relatively high solubilities and low octanol-water partition coefficients. However, sediments with high organic-matter contents or aquatic organisms with high lipid contents may accumulate significant residues if aqueous concentrations are high. Aquatic plants exposed to 10 ppm fenitrothion for five days accumulated between 216 and 286 ppm of the contaminant on a dry-weight basis (Weinberger and others, 1982). These residues decreased rapidly, however, as the fenitrothion was chemically and biologically degraded in the water column. Sharom and others (1980b) observed the sorption of a variety of OP and carbamate insecticides to soils and sediments and noted that increased sorption correlated both with decreased solubility and increased soil/sediment organic matter. The order of sorption to soil was leptophos > ethion > chlorpyrifos > parathion > diazinon > carbaryl > carbofuran > mevinphos. Sorption coefficients (K_d) for the sediment (2.8 percent organic carbon) ranged from 158 (ethion) to less than unity (mevinphos). Belluck and Felsot (1981) measured BCFs between 1 and 10 for carbofuran and malathion partitioned between water and caddisfly egg masses, indicating that bioaccumulation was minimal.

The bioaccumulation and sorption of the carbamate and OP insecticides, therefore, will vary with factors such as compound solubility and aqueous concentration, the sediment and dissolved organic matter concentration, and the lipid contents of the aquatic organisms. Because the partitioning of these solutes into the sediment organic matter and the biological lipid reservoirs are reversible processes, biological and sediment residues are likely to be short-lived as a result of the rapid chemical and biological attenuation of these compounds in surface-water systems.

Environmental Distribution

Despite the fact that the carbamate and OP insecticides are used extensively in the U.S., they are not detected frequently in surface waters. Additionally, since they have relatively high solubilities (and therefore a low tendency to partition into organic matter and biological lipid reservoirs), their residues are even less frequently detected in sediment and biota.

The U.S. Geological Survey-U.S. Environmental Protection Agency Pesticide Monitoring Network monitored the occurrence of several of the OP insecticides at 161 surface-water stations throughout the U.S. from 1975 to 1980 (Gilliom and others, 1985). Compared to chlorinated insecticide residues that also were monitored, the OP insecticides were only occasionally detected in water samples. Methyl parathion, the OP insecticide used most heavily on farms, was detected in only three of almost 3,000 water samples. The low number of detections of OP insecticides was attributed to their relatively low persistence and high aqueous detection limits (table 12). Diazinon was detected most frequently (34 detections in 2,861 water samples), and this was likely related to the fact that, of the OP insecticides included in the analysis, diazinon was the most persistent and had the lowest detection limit. For all the OP insecticides monitored, the number of sediment detections was less than the number of aqueous detections, which agrees with laboratory data demonstrating that the OP insecticides do not strongly partition into sediment organic matter. Because of the small number of detections of OP insecticides by the Pesticide Monitoring Network, no regional trends are observed either for water or sediment samples.

No studies documenting regional or temporal trends of carbamate-insecticide contamination in the U.S. were found in the reviewed literature. However, because the behavior and persistence of the carbamate and OP insecticides are similar, it is expected that the contamination of the surface waters of the U.S. by these compounds will not be widespread, and that any existing residues will rarely persist for more than several weeks. Carbamate and OP insecticide residues are expected to be highest in shallow ground water beneath agricultural areas and in streams draining these areas.

HERBICIDES

Uses, Production, Properties, and Regulatory Limits

In contrast to the declining use of insecticides in recent years, herbicide use on major crops in the U.S. has been steadily increasing, as evidenced by the data in figure 16 (Gilliom and others, 1985). Herbicides also are applied extensively to surface waters to control aquatic vegetation that may impede water flow, navigation, and recreation. The majority of herbicide use in the U.S. can be atributed to atrazine and 2,4-D. From 1971 to 1976, they accounted for 50 percent of all herbicide usage (Gilliom, 1985). Since 1976 however, their share of total herbicide application has decreased slightly. Atrazine use, for example, declined from 41 percent of the total amount of herbicide applied to corn in 1976 to 33 percent by 1980 (Gilliom, 1985).

Detection limits, water-quality criteria, and U.S. farm usage data for some of the most common herbicides are presented in table 15 (Gilliom and others, 1985). Table 16 lists the quantities of herbicides applied to 11 agricultural watersheds in Ontario during 1975 (Frank and others, 1982). Both tables indicate that atrazine and 2,4-D are the most heavily applied herbicides in those areas.

The herbicides are characterized by high aqueous solubilities and low vapor pressures (table 17). As a result, they generally do not bioconcentrate, sorb to sediments, or volatilize from solution to an appreciable extent. Figure 17 presents the structural diagrams of some of the more common terrestrial and aquatic herbicides. Based on their structural characteristics, the herbicides are broken down into four groups. The organochlorine herbicides have phenoxy, acetic, or benzoic acid functional groups attached to an aromatic ring. The other three groups are the nitrogen-substituted, urea-substituted, and dinitroaniline herbicides. Table 18 lists the four groups along with some of their associated herbicides. Paraquat and diquat, commonly referred to as the bipyridylium herbicides, are highly potent salts that exist in solution as divalent organic cations with associated chloride or bromide.

Environmental Fate

The herbicides are, in general, nonpersistent environmental contaminants. Their high solubilities greatly reduce solute partitioning into sediment organic matter or biological lipid reservoirs. Although their low vapor pressures and high solubilities combine to make volatilization an insignificant fate process, many of the herbicides are rapidly biodegraded by microbial populations or chemically attenuated by photolytic or hydrolytic reactions.

Documented sediment-water sorption coefficients (K_d) for the herbicides are small relative to compounds such as the organochlorine

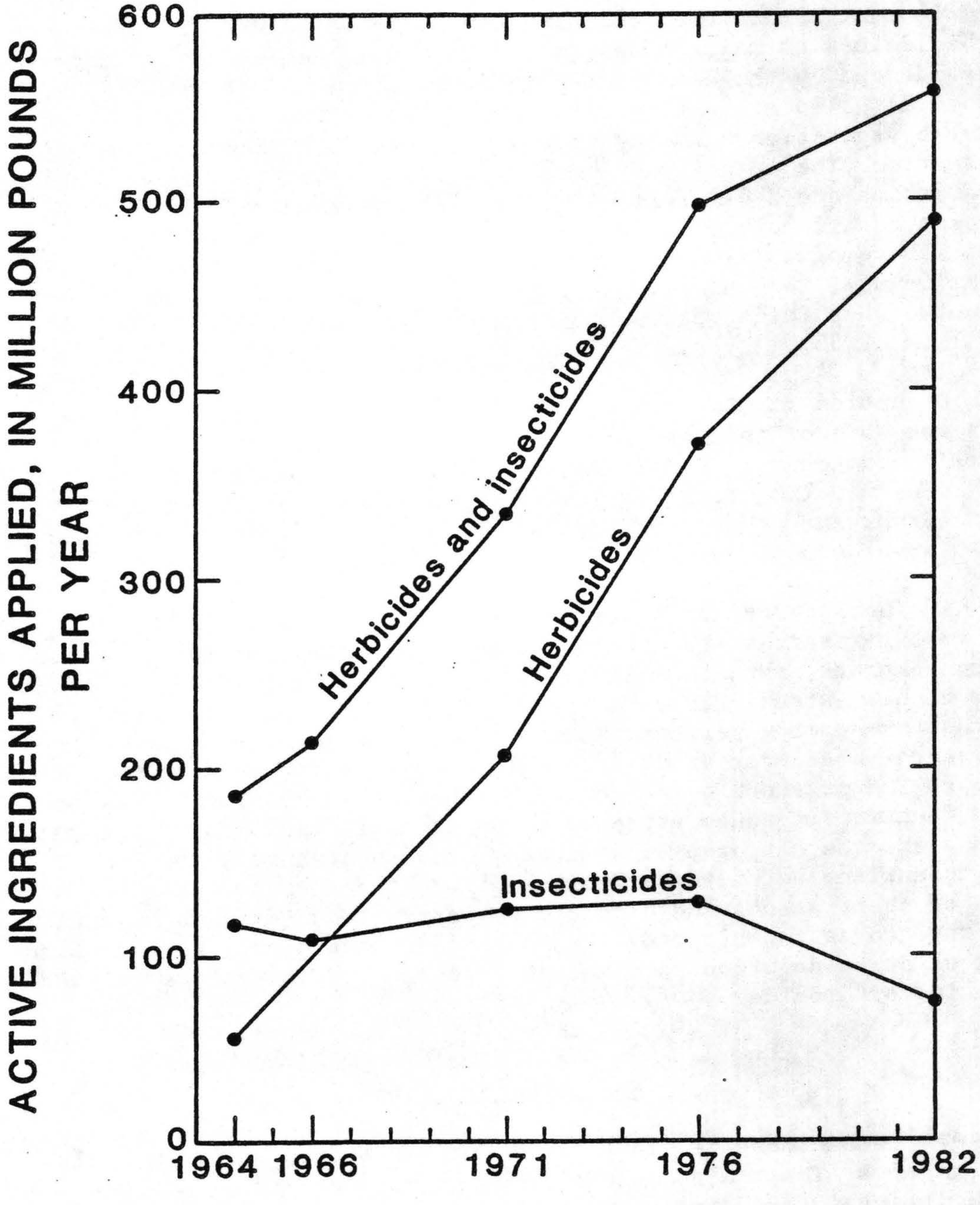


Figure 16. Trends in national use of herbicides and insecticides on major crops, 1964-82. [Reprinted from Gilliom and others, 1985)].

Table 15. Detection limits, water-quality criteria, and use data for some common herbicides.
[µg/L is micrograms per liter; lb/yr is pounds per year; from Gilliom (1985)]

Chemical	Detection limit (µg/L)[1]	Water quality Criteria[2] (µg/L)		Principal uses and sources	National use on farms[3] (million lb/yr)				Total use, 1981 (million lb/yr)
		Human health	Aquatic life		1966	1971	1976	1982	
2,4-D	0.5	100	nd	Wheat, rangeland, general purpose	4	31	38	23	60
2,4,5-T	0.5	10	nd	Rice, rangeland, general purpose	0.8	nr	nr	nr	2.2
Silvex	0.5	nd	nd	Surgarcane, rice, rangeland	nr	nr	nr	nr	0.4
Atrazine	0.5	nd	nd	Corn	24	54	90	76	92

nr = none reported; nd = no data available.

1. Detection limits are for water samples. Bed-sediment detection limits are 10 times greater and in units of micrograms per kilogram (Lucas and others, 1980).
2. U.S. Environmental Protection Agency (1977).
3. Data for 1966, Eichers and others (1970); for 1971, Andrilenas (1974); for 1976, Eichers and others (1978); for 1982, U.S. Department of Agriculture (1983).

Table 16. List of and magnitude of application of herbicides in 11 agricultural watersheds in Ontario, 1975.
[kg is kilogram; from Frank and others, 1982]

Amounts applied				
1-10 kg	11-100 kg	101-1000 kg	1001-10,000 kg	>10,000 kg
Bromacil	Amitrole	Bentazon	Alachlor (2755)[1]	Atrazine (10,570)
Monuron	Cyprazine	2,4-DB	Butylate (1708)	
Nitrofen	DCPA	Diphenamid	Chloramben (1979)	
Picloram	Diallate	EPTC	Cyanazine (2468)	
	Dicamba	Linuron	2,4-D (3098)	
	Dinitramine	MCPA	Metobromuron (1012)	
	Dinoseb	Metribuzin	Simazine (1389)	
	Mecoprop	Paraquat		
	Monolinuron	2,4,5-T		
	Naptalam	Trifluralin		
	Pebulate			
	Prometon			
	Terbacil			

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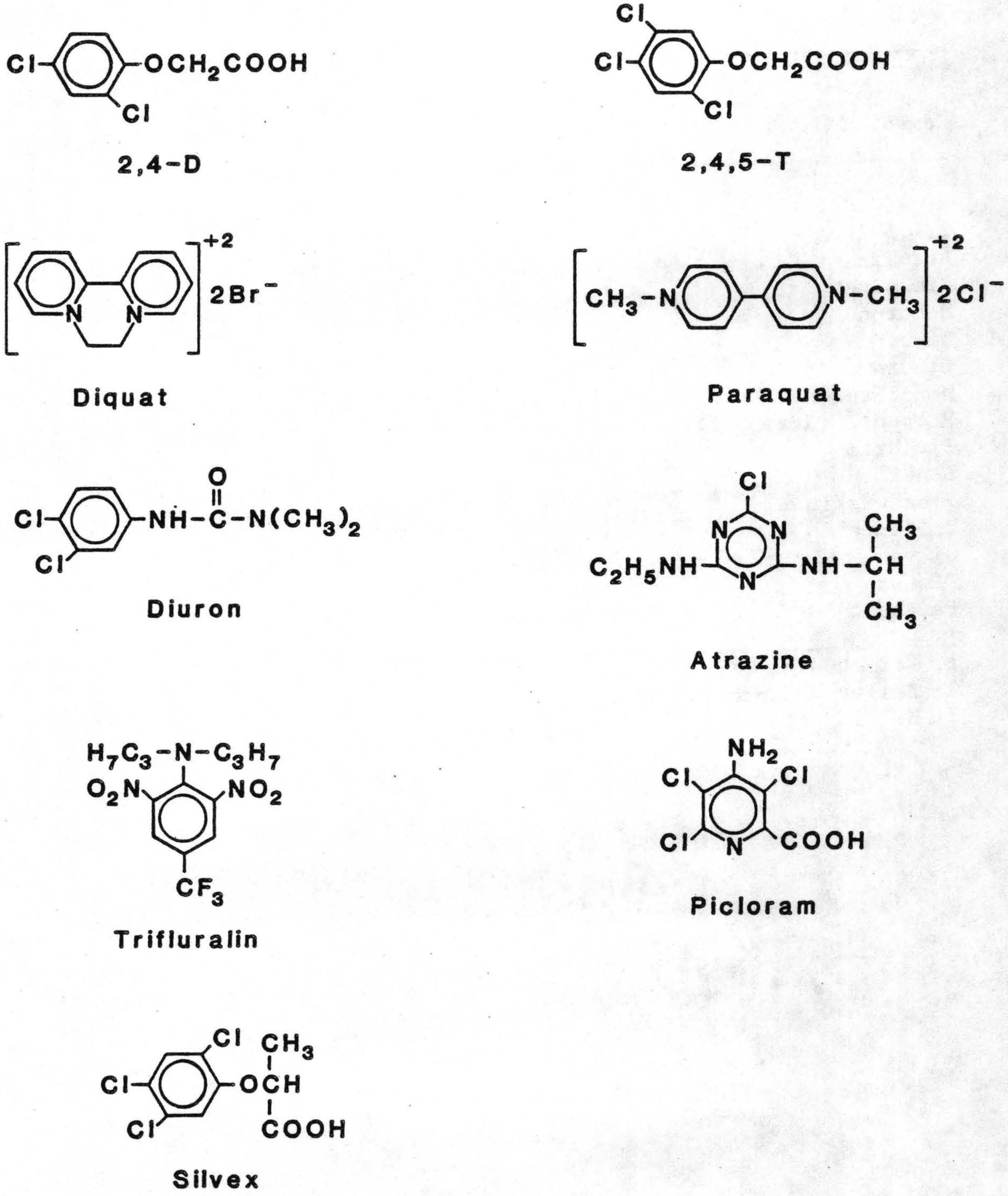
[1] Values in parentheses are actual amounts applied in kilograms.

Table 17. Experimentally determined aqueous solubilities and vapor pressures of some common herbicides.
[mg/L is milligrams per liter; mm is millimeter; dash indicates no data available]

Compound	Solubility (mg/L)	Vapor pressure (mm of Hg)	Reference
2,4-D	890	6.0×10^{-7}	1,2
2,4,5-T	278	6.5×10^{-7}	1,2
Atrazine	70	3.0×10^{-7}	1
Simazine	5	-	1
Monuron	230	5.0×10^{-7}	1
Diuron	42	3.1×10^{-6}	1
Linuron	75	1.1×10^{-5}	1
Monolinuron	735	1.5×10^{-4}	2
Propanil (Stam F-34)	50-225	9.0×10^{-5}	1
Picloram	430	6.2×10^{-7}	1
Benefin	.1	3.9×10^{-7}	3
Profluralin	.1	6.9×10^{-5}	3
Trifluralin	4	2.0×10^{-4}	1
Silvex	140		1
Diquat	700,000	-	1
Paraquat	miscible	-	1

1. Verschueren (1983)
2. Bailey and others (1968)
3. Helling (1976)



2,4-D

2,4,5-T

Diquat

Paraquat

Diuron

Atrazine

Trifluralin

Picloram

Silvex

Figure 17. Structural diagrams of selected herbicides.

Table 18. Structural groupings of selected herbicides.

Organochlorine (phenoxy, acetic, and benzoic acid)

- Amiben
- 2,4-D
- Dalapon
- Dicamba
- DNBP
- Fenac
- MCPA
- Methoxy fenac
- Picloram
- Silvex
- 2,4,5-T
- 2,3,6-TBA
- TCA
- Tricamba

Organonitrogen (triazines)

- Atrazine
- Alachlor
- Ametryn
- Atraton
- Prometone
- Prometryne
- Propazine
- Secbumeton
- Simazine
- Simetryn
- Terbutryn

Dinitroaniline herbicides

- Benefin
- Butralin
- Dinitramine
- Ethalfluralin
- Fluchloralin
- Isopropalin
- Nitralin
- Oryzalin
- Penoxalin
- Profluralin
- Prosulfalin
- Trifluralin

Substituted urea

- Buturon
- Cycluron
- Diuron
- Fenuron
- Linuron
- Monuron
- Neburon
- Norea (Herban)

insecticides, indicating sorption generally is not an important fate process. Bovey and others (1974) applied a 1:1 mixture of picloram and 2,4,5-T at a rate of 1.12 kg/ha to pastureland and then analyzed soil and runoff water for both compounds. Concentrations in runoff water (400 to 800 ppb) were significantly higher than soil concentrations (nondetectable to 238 ppb). El-Dib and Aly (1976b) studied the use of bentonite clays to remove the herbicides IPC, CIPC, linuron, and monuron from contaminated surface waters and concluded that the clay minerals would be unable to remove significant amounts of the herbicides from solution. Endothall, an aquatic herbicide, was shown to have a sorption coefficient of 0.958 in a sediment/water system investigated by Reinert and Rodgers (1984). Similarly, Muir and others (1980) determined that distribution coefficients for fluridone sorption to pond and river sediments were relatively low, ranging from 20 to 137. Wauchope and Myers (1985) observed atrazine and linuron sorption to fresh water sediments to be rapid and reversible. Once again, sorption coefficients were low, ranging from 1.3 to 18 for atrazine and 1.5 to 24 for linuron.

Although the majority of herbicides do not sorb appreciably to sediments, their are some exceptions. The dinitroaniline and bipyridylium herbicides have demonstrated a strong tendency to sorb to sediments. Juo and Oginni (1978) observed that sorption maximums for paraquat sorbed to a variety of tropical soils ranged from 1200 to 7500 mg/kg of soil. Karickhoff and Brown (1978) reported similar paraquat concentrations for the silt- and clay-size fractions of five natural sediments, with the extent of sorption increasing with the sediment fraction's cation exchange capacity. Distribution coefficients were greater than 1,000 for the clay fraction of one of the sediments. Khan (1974a) noted that paraquat and diquat sorb by ion exchange, and that their magnitudes of sorption are comparable. LaFleur (1979) noted that sorption of trifluralin to several model soils was extensive and rapid, with practically 100 percent of the applied herbicide being sorbed to the soil within 100 minutes of batch mixing. Therefore, the low solubilities of the dinitroaniline herbicides (relative to the other herbicides) and the strongly cationic nature of the bipyridylium herbicides cause them to strongly sorb to natural sediments.

The herbicides are not readily bioaccumulated because of their high solubilities and the ability of biota to metabolize them easily. Muir and others (1980) observed that BCFs for minnows exposed to fluridone in small ponds ranged from less than 1 to 64. BCFs for duckweed in the ponds were also low, ranging from 19 to 85. Hoeppel and Westerdahl (1983) noted only minor accumulations of 2,4-D by fish in a Georgia Lake treated with the dimethylamine (DMA) and butylethanol (BEE) salts of 2,4-D. All fish collected 13 days after application of the herbicide contained nondetectable residues of 2,4-D. However, fish subjected to the 2,4-D BEE treatment initially appeared to accumulate greater amounts of 2,4-D than fish subjected to the treatment with 2,4-D DMA. In a laboratory study documenting the BCFs of a variety of pesticides by caddisfly egg masses, Belluck and Felsot (1981) observed that monuron had the lowest BCF of the group, having a value of approximately unity. Monuron's low BCF was attributed to its high solubility relative to the other pesticides studied. With regard to the herbicides as a group, bioconcentration varies inversely with herbicide solubility, with some of the dinitroaniline herbicides probably exhibiting the greatest ability to bioconcentrate.

The majority of the herbicides are rapidly degraded in surface-water systems, and therefore are not persistent environmental contaminants. Averitt and Gangstad (1976) observed the dissipation of 2,4-D in static water as a function of water depth, temperature, and time. Using a treatment rate of 4.48 kg acid equivalent per hectare, they observed a 58-ppb residue decrease for each 0.61 m increase in water depth, a 115-ppb residue decrease for each 7^{0}C increase in temperature, and a 53-ppb concentration decrease for every 7 day interval after treatment. Delaune and Salinas (1985) found that anaerobic conditions retard the microbial degradation of 2,4-D, and that rapid degradation is most likely to occur in the oxidized surface layer of sediments. Complete degradation of 2,4-D to CO_2 has been reported, with interim soil degradation products of 2,4-dichlorophenol and 2,4-dichloroanisole being detected (Smith, 1985). Jones and others (1982) documented half-lives of atrazine in an aqueous estuarine environment to range from 3 to 12 days, with the major metabolite being hydroxyatrazine. In contrast to 2,4-D degradation, oxygen levels had little affect on atrazine degradation. Humic substances have been shown to inhibit base-catalyzed hydrolytic reactions and accelerate acid-catalyzed hydrolytic reactions (Purdue, 1983). For example, Li and Felbeck (1972) have shown that the hydrolytic half-life of atrazine decreases with decreasing pH and increasing humic acid concentration. Muir and others (1980) reported fluridone half-lives in pond water ranged from 4 to 7 days. Similarly, Bovey and others (1974) observed that the picloram and 2,4,5-T applied to pastureland dissipated rapidly with no evidence of accumulation.

Some herbicides have demonstrated greater persistence than compounds such as atrazine and 2,4-D. Anderson (1985) determined that residues of chlorsulfuron and metsulfuron (two sulfonylurea herbicides applied to winter wheat and barley) were persistent in soils for as long as 500 days. Their ultimate attenuation was attributed to hydrolysis and biodegradation, the rates of which decreased with decreasing temperature. El-Dib and Aly (1976a, 1976c) investigated the hydrolysis and biodegradation of some of the phenylamide herbicides. They found that hydrolysis was only a significant degradation process at pH values above typical environmental levels. Additionally, they were not significantly biodegraded by mixed microbial cultures taken from Nile River water. Biodegradation did occur, however, when Bacillus cereus was added to the aqueous system. Despite these examples, the herbicides are relatively nonpersistent contaminants of surface-water environments, with aquatic half lives usually less than 60 days.

Environmental Distribution

Since the herbicides do not readily partition into sediment organic matter or the lipid reservoirs of aquatic organisms, the highest environmental residues of these compounds are typically found in the aqueous phase of surface-water systems. Bovey and others (1974) observed that picloram and 2,4,5-T residues in runoff from pastureland were primarily in the aqueous phase, with only small amounts sorbed to soil particles. Green and others (1977) noted that diuron residues in Hawaiian estuaries were transported primarily in solution. In a study of an Iowa reservoir, Leung and others (1982) only detected residues of atrazine, alachlor, and cyanazine in the aqueous phase. In samples taken from more than 150 surface-water stations across the U.S. during a three-year period, Gilliom and others (1985) reported that all herbicide detections were in water samples, with no detections reported for bed sediment samples. Table 19 presents some herbicide residues that have been detected in natural surface waters in the U.S.

Herbicides enter surface-water systems in a variety of ways, including the application of aquatic herbicides directly to the body of water to control aquatic vegetation. As a result, residues of aquatic herbicides will be greatest immediately following application. Terrestrial herbicides are carried into surface waters by runoff and base flow, and consequently, surface-water residues are highest if a heavy rain immediately follows the application of the herbicide. During the spraying season of herbicides, residues are commonly caused by misuse of equipment resulting in accidental discharges of the herbicide into surface waters. Frank and others (1982) noted that 82 percent of the pesticides lost to water in 11 agricultural watersheds in Canada during the spraying season could be attributed to careless use of the pesticides near surface waters. On an annual basis, however, spills accounted for only 22 percent of the loss to water, while runoff accounted for 60 percent and base flow resulted in 18 percent of the pesticide loss.

No definitive regional contamination trends of herbicides in U.S. surface waters have been reported in the literature, but regional herbicide-contamination trends can be expected to parallel usage patterns. For example, Gilliom and others (1985) noted that stations in the U.S. Geological Survey-U.S. Environmental Protection Agency Pesticide Monitoring Network where atrazine was detected more than once were all located downriver of large corn-producing areas, where atrazine is heavily applied. The low persistence of the herbicides coupled with relatively high analytical detection limits, however, prevented any other determinations of regional trends.

Aside from the fact that the highest herbicide residues in surface-water systems usually occur during spraying seasons, there are little data in the literature indicating temporal contamination trends in U.S. surface waters. Frequency of detection data for some of the chlorophenoxy and triazine herbicides monitored during the Pesticide Monitoring Network were inconclusive with regard to temporal trends (Gilliom, 1985). This is primarily attributable to the relatively

Table 19. Herbicide residues in North American surface waters.

Compound	Locality	Mean, ppb	Maximum, ppb	Reference
Atrazine	Rhode River, Maryland	0.13	3.3	1
Atrazine	Ontario surface waters	5.5	32	2
Atrazine	Saylorville Reservoir, Iowa	.22	.67	3
2,4-D	New Iberia, Louisiana	359	-	4
2,4-D	Ontario surface waters	5.2	320	2
2,4,5-T	Runoff; Reisel, Texas	26	287	5
Picloram	Runoff; Reisel, Texas	10	19	5
Diuron	Pearl Harbor, Hawaii	.33	1	6
Alachlor	Saylorville Reservoir, Iowa	.08	.41	3
Simazine	Ontario surface waters	.37	3.4	2
Cyanazine	Saylorville Reservoir, Iowa	.09	.32	3

1. Wu and others (1980)
2. Frank and others (1982)
3. Leung and others (1982)
4. Averitt and Gangstad (1976)
5. Bovey and others (1974)
6. Green and others (1977)

short persistence of the herbicides combined with the fact that herbicide data at most stations of the network were only collected during 1976, 1977, and 1978. Atrazine and 2,4-D were the most frequently detected herbicides, which can be explained by the heavy agricultural use of these two compounds. Atrazine also was the most frequently detected herbicide in the water of 11 Canadian agricultural watersheds from 1975-1977 (Frank and others, 1982). Although the available literature does not reveal any clear temporal trends in herbicide detections in the U.S., the escalating use of herbicides over the last 20 years (fig. 16) indicates that the amount of herbicides in the Nation's surface waters is not likely to decrease in the near future.

PHENOLS

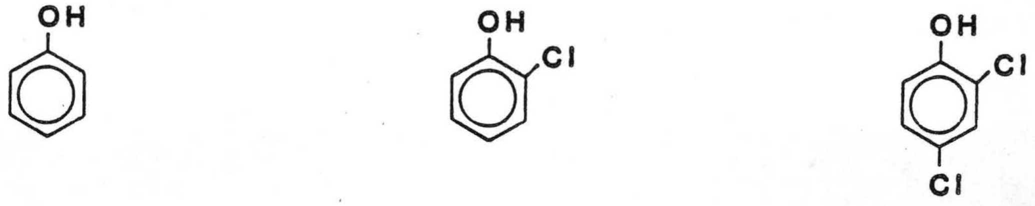
Uses, Production, Properties, and Regulatory Limits

Phenols are a widely used group of compounds characterized by a benzene ring with one or more hydroxyl groups. The dihydroxy phenols can have the second hydroxyl on the ortho, meta, or para position of the benzene ring, and these isomers are commonly referred to by their trivial names, catechol, hydroquinone, and resorcinol, respectively. Although phenols were first produced by the distillation of coal tar in 1834, most current production is on a commercial scale, employing either the cumene (isopropylbenzene) process, the toluene oxidation process, or the benzene sulfonation process (U.S. Environmental Protection Agency, 1980b). The basic phenol molecule can then be ammended with chlorine, nitro, or methyl groups. In addition to manufacturing processes, chlorophenols are produced by the chlorination of treated wastewaters and drinking waters containing phenol. In solutions containing as little as 10 mg/L phenol and 20 mg/L chlorine, 2-chlorophenol has been synthesized in a one-hour period (Callahan and others, 1979). Similar results have been reported for di- and trichlorophenol isomers. Structural diagrams of some of the more common phenolic compounds are presented in figure 18.

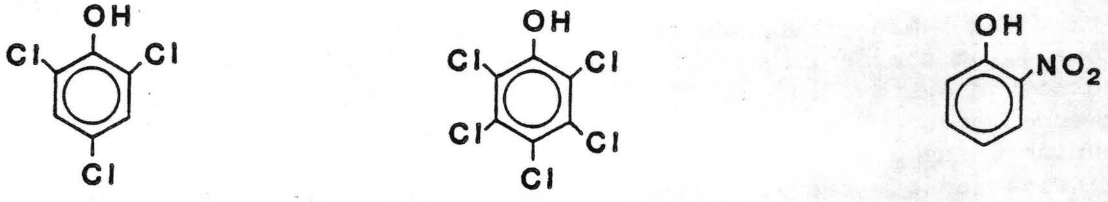
Phenol, C_6H_5OH, is a monohydroxybenzene that exhibits the properties of a weak acid ($pK_a = 10$) due to the delocalization (via resonance) of the negative phenoxide ion throughout the benzene ring (Baum, 1982). It is this acidity that differentiates phenols from the alcohols. Phenol is a colorless, crystalline solid with a characteristic taste and odor. It is primarily an industrial chemical that is used as an intermediate in the production of other compounds such as phenolic resins, germicides, pharmaceuticals, fungicides, dyes, herbicides, plastics (such as Bakelite), explosives (such as picric acid or 2,4,6-trinitrophenol), antiseptic throat lozenges, and skin medications. Production data for phenol are presented in table 20.

Established U.S. Environmental Protection Agency criteria for phenol state that chronic toxicity to freshwater aquatic life will occur at a concentration of 2.56 mg/L, and a limit of 3.5 mg/L is imposed as the maximum level allowable to insure a lack of hazardous effects to humans (U.S. Environmental Protection Agency, 1980b). In addition, in order to prevent undesirable tastes and odors in stream water, phenol concentrations must not exceed 0.3 mg/L.

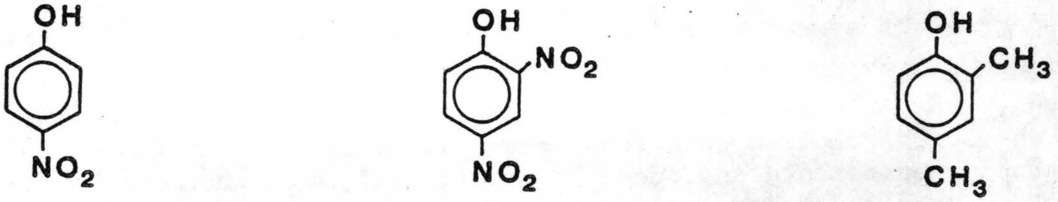
Monochlorophenols are primarily used as intermediates in the production of more highly chlorinated phenols, and their approximate annual production in the U.S. is 18,800 metric tons--significantly less than the 39,000-metric-ton production of 2,4-dichlorophenol (Moore and Ramamoorthy, 1984). This compound is used extensively to manufacture the herbicide 2,4-D. Trichlorophenols are used as antimicrobial agents, as anti-mildew agents for textiles, and in the



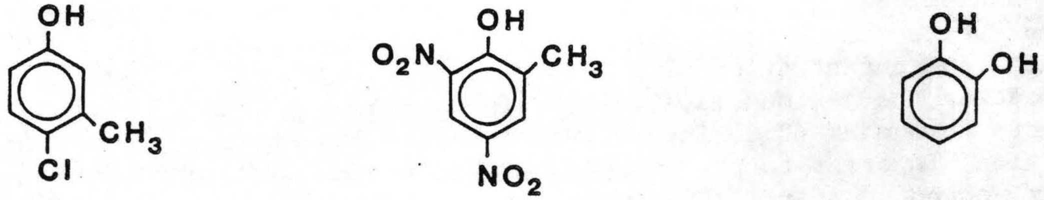
Phenol 2-Chlorophenol 2,4-Dichlorophenol



2,4,6-Trichlorophenol Pentachlorophenol 2-Nitrophenol



4-Nitrophenol 2,4-Dinitrophenol 2,4-Dimethylphenol



P-chloro-m-cresol 4,6-Dinitro-o-cresol Catechol

Figure 18. Structural diagrams of selected phenolic compounds.

Table 20. World production figures for phenol in 1978.
[From Moore and Ramamoorthy, 1984]

Country	Production (10^3 metric tons)	Country	Production (10^3 metric tons)
North America		Western Europe	
Canada	50	Belgium/Luxemborg	140
Mexico	25	France	125
U.S.	1,589	West Germany	420
		Italy	280
South America		United Kingdom	267
Argentina	12		
Brazil	65	Eastern Europe	>360
Far East		Australia	17
Japan	289		
Other	22	World Total	3,711

manufacture of wood and glue preservatives. More specifically, 2,4,5-trichlorophenol is used to manufacture 2,4,5-T, and 2,4,6-trichlorophenol is used to produce tetrachlorophenol. The combined annual production of tri- and tetrachlorophenols in the U.S. is less than 7000 metric tons (Moore and Ramamoorthy, 1984).

Pentachlorophenol (PCP) has probably seen the most extensive use of all the chlorophenols, and it is manufactured primarily by the organic chemical and pesticide industries. PCP was the second most heavily used pesticide in the U.S. in 1977, when approximately 80 million pounds were produced (Guthrie and others, 1984). As a herbicide in Japan, it accounted for 50 percent of all herbicide use in the country until its use was regulated in 1971 (Murthy and others, 1979). It is also used extensively as a wood preservative, as a fungicide/bactericide in cooling tower water, and as an additive in adhesives, construction materials, textiles, leather, paint, paper, and oil-well-drilling mud.

Annual U.S. production of 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol has been estimated to be 6800, less than 500, 19,000, and 500 metric tons, respectively (Moore and Ramamoorthy, 1984). For the most part, the nitrophenols serve as intermediates in the production of pesticides, pharmaceuticals, dyes, explosives, and wood preservatives.

Only sparse production data were found for some of the other phenolic compounds. Moore and Ramamoorthy (1984) noted that annual U.S. production of 4-methyl-2,6-dibutyl phenol is about 16,000 metric tons, and production of nonylphenol was about 69,000 metric tons 1981. The latter compound's uses include nonionic surfactants, phenolic resins and plasticizers, adhesives, lube oil additives, stabilizers, and petroleum demulsifiers (Verschueren, 1983).

Table 21 presents some physicochemical data for the phenols. In general, they have high solubility, with relatively low vapor pressures and octanol-water partition coefficients. Among the chlorinated phenols, however, compound solubility decreases and octanol-water partition coefficient increases with increased chlorination of the aromatic ring. PCP, the most highly chlorinated phenol, has a solubility of only 14 mg/L and an octanol-water partition coefficient of 5.0.

Environmental Fate

Primary fate mechanisms for phenolic compounds include biodegradation and photolysis. Sorption to natural sediments and bioaccumulation is generally minor, with the exception of the highly chlorinated phenols. Volatilization, hydrolysis, and nonphotolytic oxidation are also relatively insignificant fate processes.

Numerous researchers have documented the biological degradation of the phenols. Studies by Baird and others (1974), Hickman and Novak

Table 21. Experimentally determined physicochemical properties of selected phenolic compounds.
[From Callahan and others, 1979]

Compound	Solubility (mg/L)	K_{ow}	Vapor pressure (torrs)	pK_a
Phenol	93,000	1.46	0.53	10.02
2-Chlorophenol	28,500	2.17	2.2	8.52
2,4-Dichlorophenol	4,500	2.75	0.12	7.85
2,4,6-Trichlorophenol	800	3.38	1.0	5.99
Pentachlorophenol	14	5.01	0.00011	4.74
2-Nitrophenol	2,100	1.76	1.0	7.21
4-Nitrophenol	16,000	1.91	2.2	7.15
2,4-Dinitrophenol	5,600	1.53	-	4.09
2,4-Dimethylphenol	17,000	2.50	0.0621	10.60
p-Chloro-m-cresol	3,850	2.95	-	-
4,6-Dinitro-o-cresol	-	2.85	-	4.35

(1984), and Tabak and others (1964) reported significant phenolic biodegradation in activated sludge systems. Other researchers (Chu and Kirsch, 1972; Knackmuss and Helwig, 1978; Banerjee and others, 1984a; Tabak and others, 1981) have noted the biodegradation of phenols by isolated bacterial cultures.

Biodegradation of phenol in surface waters has also been observed. Borighem and Vereecken (1978) used in situ batch studies in both polluted and unpolluted reaches of the River Samber in Belgium to determine the effects of certain parameters on the degradation of phenol. They found that biodegradation rates increased with both increased oxygen transfer to the water and with increased initial phenol concentration. Visser and others (1977) used in situ studies in the St. Lawrence River to also quantify phenol biodegradation. During the summer, they observed that phenol concentrations as high as 125 ppb were reduced to less than 10 ppb within 4 hours. The phenol degradation was accompanied by a concurrent increase in the microbial population in the river water sample. During the coldest part of the winter, however, phenol biodegradation was negligible, probably due to the absence of phenol-degrading bacteria. Table 22 lists the bacteria present in the St. Lawrence River water during the winter and summer months and the maximum phenol levels they tolerated after adaptation. Other microorganisms that have been shown to successfully degrade phenol include Pseudomonas putida, Bacillus stearothermophilus, and yeast such as Oospora, Saccaromycetes, Candida, Debarymyces, and Trichosporon cutaneum (Callahan and others, 1979).

Most of the other phenols have been biodegraded under laboratory conditions. Using mixed microbial cultures obtained from soils and sediments, Tabak and others (1964) measured the biotransformation of 95 percent of a variety of parent phenolic compounds in 1 to 10 days (table 23). Knackmuss and Helwig (1978) reported the biodegradation of a variety mono- and dichlorophenols by a strain of 4-chlorophenol-grown cells. With the exception of 3,5- and 2,4-dichlorophenol, all half-lives were less than 12 days. Stanlake and Finn (1982) isolated a variety of PCP-degrading bacteria from soil, water, and sewage and noted that the length of the lag phase for bacterial growth on PCP decreased when the pH was raised from 6.8 to 7.8. Murthy and others (1979) examined PCP degradation in aerobic and anaerobic soils, and noted that pentachloroanisole was a primary degradation product of PCP, along with 2,3,5,6- and 2,3,4,5-tetrachlorophenols and 2,3,6-trichlorophenol. Their proposed degradation pathway of PCP is presented in figure 19.

The biodegradability of the chlorophenols differs with chlorine substitution. However, increased biodegradability does not always correlate with decreased chlorination of the phenolic molecule. In a study involving a variety of phenolic compounds, Alexander and Aleem (1961) found that chlorine substitution in the meta position of the aromatic ring increases the ring's resistance to biological cleavage. With the exception of these metachlorophenols, the authors observed virtually 100 percent ring cleavage within 47 days of all the chlorophenols in a soil suspension. Under aerobic, room temperature

Table 22. Phenol bacteria present during the winter and/or summer season in the St. Lawrence River water and the maximum phenol levels that could be tolerated.
[mg/L is milligrams per liter; from Visser and others, 1977]

Bacterial species	Winter	Summer	Maximum phenol levels tolerated after adaptation (mg/L)
Achromobacter eurydice		x	2,400
A. cycloclastes or guttatus	x	x	1,200
A. iophagus		x	1,200
Arthrobacter terregens		x	1,200
Azotobacter agilis		x	2,400
Bacillus brevis		x	2,400
B. cereus		x	600
B. circulans		x	600
Brevibacterium maris		x	2,400
B. sulfureum		x	150
Brevibacterium sp.	x	x	600
Clostridium carnis or tertium		x	300
Flavobacterium aquatile	x	x	600
F. breve or peregrinum		x	1,200
F. lutescens		x	600
F. marinum	x	x	300
F. solare		x	150
Flavobacterium (marinum ?)	x	x	600
Flavobacterium sp.		x	1,200
Micrococcus conglomeratus		x	1,200
Micrococcus (?)		x	600
Mycobacterium phlei		x	600
Paracolobactrum coliforme		x	2,400
Pseudomonas fragi	x	x	600
Pseudomonas sp.		x	150
Pseudomonas sp.		x	300
Pseudomonas sp.		x	600
Pseudomonas sp.	x	x	1,200
Pseudomonas sp.		x	2,400
Sarcina flava		x	1,200
S. hansenii		x	2,400

Table 23. Time required for bacteria to utilize 95 percent of parent substrate.
[From Tabak and others, 1964].

Compounds degraded in:*		
1 to 2 days	3 to 6 days	7 to 10 days
Phenol Catechol Resorcinol Quinol Phloroglucinol o-Cresol m-Cresol p-Cresol	o-Nitrophenol m-Nitrophenol p-Nitrophenol 2,4,6-Trinitrophenol (250 ppm) 2-Chloro-4-nitrophenol 2,6-Dichloro-4-nitrophenol m-Chlorophenol (150 ppm) p-Chlorophenol o-Phenylphenol (100 ppm) Thymol (150 ppm)	2,4-Dinitrophenol 2,6-Dimethylphenol (200 ppm) 2,4-Dichlorophenol (200 ppm) 2,4,6-Trichlorophenol

*Initial concentration was 300 parts per million (ppm) unless noted in parentheses.

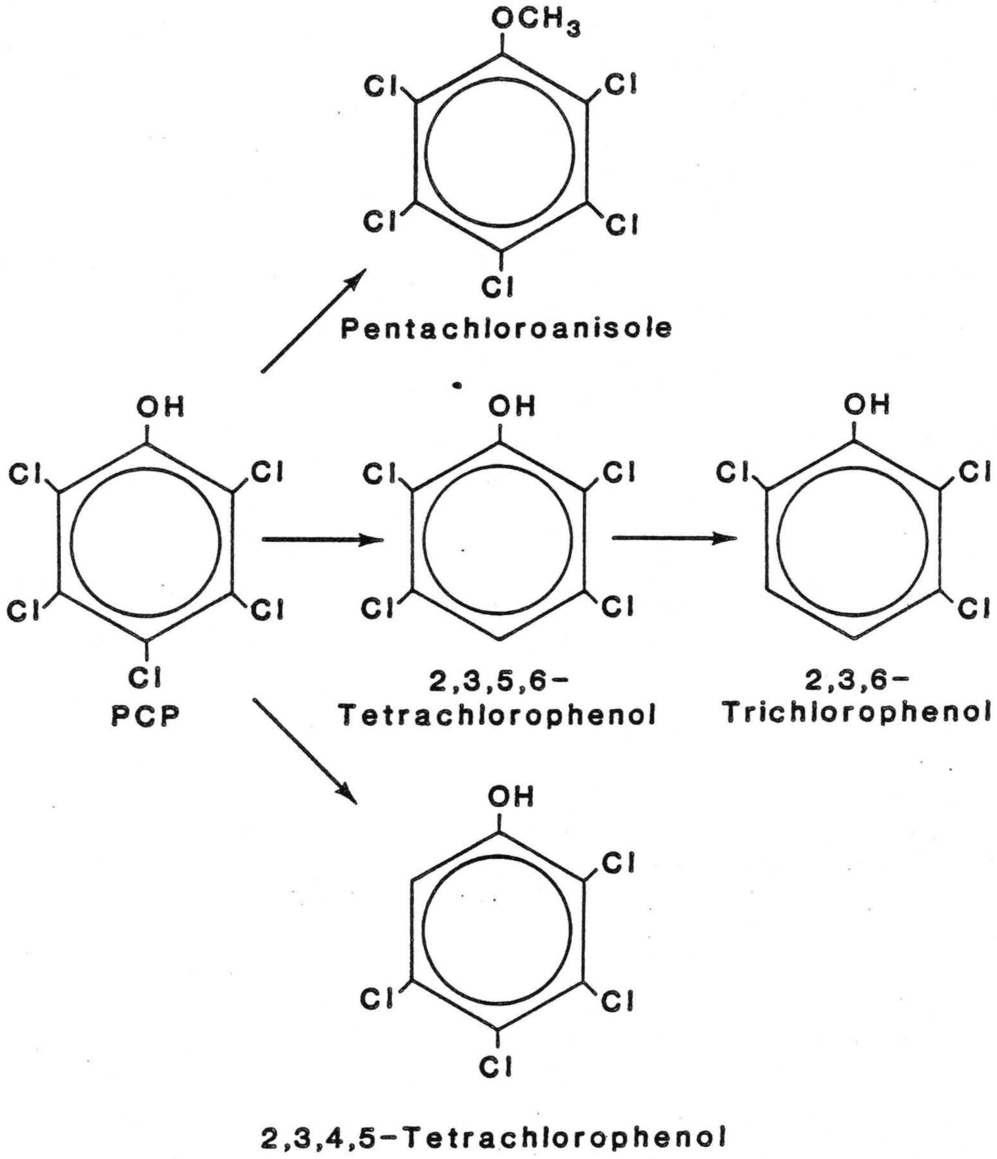


Figure 19. Degradation pathway of PCP in soils. [Reprinted with permission from the Journal of Environmental Science and Health B14, 13 (1979). Copyright 1979 by Marcel Dekker, Inc.]

conditions, Banerjee and others (1984a) observed zero-order biodegradation kinetics for a variety of phenolic compounds in natural water samples. They also stated that degradation rates decreased with increased chlorine substitution. However, biodegradation studies in their second collection of Seneca River water indicated that 2,4-dichlorophenol was more resistant to biodegradation than 2,4,5-trichlorophenol, which in turn was more resistant to degradation than PCP. Data indicating that decreased phenolic biodegradation rates do not strictly correspond to increasing chlorination of the aromatic ring have also been reported by Tabak and others (1964), Alexander and Aleem (1961), and Smith and Novak (1987).

Available data indicate that photolytic oxidation may also be a significant fate mechanism for many phenols. Phenol can be photolytically degraded to a reddish, high molecular weight material. Photolytic end products of phenol degradation include 4,4′-, 2,4′-, and 2,2′-dihydroxybiphenyl, hydroquinone, and catechol (Joschek and Miller, 1966). Callahan and others (1979) have indicated that metal coordinated phenols can have their absorption maximums significantly extended. In the near-ultraviolet spectral region, the absorption maximum of phenol does not extend beyond 290 nanometers. However, when phenol is complexed with metal cations such as Fe(III), the absorption maximum is extended to 600 nm. Similarly, the aqueous Fe(III) complex with 2-chlorophenol has an absorption maximum of about 550 nm, which is significantly greater than the absorption maximum of the chlorophenolate anion (310) or undissociated 2-chlorophenol (290 nm). Table 24 details some of the photolytic degradation products of the phenols.

Based on their relatively high solubilities, low octanol-water partition coefficients, and anionic nature, most of the phenols do not strongly sorb to sediments or bioaccumulate. However, increased chlorination of the phenol molecule decreases compound solubility and increases the octanol-water partition coefficients. Therefore, the more highly chlorinated phenols such as PCP or the tetrachlorophenols can exhibit significant sorption and bioaccumulation in surface-water systems.

Table 25 lists experimentally determined sorption coefficients (K_d, equal to the equilibrium solute concentration in sediment divided by its equilibrium aqueous concentration) for nonionized chlorophenols sorbed to four different natural sediments (Schellenberg and others, 1984). The authors determined that in natural waters of low ionic strength (less than 10^3 M) and of pH not more than one log unit greater than the phenolic compound's pK_a, sorption of the phenolate anion can be neglected. The data indicate that sorption coefficients increase with increasing chlorination of the phenolic compound and with increased sediment organic-matter content. The less-chlorinated phenols are not sorbed significantly to any of the soils. In soils with low organic-matter content, even sorption of PCP will not be substantial. Similarly, Scott and others (1982) observed that phenol did not sorb strongly to soils, with sorption coefficients ranging

Table 24. Photolysis of phenols and their degradation products.
[nm is nanometer; ppm is parts per million; from Callahan and others, 1979]

Compound	Light source	Experimental conditions	Products
Phenol	254 nm	Aqueous, oxygenated solutions	4,4'-, 2,4'-, and 2,2'-dihydroxybiphenyl; hydroquinone; catechol
2-Chlorophenol	313 nm	Aqueous alkali	Catechol
4-Chlorophenol	254 and >290 nm	Aqueous solution with cyanide	4-cyanophenol
2,4-Dichlorophenol	Solar radiation	Aerated aqueous solution	Complete disappearance after 10 days; insoluble, dark, tarry substance produced
2,4,6-Trichlorophenol	-	In presence of electron acceptor	2,6-dichlorophenoxyl semiquinone radical anion
Pentachlorophenol	Sunlight	2% solution of NaPCP	50% degradation after 10 days; products: chloranilic acid, tetrachlororesorcinol, and several complex chlorinated benzoquinones
4-Nitrophenol	Sunlight	Aqueous solution of 200 ppm	Degraded in 1-2 month period to hydroquinone, 4-nitrocatechol, and a dark, acidic polymer

Table 25. Experimentally determined sorption coefficients of nonionized chlorinated phenols for different natural sorbents.
[From Schellenberg and others, 1984]

	Sorption coefficient for sorbent*			
Compound	1	2	3	4
2,3-DCP	21	12	5	<1
2,4-DCP	25	17	6	<1
2,4,6-TCP	78	34	9	<1
2,4,5-TCP	165	74	20	<1
3,4,5-TCP	276	115	31	<1
2,3,4,6-TeCP**	568	200	52	<3
2,3,4,5-TeCP	1237	362	105	7
PCP**	3670	930	200	<13

*1. Lake sediment; organic carbon content (OC) = 9.4%
2. River sediment; OC = 2.6%
3. Aquifer material; OC = 0.84%
4. Aquifer material; OC = 0.03%

**Sorption coefficients for compound calculated from chromatographic data.

from 0.57 to 1.19. For the case of the higher chlorinated phenols such as PCP, sorption will likely be greatest in acidic soils/sediments having high organic-matter contents.

Similar to sediment sorption, phenols are not readily bioaccumulated in surface-water systems, but increased accumulation has been correlated to increased chlorination of the phenol molecule (Biddinger and Gloss, 1984). Little bioaccumulation data were found in the reviewed literature for the majority of the phenols, with the exception of PCP. Callahan and others (1979) cite several studies were PCP was accumulated to concentrations well beyond its aqueous concentration. An eel exposed to a pulp-mill discharge bioaccumulated an aqueous PCP concentration of 3 μg/L to a tissue concentration of 3000 μg/L. Similarly, a 72-hour exposure to 100 μg/L PCP resulted in a 900-fold concentration increase of the compound in goldfish, indicating that PCP can be bioaccumulated in substantial amounts. For the other phenols, bioaccumulation is likely to be an insignificant fate process due to the compounds' generally low octanol-water partition coefficients.

Volatilization, nonphotolytic oxidation, and hydrolysis are not significant fate processes for the phenols. 2-Chlorophenol has the highest vapor pressure of the phenols, but its high solubility prevents any substantial volatilization losses. Phenol can be oxidized in aqueous solution by molecular oxygen, but the higher chlorinated phenols are resistant to oxidation under typical environmental conditions (Moore and Ramamoorthy, 1984). The phenols also are resistant to hydrolysis due to the high negative charge density of the aromatic ring, making the covalent bonds relatively stable to hydrolytic degradation (Moore and Ramamoorthy, 1984).

Environmental Distribution

Phenols may enter surface-water systems directly as components of industrial effluents and indirectly as transformation products of other compounds. For example, pulp-mill effluents commonly contain elevated concentrations of phenolic compounds (Landner and others, 1977), and the chlorination of wastewaters can convert phenol to monochlorophenol, dichlorophenol, or even trichlorophenol (Callahan and others, 1979). Table 26 lists the concentrations of phenol and some of its chlorinated derivatives in municipal and industrial wastewater.

Because of their generally high solubilities, the phenols can be found in relatively high aqueous concentrations in natural surface waters. Sheldon and Hites (1979) detected isomers of bromochlorophenol, dibromophenol, dichlorobromophenol, and dibromochlorophenol in water of the Delaware River near Philadelphia. Yasuhara and others (1981) reported extremely high concentrations of PCP in the waters of the Hayashida River in Japan. Concentrations ranged from 306 to 895 μg/L and were attributed to the unregulated discharge of leather-tannery wastewaters. Visser and others (1977)

Table 26. Concentration of phenol and some of its chlorinated derivatives in municipal and industrial wastewater.
[μg/L is micrograms per liter; from Moore and Ramamoorthy, 1984]

Compound	Concentration (μg/L)	Source
Phenol	0.03-20	Treated sewage, European cities
	200-3,016,000	3 petroleum refineries (USA)
	3200	2 coal gasifacation plants (USA)
	38,000-1,240,000	Coke plant (USA)
	10-300	Specialty chemical plant (USA)
2,4-DCP	220	Chemical plant (Vancouver)
	<0.1	Wood preservation plant (British Columbia)
	<0.1	Landfill leachate (Vancouver)
2,6-DCP	220	Chemical plant (Vancouver)
	2.4	Wood preservation plant (British Columbia)
	1.2-5.6	Landfill leachate (British Columbia)
2,4,5-TCP	<0.05	Treated sewage, 4 plants (Vancouver)
	0.5-2400	2 chemical plants (Vancouver)
	<0.05	Wood preservation plant (British Columbia)
	0.05-2	Landfill leachate (Vancouver)
2,4,6-TCP	<0.05-1	Treated sewage, 4 plants (Vancouver)
	<0.05-3120	3 chemical plants (Vancouver)
	0.5-1	Wood preservation plant (British Columbia)
	0.4-1	Landfill leachate (Vancouver)
	25-115	Pulpmill effluent (Vancouver)
2,3,4,6-TeCP	0.6-28	Treated sewage, 4 plants (Vancouver)
	1.2-8270	4 wood preservation plants (British Columbia)
	0.3-166	3 chemical plants (Vancouver)
	0.2-0.8	Landfill leachate (Vancouver)
PCP	0.5-4.7	Treated sewage, 4 plants (Vancouver)
	0.25-1.3	Treated sewage, 6 cities (Ontario)
	0.05-2760	Wood preservation plants (British Columbia)
	5,400,000	Chemical plant (Philadelphia)
	0.6-42	Landfill leachate (Vancouver)

observed that ambient phenol concentrations in the waters of the St. Lawrence River were approximately 10 to 15 µg/L. Borighem and Vereecken (1978) noted that phenol levels in polluted stretches of the River Samber in Belgium were considerably higher, ranging from 0.2 to 0.7 mg/L. In a study of water and sediment quality in the Netherlands, Wegman and Van den Broek (1983) detected all the isomers of mono-, di-, tri-, tetra-, and pentachlorophenol in water samples taken from the Ijssel River near Kampen. Maximum compound concentrations ranged from 0.02 µg/L (2,3,4,5-tetrachlorophenol) to 3.4 µg/L (3-chlorophenol). Despite these detections, the ability of phenolic compounds to be biologically and photolytically attenuated makes them relativley nonpersistent contaminants. This is confirmed by data from the U.S. Environmental Protection Agency, which reported that of 110 raw-water samples taken throughout the U.S., phenol was detected in only 2 of the samples (U.S. Environmental Protection Agency, 1980b).

Sediment residues of phenols rarely exceed the µg/kg range. However, higher residues have been occasionally reported. For example, Van Luik (1984) reported that phenol concentrations in the sediments of the Calumet-Sag Channel ranged from 1 to 6.9 mg/kg. Pierce and others (1977) documented sediment PCP concentrations in a small stream to range from 1.1 to 1.3 mg/kg as a result of an accidental discharge of the compound. Concentrations typical of a phenol-contaminated surface-water system were reported by Wegman and van den Broek (1983). They determined that 100 percent of the sediment samples collected from Lake Ketelmeer in the Netherlands were contaminated with 2,5-dichlorophenol, 2,3,5- and 2,4,5-trichlorophenol, 2,3,4,5- and 2,3,4,6-tetrachlorophenol, and PCP. The respective median concentrations were 6.3, 2.4, 6.4, 0.9, 1.7, and 8.4 µg/kg. The authors also noted that areas of highest phenol contamination were near industrial areas.

Biological phenolic residues also have been reported. DeVault (1985) found that fish taken from harbors and tributary mouths of the Great Lakes contained PCP concentrations ranging from <0.08 mg/kg to 4.52 mg/kg. In Lake Ontario, Niimi and Cho (1983) found lower PCP concentrations in a variety of sampled fish. Mean residue levels ranged from 0.3 to 24 µg/kg. Rudling (1970) analyzed fish taken from a lake into which PCP was discharged and determined that concentrations in the tissues of pike, perch, and eel were 0.2, 0.15, and 3.0 mg/kg, respectively. The elevated PCP concentrations found in the eel were attributed to its relatively high lipid content. Similarly, Landner and others (1977) analyzed perch and northern pike caught in the vicinity of a pulp mill. Phenolic residues were concentrated in the liver fat of the sampled fish, with mean concentrations of 2,4,6-trichlorophenol, trichloroguaiacol, and tetrachloroguaiacol of 1.2, 5.0, and 4.4 mg/kg fat, respectively. In general, biological residues of phenolic compounds will be dependent on aqueous concentrations, biological lipid content, and the solubility of the phenolic compound.

HALOGENATED ALIPHATIC AND MONOCYCLIC AROMATIC HYDROCARBONS

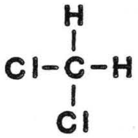
Uses, Production, and Properties

The aliphatic hydrocarbons are straight-chain molecules composed only of hydrogen and carbon. The saturated aliphatic hydrocarbons, commonly referred to as the alkanes or parrafin hydrocarbons, are molecules in which each carbon atom is bonded covalently to four other atoms by single bonds. The general formula for alkanes is C_nH_{2n+2}. Because of double and triple carbon-carbon bonds, unsaturated aliphatic hydrocarbons contain fewer hydrogen atoms per carbon atom than the alkanes. The family of unsaturated aliphatic hydrocarbons containing carbon-carbon double bonds are called the alkenes, or olefins. The family of compounds containing carbon-carbon triple bonds are called the alkynes, or acetylenes. The general formulas for the alkenes and alkynes are C_nH_{2n} and C_nH_{2n-2}, respectively. The industrial halogenation of the aliphatic hydrocarbons results in the production of many toxic chemicals that are widely used as solvent degreasers, refrigerants, fumigants, and in dry-cleaning operations and the pharmaceutical industry.

Benzene, first isolated in 1825 by Michael Faraday, exhibits the common structural feature of the aromatic hydrocarbons. The benzene molecule consists of six carbon atoms bound together in a cyclic structure. Each carbon atom also is bound to one hydrogen atom. X-ray diffraction analysis of benzene indicates that all the carbon-carbon bonds have a length of 1.39 angstroms, intermediate to the length of a carbon-carbon single bond (1.54 angstroms) and a carbon-carbon double bond (1.34 angstroms) (Baum, 1982). The molecule's stability and intermediate carbon-carbon bond length are attributable to a resonating electron structure within the molecule. Benzene and other aromatic compounds having halogens or other functional groups substituted for hydrogen atoms have found wide industrial use. Many of these compounds are highly toxic and, therefore, pose a serious threat to surface-water quality. Figure 20 gives the structural diagrams of some of the more common monocyclic aromatic hydrocarbons (MAHs), together with some of the halogenated aliphatic hydrocarbons.

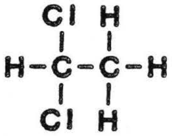
Table 27 presents U.S. production data for the halogenated aliphatic and MAHs. Benzene, toluene, xylene, 1,2-dichloroethane, vinyl chloride, ethyl benzene, carbon tetrachloride, and nitrobenzene are among the compounds that have seen the largest production over the last 20 years. Although production of some of the compounds in table 27 has slowed since 1979, the data indicate that the production of both the halogenated aliphatic and MAHs was significantly greater in 1981-82 than the production of these same compounds from 1965-69. Table 28 documents the numerous uses of the halogenated aliphatic and MAHs.

With the exception of the phenols discussed previously, the halogenated aliphatic and MAHs are characterized by high vapor



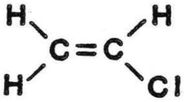
$$\begin{array}{c} H \\ | \\ Cl-C-H \\ | \\ Cl \end{array}$$

Dichloromethane

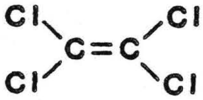


$$\begin{array}{c} Cl\ \ H \\ |\ \ \ \ | \\ H-C-C-H \\ |\ \ \ \ | \\ Cl\ \ H \end{array}$$

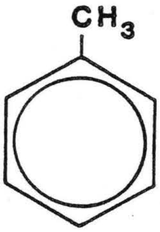
1,1-Dichloroethane



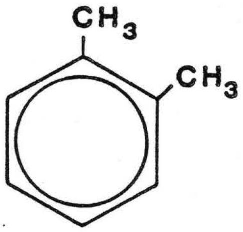
Vinyl chloride



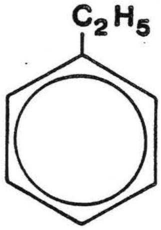
Tetrachloroethylene



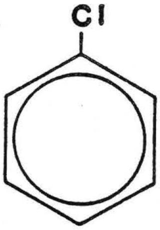
Toluene



o-Xylene



Ethyl benzene



Chlorobenzene

Figure 20. Structural diagrams of selected halogenated aliphatic and monocyclic aromatic hydrocarbons.

Table 27. U.S. production (metric tons X 10^4)* of selected halogenated aliphatic and monocyclic aromatic hydrocarbons. [From Moore and Ramamoorthy, 1984]

Compound	1961-65**	1966-70**	1971-75**	1976	1977	1978	1979	1980	1981	1982
Chloromethane	5.5	14.9	20.8	17.1	21.6	20.6	21.0	16.4	18.4	16.0
Dichloromethane	6.9	14.5	19.0	24.4	21.7	25.9	28.7	25.5	26.8	23.8
Chloroform	3.6	9.1	11.6	13.2	13.7	15.8	16.1	16.0	18.3	13.5
Carbon tetrachloride	21.8	36.5	45.9	38.9	36.7	33.4	32.4	32.1	32.9	nd
Chloroethane	26.6	23.1	28.1	30.4	27.8	24.5	26.4	17.9	14.7	13.1
1,2-dichloroethane	82.1	234.8	379.2	364.6	498.7	498.9	534.9	503.7	452.3	nd
1,1,1-trichloroethane	nd	14.0	21.9	28.6	28.8	29.2	32.5	31.4	27.8	25.0
Chlorodifluoromethane	nd	nd	nd	7.7	8.1	9.3	9.6	10.3	11.4	nd
Trichlorofluoromethane	5.6	10.4	13.6	11.6	9.7	8.8	7.6	10.3	7.4	nd
Dichlorodifluoromethane	9.6	15.1	19.9	17.8	16.2	14.8	13.3	13.4	14.7	nd
Vinyl chloride	63.8	142.1	223.1	257.5	271.5	315.8	289.7	293.2	311.7	nd
Trichloroethylene	13.9	24.5	18.8	14.3	13.5	13.6	14.5	12.1	11.7	8.1
Tetrachloroethylene	14.2	27.0	32.3	16.3	27.8	32.9	35.1	34.7	31.3	nd
Bromoform	0.6	0.9	1.2	nd	1.6	1.6	nd	nd	nd	nd
Ethylene dibromide	nd	13.8	14.0	9.1	11.1	10.4	13.0	8.8	7.6	nd
Benzene	62.6	104.8	125.8	142.5	143.5	148.8	167.2	200.7	133.9	107.0
Toluene	39.1	70.2	87.5	99.9	101.8	105.4	101.0	101.7	85.6	105.2
Xylene	31.9	44.9	53.2	72.2	81.1	84.5	97.2	90.8	88.2	73.0
Monochlorobenzene	25.0	25.0	17.2	14.9	14.8	13.4	14.7	12.8	12.9	nd
1,2-dichlorobenzene	1.9	2.7	2.7	2.2	2.1	1.9	2.6	2.2	2.3	nd
1,4-dichlorobenzene	3.2	2.9	2.9	1.7	3.0	1.9	3.8	3.4	3.3	nd
Alkyl benzenes	28.3	29.4	23.6	nd	23.6	23.8	28.4	40.6	24.2	nd
2,4 + 2,6-dinitrotoluene	nd	12.6	18.6	18.0	nd	29.8	31.2	nd	22.8	nd
Ethyl benzene	106.1	184.7	246.9	261.7	376.9	380.3	383.1	346.5	354.3	299.7
Nitrobenzene	9.7	19.1	20.2	18.6	25.0	26.1	43.2	27.7	40.8	nd

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* For benzene, toluene, and xylene, units are X 10^7 gallons.

**Annual average

nd - no data available

Table 28. Uses of selected halogenated aliphatic and aromatic hydrocarbons.
[From Verschueren, 1983]

Compound	Uses
Chloromethane	Mfg.* of silicones, tetraethyllead, synthetic rubber and methyl cellulose; refrigerant mfg.; mfg. of organic chemicals (methylene chloride, chloroform, etc.); mfg. of fumigants; extractant
Dichloromethane	Paint stripping and solvent degreasing; mfg. of aerosols, photographic film, synthetic fibers; refrigerant; fumigant; solvent; textile and leather coatings; pharmaceutical; spotting agent
Chloroform	Mfg. of fluorocarbon refrigerants and propellants and plastics; mfg. of anesthetics and pharmaceuticals, primary source for chlorodifluoromethane; fumigant; solvent; sweetener
Carbon tetrachloride	Mfg. of fire extinguishers; dry cleaning operations; mfg. of refrigerants, aerosols and propellants; mfg. of chlorofluoromethanes; extractant; solvent; veterinary medicine; metal degreasing; fumigant; chlorinating organic compounds
1,2-dichloroethane	Mfg. of vinyl chloride; mfg. of tetraethyllead; intermediate insecticidal fumigant (peachtree borer, japanese beetle, root-knot nematodes); tobacco flavoring; constituent in paint, varnish and finish removers, metal degreaser, soaps and scouring compounds
Vinyl chloride	Mfg. of polyvinyl chlorides and copolymers; adhesives for plastics
Tetrachloroethylene	Dry cleaning operations; metal degreasing; solvents for fats, greases, waxes, rubber, gums, caffeine from coffee; remove soot from industrial boilers; mfg. of paint removers
Ethylene dibromide	Scavenger for lead in gasoline; grain and fruit fumigant, general solvent, waterproofing preparations, organic synthesis, insecticide
Trichlorofluoromethane	Mfg. of aerosol sprays; mfg. of commercial refrigeration equipment; blowing agent for polyurethane foams; cleaning compounds; solvent; fire extinguisher
Benzene	Mfg. of styrene, phenol, detergents, organic chemicals, pesticides, plastics and resins, synthetic rubber, aviation fuel, pharmaceuticals, dye, explosives, flavors and perfumes, paints and coatings; nylon intermediates; food processing; photographic chemicals
Toluene	Mfg. of benzene derivatives, caprolactam, saccharin, medicines, dyes, perfumes, TNT; solvent recovery plants; component gasoline; solvent for paints and coatings, gums, resins, rubber and vinyl organosols; diluent and thinner in nitrocellulose lacquers
Xylene	Mfg. phthalic acid and anhydride; mfg. of terepthalic acid for polyester; solvent recovery plants; specialty chemical manufacture; mfg. isophthalic acid, aviation gasoline, protective coatings mfg.; solvent for alkyd resins, lacquers, enamels, rubber cements; dye mfg.
Chlorobenzene	Solvent recovery plants; intermediate in dyestuffs mfg.; mfg. aniline, insecticide, phenol, chloronitrobenzene
1,2-dichlorobenzene	Mfg. of 3,4-dichloroaniline; solvent; dye mfg.;fumigant and insecticide; metal polishes; industrial odor control
1,4-dichlorobenzene	Mfg. moth repellants, mfg. air deodorizers, mfg. dyes and intermediates; pharmaceuticals mfg.; soil fumigant; pesticide
1,2,4-trichlorobenzene	Solvent in chemical manufacturing; dyes and intermediates; dielectric fluid; synthetic transformer oils; lubricants; insecticides
2,6-dinitrotoluene	Mfg. of TNT; urethane polymers, flexible and rigid foams and surface coatings, dyes; organic synthesis
Ethyl benzene	Styrene mfg.; acetophenone mfg.; solvent; asphalt constituent; naphtha constituent
Nitrobenzene	Mfg. aniline and dyestuffs; solvent recovery plants; mfg. rubber chemicals, drugs, photographic chemicals; refining lubricants oils; solvent in TNT production; solvent for cellulose ethers; cellulose acetate mfg.
Bromobenzene	Solvent (fats, waxes, or resins); intermediates in specialty organic chmeicals synthesis; additive to motor oil and fuels

* - manufacturing.

pressures, high solubilities, and low octanol-water partition coefficients. Table 29 quantifies these physicochemical parameters.

Environmental Fate

The primary fate of most of the halogenated aliphatic and MAHs in surface-water systems is volatilization followed by photolytic degradation in the atmosphere. Dilling and others (1975) studied the volatilization, sorption, and chemical degradation of five chlorinated aliphatic compounds at aqueous concentrations of 1 ppm. In water at 25^{o}C and stirred at 200 rpm (revolutions per minute), all five compounds (methylene chloride, chloroform, 1,1,1-trichoroethane, trichloroethylene, and tetrachloroethylene) demonstrated 50 percent volatilization in less than 30 minutes and 90 percent volatilization in less than 90 minutes. The addition of other material (clay, limestone, sand, salt, peat moss, and kerosene) to the water had little effect on the rate of volatilization, indicating that sorptive processes were unable to compete with solute evaporation. Furthermore, the authors determined that chemical degradation half lives for the five compounds ranged from 6 to 18 months. Table 30 presents the times for 50 and 90 percent removal of the five compounds from water, along with the evaporation times of 22 other chlorinated aliphatic hydrocarbons as determined by Dilling and others (1975).

Other researchers similarly have noted the importance of volatilization. Helz and Hsu (1978) determined that evaporative losses were the primary cause of the attenuation of halogenated aliphatic hydrocarbons discharged into the Back River estuary in Maryland. Hill and others (1976) found that the rate of bulk exchange of gaseous vinyl chloride between water and air is about twice that of oxygen, and they concluded that volatilization probably is the most important process in its distribution. Within an 8-day period, Jensen and Rosenberg (1975) observed 80 percent removal of trichloroethylene from an open aquarium kept in the light. Concentrations of chloroform, 1,1,1-trichloroethane, and tetrachloroethylene were decreased by 40 to 50 percent over the same period. When the same compounds were incubated in closed systems (both light and dark), compound disappearance typically was less than 5 percent, indicating that solute volatilization was the most important fate process. Similarly, Wakeham and others (1983) stated that volatilization appeared to be the major process responsible for the removal of a variety of aromatic and chlorinated aromatic hydrocarbons from seawater.

Using theoretical considerations, Cadena and others (1984) presented a model to predict the aqueous concentrations of volatile organic contaminants (compounds with Henry's law constants greater than 1.6×10^{-4} atm/m^3mole) in streams as a function of traveltime and stream-reaeration coefficient. The derived relationship is given by

$$C/C_i = \exp\left(-K_2 t(K/K') \right) ,$$

Table 29. Experimentally determined octanol-water partition coefficients (K_{ow}), solubilities, and vapor pressures of selected halogenated aliphatic and monocyclic aromatic hydrocarbons. [mg/L is milligrams per liter; mm is millimeters]

Compound	Log K_{ow}	Solubility (mg/L)	Vapor pressure (mm of Hg)	Refs.
Dichloromethane	-	20,000	349	1
Chloroform	1.97	7,950	160	1,2
Carbon tetrachloride	2.64	800	90	1,2
1,2-Dichloroethane	-	8,450	61	1,3
1,1,1-Trichloroethane	-	1,360	100	1,3
1,1,2,2-Tetrachloroethane	-	3,230	5	1,3
1,2-Dibromoethane	-	3,520	11	1,3
Vinyl chloride	-	2,700	2,660	4,1
1,1,2,2-Tetrachloroethylene	2.60	400	14	1,2
Bromoform	-	3,190	5.6	1
1,2-Dichloropropane	-	3,570	42	1,3
Benzene	2.13	1,780	76	1,2,5
Toluene	2.69	470	22	1,2
o-Xylene	2.77	175	5	1
Chlorobenzene	2.84	448	8.8	1,2
1,2-Dichlorobenzene	3.38	148	1.5	1,3
1,4-Dichlorobenzene	3.38	79	0.6	1,2
1,2,4-Trichlorobenzene	4.02	19	-	1,6
Ethyl benzene	3.15	152	7	1,6
Nitrobenzene	1.85	1,900	0.15	1
Fluorobenzene	2.27	1,540	-	2
Bromobenzene	2.99	446	3.3	1,2
Iodobenzene	3.25	340	-	2

1. Verschueren (1983)
2. Chiou and others (1977)
3. Chiou and others (1979)
4. Dilling (1977)
5. Mackay (1977)
6. Chiou and others (1983b)

Table 30. Evaporation times for 50 and 90 percent removal of chlorinated aliphatic hydrocarbons [1 milligram per liter] at 25°C, 200 revolutions per minute of stirring, and a depth of 6.5 centimeters.
[From Dilling and others, 1975]

	Time (minutes) for evaporation from water	
Compound	50 percent	90 percent
Chloromethane	27	91
Dichloromethane	19	60
Chloroform	20	68
Carbon tetrachloride	29	97
Chloroethane	21	79
1,1-Dichloroethane	22	109
1,2-Dichloroethane	29	96
1,1,1-Trichloroethane	20	65
1,1,2-Trichloroethane	21	102
1,1,1,2-Tetrachloroethane	43	>120
1,1,2,2-Tetrachloroethane	56	>120
Pentachloroethane	48	>140
Hexachloroethane	45	>120
Vinyl chloride	26	96
1,1-Dichloroethylene	22	89
cis-Dichloroethylene	18	64
trans-Dichloroethylene	24	83
Trichloroethylene	21	63
Tetrachloroethylene	25	86
1,1,2,3-Tetrachloropropane	51	>120
1,2,2,3-Tetrachloropropane	47	>120
3-Chloropropene	27	89
2-Chloropropene	29	110
1-Chloropropene	16	59
2,3-Dichloropropene	20	68
1,3-Dichloropropene (cis and trans)	31	98
1,2,3-Trichloropropene	49	>140

where C/C_i is the ratio of the concentration of the contaminant at travel time t to its initial concentration, K_2 is the stream reaeration constant, and K/K' is the ratio of the overall transfer coefficient for the volatile contaminant to the overall transfer coefficient of a tracer compound. The value of K_2 is given by

$$K_2 = 5.015\ v^{0.969}/L^{1.673},$$

where v is the stream velocity (m/s) and L is the mean stream depth. The value of K_2 can be corrected for temperature by multiplying K_2 at 20°C by $(1.0238)^{T-20}$, where T is the stream temperature in degrees Celsius. Ratios of K/K' are presented in table 31 for a variety of halogenated aliphatic and MAHs.

The authors verified their model by a pilot study using benzene and chlorobenzene at a variety of concentrations and reaeration rates. Figure 21 presents the results of their model applied to a hypothetical contamination problem in the Rio Grande River in New Mexico. The concentrations of both methylene chloride and dichlorobenzene are predicted to be below 10 percent of their initial concentration within 60 km from the point of discharge. The authors state that other halogenated aliphatic and MAHs also are likely to volatilize at similar rates, inasmuch as methylene chloride and dichlorobenzene represent the extremes in volatility of the compounds tested in this study.

Once volatilized from solution, many halogenated aliphatic and MAHs are degraded photolytically in the atmosphere. In laboratory experiments simulating atmospheric conditions, photolysis half lives for vinylidene chloride, cis- and trans-dichloroethylene, trichloroethylene, and vinyl chloride ranged from 5 to 12 hours under bright sunlight and in the presence of nitric oxide (Dilling and others, 1976). Half lives for chlorobenzene, tetrachloroethylene, and 1,1,2-trichloroethane were slightly longer, ranging from 20 to 40 hours. Methylene chloride and 1,1,1-trichloroethane, however, were resistant to photolysis, with respective half-lives of >250 and >1700 hours reported. While the aqueous photodecomposition of many of the aliphatic and MAHs will not be considerable because of rapid volatilization, the atmospheric photodecomposition of these compounds may be their ultimate fate (Helz and Hsu, 1978; Hill and others, 1976).

Analysis of available data suggests that some of the halogenated aliphatic and MAHs can be biologically and/or chemically degraded in surface-water systems, but the degradation rates are slow compared to volatilization rates for these compounds. Helz and Hsu (1978) noted that many halogenated aliphatic compounds were rapidly volatilized from a Maryland estuary. However, they also observed nonconservative downstream mixing of the contaminants during the winter when the river was ice covered and substrate evaporation was minimal. They concluded that some biological or chemical degradation also was occurring.

Table 31. Ratios of overall transfer coefficients for selected aliphatic and monocyclic aromatic hydrocarbons (K) to overall transfer coefficients for oxygen (K').
[From Cadena and others, 1984]

Compound	K/K'
1,4-Dichlorobenzene	0.45
1,2-Dichlorobenzene	.46
1,3-Dichlorobenzene	.46
Chlorobenzene	.49
1,1,2-Trichloroethane	.49
Tetrachloroethylene	.50
Carbon tetrachloride	.51
Benzene	.53
Trichlorofluoromethane	.54
Chloroform	.55
1,1-Dichloroethane	.55
1,2-Dichloropropane	.57
1,2-Dichloroethane	.58
Dichlorodifluoromethane	.58
Acrylonitrile	.59
Chloroethane	.61
Dichloromethane	.62
Vinyl chloride	.66
Methylene chloride	.73

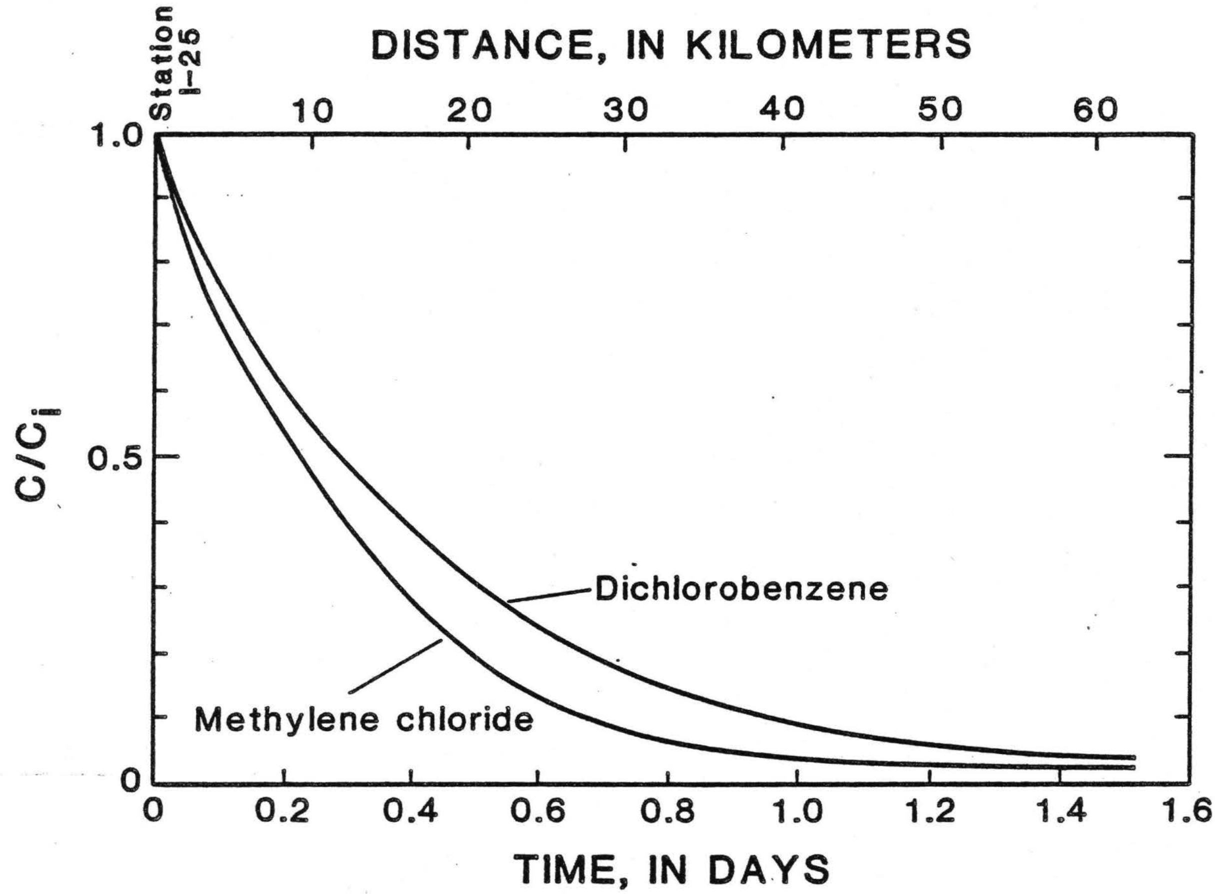


Figure 21. Predicted volatilization rates of methylene chloride and dichlorobenzene in the Rio Grande River. [Reprinted with permission from Journal of the Water Pollution Control Federation 56, 460 (1984).]

Wakeham and others (1983) also reported that volatilization was the primary fate process for aromatic hydrocarbons in seawater, but noted that summer biodegradation of these compounds can also be an important process. In closed systems incubated in the dark, Jensen and Rosenberg (1975) observed slow degradation of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethylene. Other compounds, such as vinyl chloride, have high resistance to biological or chemical degradation in natural surface waters (Hill and others, 1976).

Because of their high solubilities and low octanol-water partition coefficients, the majority of the halogenated aliphatic and MAHs will not strongly partition into sediment organic matter or biological lipid reservoirs. However, some of the chlorinated benzenes have been observed to bioaccumulate. Konemann and van Leeuwen (1980) found that the increasing octanol-water partition coefficients of the chlorobenzenes correlated with increased BCFs. Guppies exposed to aqueous chlorobenzene concentrations exhibited lipid-normalized BCFs ranging from 1,800 (1,4-dichlorobenzene) to 72,000 (1,2,3,5-tetrachlorobenzene). Oliver and Niimi (1983) observed a similar bioconcentration trend for the chlorobenzenes accumulated by rainbow trout, with BCFs as high as 4,100 reported for 1,3,5-trichlorobenzene. Lower BCFs were reported for the less-chlorinated benzenes. Sediments rich in organic matter also can accumulate appreciable amounts of tri- and tetrachlorobenzenes. Chiou and others (1983b) reported organic-matter-normalized sorption coefficients of 500 and 190 for 1,2,4-trichlorobenzene and 1,4-dichlorobenzene partitioned between water and a Woodburn silt loam soil with 1.9 percent organic-matter content. In contrast, the distribution coefficient for chlorobenzene was only 50.

Based on their tendency to rapidly volatilize from solution, the aliphatic and MAHs are not persistent environmental contaminants in surface-water systems. Secondary fate processes include biological and chemical degradation, but these rates are slow relative to evaporative loss rates. With the possible exception of some of the highly chlorinated benzenes, sorption and bioaccumulation are not important fate mechanisms.

Environmental Distribution

Aliphatic and MAHs are natural components of oil deposits, and commonly find their way into surface waters as a result of discharges from refineries, waste oil disposal, and accidental spills. Municipal wastewater discharges also have been recognized as sources of aliphatic and MAH discharges (Barrick, 1982). Chlorinated aliphatic hydrocarbons are commonly found in chlorinated water and wastewater effluents and in industrial discharges. Chlorinated benzenes may enter the environment as a result of their use as solvents, heat transfer fluids, flame retardants or chemical intermediates, or as waste products of the electro-industry (Jan and Malnersic, 1980).

Point discharges have contributed large amounts of aliphatic and MAHs to surface waters. Barrick (1982) determined that primary sewage effluent from Seattle discharges an average of 475 megagrams per year of aliphatic hydrocarbons into central Puget Sound. Eganhouse and Kaplan (1982) similarly noted that southern California treatment plants discharge hydrocarbons into coastal waters at an annual rate of 17,400 megagrams. Brooks and others (1981) documented concentrations of aliphatic hydrocarbons with 5 to 14 carbon atoms to be as high as 400 μg/L as the result of an oil well blowout in the Gulf of Mexico. Middleditch and Basile (1980) have reported that oil platforms in the northwest portion of the Gulf routinely discharge 200 grams per day of alkanes. Halogenated aliphatic and MAHs such as methylene chloride (3 to 8 ppm), toluene (13 to 20 ppm), and chlorobenzenes (0.50 ppm) have been detected in the effluents of chemical-manufacturing plants (Jungclaus and others, 1978; Sheldon and Hites, 1979). Because of the volatility of the halogenated aliphatic and MAHs, however, these effluent concentrations are usually rapidly reduced to much lower levels.

Because of the large quantities of halogenated aliphatic and MAHs that are produced annually in the U.S., these compounds are ubiquitous contaminants in surface waters. Their aqueous concentrations, however, are usually in the part-per-billion range as a result of their tendency to volatilize into the atmosphere. Higher concentrations usually are limited to specific discharge points. While Brooks and others (1981) reported volatile hydrocarbon residues as high as 400 μg/L in the vicinity of an oil well blowout, residues 6 and 12 miles down plume were reduced to 63 and 4 μg/L respectively. Oliver and Nicol (1982) reported low concentrations of chlorobenzenes in the Great Lakes, with the highest mean concentration being observed for 1,4-dichlorobenzene (45 ng/L) in Lake Ontario. Part-per-trillion residues have also been reported by Schwarzenbach and others (1979) in Lake Zurich, Switzerland. Concentrations of 1,4-dichlorobenzene and tetrachloroethylene in the lake's upper basin were 10 and 40 ng/L, respectively.

With the possible exception of some of the chlorobenzenes, biological residues of the aliphatic and MAHs are generally in the part per billion range. Ferrario and others (1985) detected a variety of chlorinated aliphatic and MAHs in clams and oysters from Lake Pontchartrain, Louisiana. Detectable concentrations ranged from 0.04 ppb for chlorobenzene to 310 ppb for 1,1,1-trichloroethane. Jan and Malnersic (1980) reported total chlorobenzene residues in fish taken from Yugoslavian surface waters to range from 1.8 ppm (expressed on a fat basis) near industrial areas to 0.2 ppm near agricultural and wooded areas. Oliver and Nicol (1982) also quantified the concentrations of a variety of chlorobenzenes in trout taken from the Great Lakes. Again, residues were in the parts-per-billion range, varying from 0.05 ppb (1,2,3,5-tetrachlorobenzene) to 12 ppb (1,2,3,4-tetrachloro-benzene).

Similar to biological residues, sediment residues of halogenated aliphatic and MAHs are typically in the parts-per-billion range. Chlorobenzene residues in the surficial sediments of Lake Ontario have been reported to range from 1 to 320 ppb (Oliver and Nicol, 1982). Lower concentrations were reported for Lakes Superior, Huron, and

Erie. Chlorobenzenes sorbed to suspended sediments in the Niagara River also had concentrations in the parts-per-billion range, with the highest concentration being reported for 1,4-dichlorobenzene (160 ppb) (Oliver and Charlton, 1984). Benzene (21 ppb) and chloroform (18 ppb) had the highest concentrations of a variety of chlorinated aliphatic and MAHs detected in the sediments of Lake Pontchartrain, Louisiana, (Ferrario and others, 1985). In a study of the effects of an industrial discharge on a stream, Jungclaus and others (1978) found that effluent toluene and methylene chloride concentrations of 13 to 20 and 3 to 8 ppm, respectively, caused no detectable residues of either compound in the stream sediment.

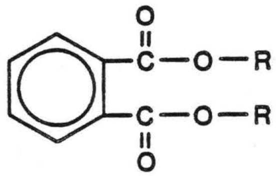
Little data were found in the reviewed literature with regard to spatial or temporal contamination trends in the U.S.; however, based on production and use data, some general conclusions can be drawn. The production of halogenated aliphatic and MAHs increased significantly until the late 1970's, when production of many of the compounds either slowed or declined (table 27). Therefore, temporal trends in surface-water contamination are likely to mirror production. Sediment-core data from the Great Lakes confirm this hypothesis. Oliver and Nicol (1982) reported that chlorobenzene residues in Great Lakes sediments increased rapidly from about 1940 (6- to 7-cm sediment core depth) to the early 1970's (1- to 2-cm sediment core depth). Surficial sediment residues (0- to 1-cm sediment core depth) however, were generally lower than residues at a 1- to 2-cm depth, parallelling the decreased production of chlorobenzenes in the late 1970's. Despite this decline, surficial sediment residues were still higher than sediment residues at the 2- to 3-cm depth (1965-1971).

Halogenated aliphatic and MAHs are found principally in industrial and municipal wastewater effluents, and, as a result, significant environmental residues of these contaminants are most commonly found near industrial areas (Jan and Malnersic, 1980). Surface waters draining agricultural or forested areas are less likely to have significant residues of halogenated aliphatic and MAHs than densely populated and industrialized areas. Nonhalogenated aliphatic and MAHs also are commonly found in coastal waters near oil-drilling and production areas because of their presence in natural oil.

PHTHALATE ESTERS

Uses, Production, and Properties

The phthalate esters are derivatives of phthalic acid (the ortho isomer of benzene dicarboxylic acid) and are characterized by the following structure:

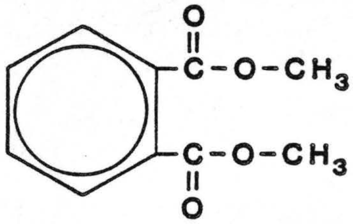


where R is either an alkyl or aryl group. Structural diagrams of some of the phthalate esters are presented in figure 22.

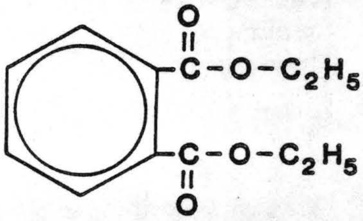
The phthalate esters are manufactured by the oxidation of either naphthalene or o-xylene to produce phthalic anhydride, which is subsequently combined with the desired alcohol (Peakall, 1975). Phthalate esters are used extensively as plasticizers to produce useful products from polymers of vinyl chloride, propylene, ethylene, and styrene. Commonly, their contribution to the weight of the plastic is second only to the weight of the polymer itself (Mathur, 1974). Uses of plastics include home construction, appliances, furnishings, automobiles, apparels, and food containers and wrappings. Table 32 documents the relative use of phthalate esters for these various products in the U.S., along with the small proportion of nonplasticizer use. The amount of solid waste generated from these uses has been estimated to be in excess of 12 billion kilograms annually in the U.S. (Mathur, 1974).

The manufacture of phthalate esters in the U.S. has increased rapidly over the last 25 years. Production from 1961 to 1970 increased at an average annual rate of 10 percent (Peakall, 1975). The total annual production of phthalate esters in the U.S. reached nearly 5 X 10^8 kg in 1978, and has continued to increase (Giam and others, 1978). World production has been estimated to be 3 to 4 times the U.S. production, and some of the leading foreign manufacturers of phthalate esters include Japan, the U.S.S.R., and Germany (Peakall, 1975). Of the various esters of phthalic acid, bis(2-ethylhexyl) phthalate is one of the most widely used, with 158.8 million kg produced in the U.S. in 1970 (Mathur, 1974). As a result of their large-scale production, phthalates are frequently identified as contaminants in the water, sediment, and biota of surface-water systems.

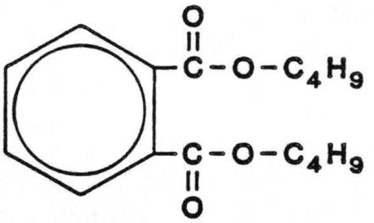
The phthalate esters are relatively stable, colorless liquids of medium viscosity and low volatility. Table 33 presents some of the physicochemical properties of the phthalate esters.



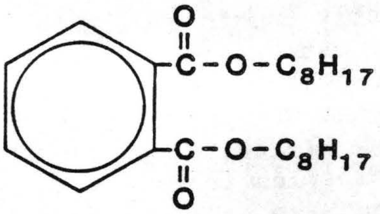
o-Dimethyl phthalate



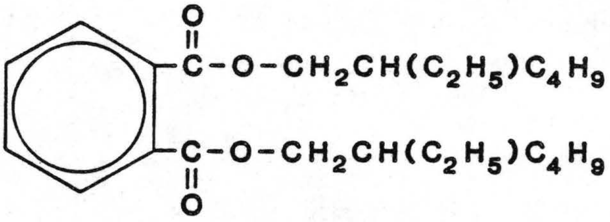
Diethyl phthalate



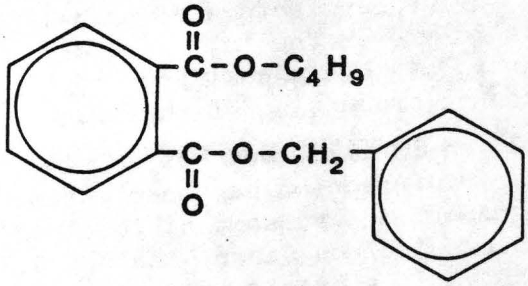
Di-n-butyl phthalate



Di-n-octyl phthalate



Bis(2-ethylhexyl) phthalate



Butyl benzyl phthalate

Figure 22. Structural diagrams of some common phthalate esters.

Table 32. Uses of phthalate esters in the U.S.
[From Peakall, 1975]

	Percentage of total use[1]
A. As plasticizers	
Building and construction	
Wire and cable	21
Flooring	17
Swimming pool liners	2
Miscellaneous	4
Home furnishings	
Furniture upholstery	10
Wall coverings	4
Houseware	3
Miscellaneous	6
Cars (upholstery, tops, etc.)	13
Wearing apparel	8
Food wrapping and closures	3
Medical tubing and intravenous bags	3
Total as plasticizers	94
B. As nonplasticizers	
Pesticide carriers	-
Oils	-
Insect repellent	-
Total as nonplasticizers	6

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[1] A dash indicates that exact data are not available.

Table 33. Solubilities and vapor pressures of selected phthalate esters.
[mg/L is milligrams per liter; mm is millimeters]

Compound	Solubility (mg/L)	Vapor pressure (mm of Hg)	Reference
Dimethyl phthalate	5000 (20°C)	0.01 (20°C)	1
Diethyl phthalate	896 (25°C)	.05 (70°C)	1
Di-n-butyl phthalate	13 (20°C)	.10 (115°C)	1
Di-n-octyl phthalate	3 (25°C)	.20 (150°C)	1
Bis(2-ethylhexyl) phthalate	0.4 (25°C)	2 X 10^{-7} (20°C)	1
Butyl benzyl phthalate	2.9	8.6 X 10^{-6} (20°C)	1,2

1. Callahan and others (1979)
2. Verschueren (1983)

Environmental Fate

The reviewed literature contained only sparse information on the environmental fate of the phthalate esters, and most studies were limited to bis(2-ethylhexyl) phthalate. Based on the available data, however, biodegradation, sorption, and bioaccumulation appear to be important fate-determining processes.

Phthalate esters have been metabolized both by isolated and mixed bacterial cultures, undergoing primary and ultimate biodegradation by enzyme-catalyzed hydrolysis. Of the group, bis(2-ethylhexyl) and di-n-octyl phthalate have been determined to be the most resistant to biodegradation, but data indicate that even these two compounds can be at least partially degraded (Tabak and others, 1981). Mathur and Rouatt (1975) isolated a bacterium, Serratia marcescens Bizio, capable of utilizing both bis(2-ethylhexyl) phthalate and di-n-octyl phthalate as sole sources of carbon and energy. The primary degradation product of these phthalates appeared to be o-phthalic acid. Fairbanks and others (1985) observed the degradation of bis(2-ethylhexyl) phthalate to CO_2 in sludge-amended soils. Half lives ranged from 8 to 72 days, and, after 146 days, 76 to 93 percent of the phthalate ester was degraded to CO_2. A strain of Enterobacter aerogenes, isolated from the inside of plastic tubing used as an outlet for deionized water, degraded dimethyl phthalate as a sole carbon source (Perez and others, 1977). The culture degraded a dimethyl phthalate concentration of 1000 ppm to less than 400 ppm in 41 days. Engelhardt and Wallnofer (1975) determined that a variety of microorganisms were capable of degrading di-n-butyl, di-n-octyl, bis(2-ethylhexyl), and dimethyl phthalates, and suggested that mixed microbial populations can readily metabolize phthalate esters. Their proposed pathway for the degradation of di-n-butyl phthalate by different soil microorganisms is presented in figure 23.

As a result of their low solubilities, some of the phthalate esters strongly partition into the lipid reservoirs of aquatic organisms and sediment organic matter. Table 34 documents BCFs for bis(2-ethylhexyl), di-n-octyl, and di-n-butyl phthalates for a variety of aquatic organisms (Callahan and others, 1979; Sanborn and others, 1975). The data indicate that all three compounds exhibit significant bioaccumulation. The BCFs range from 130 to 100,000, with variations reflecting differences in organism lipid content, compound solubility, and duration of exposure. Little sorption data are available for the phthalate esters. However, Matsuda and Schnitzer (1971) presented data indicating that a variety of dialkyl phthalates can partition into dissolved fulvic acid, significantly enhancing their apparent solubilities. Using batch sorption studies with solution/soil ratios ranging from 5 to 300, Fairbanks and others (1985) noted that as much as 87 percent of the bis(2-ethylhexyl) phthalate added to centrifuge tubes was sorbed to the glass. Of the amount remaining, 96 to 99 percent was sorbed to the soil, suggesting that significant sorption to sediments may occur in natural systems. Because phthalate esters have been frequently detected in surface-water sediments and biota, it

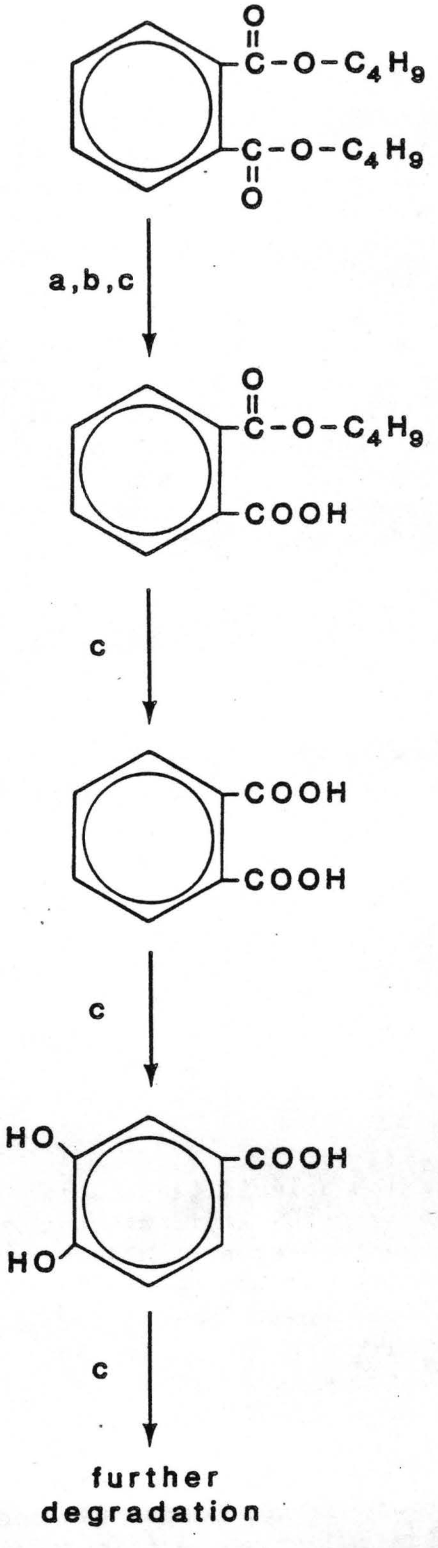


Figure 23. Structural diagram of degradation of di-n-butyl phthalate (DBP), mono-n-butyl phthalate, and phthalic acid by different microorganisms: (a) organisms isolated with DBP as carbon source for enrichment, (b) stock cultures, (c) bacteria isolated from phthalic acid enrichment medium. [Reprinted with permission from Bulletin of Environmental Contamination and Toxicology **13**, 344 (1975). Copyright 1975 by Springer-Verlag New York Inc.]

Table 34. Selected bioconcentration factors (BCFs) of phthalate esters in aquatic systems.
[From Callahan and others (1979) and Sanborn and others (1975)]

Phthalate ester	Aquatic organism	Exposure time (days)	BCF
Bis(2-ethylhexyl)	Fish	-	130
Bis(2-ethylhexyl)	Sowbug	14	230
Bis(2-ethylhexyl)	Fathead minnow	28	800
Bis(2-ethylhexyl)	Scud	14	13,400
Bis(2-ethylhexyl)	Snail	-	21,000
Bis(2-ethylhexyl)	Mosquito larvae	-	100,000
Di-n-octyl	Daphnia	33	2,600
Di-n-octyl	Fish	33	9,400
Di-n-octyl	Algae	33	28,500
Di-n-butyl	Waterflea	14	5,000
Di-n-butyl	Scud	14	6,700

is likely that both bioaccumulation and sorption will influence their environmental fate.

Nonbiological hydrolysis, volatilization, and photolysis do not appear to be significant fate-determining processes for the phthalate esters. Estimated hydrolytic half lives range from 3.2 years for dimethyl phthalate to 2000 years for bis(2-ethylhexyl) phthalate (Callahan and others, 1979). Evaporative losses of phthalate esters from surface waters also are minor because of their relatively low vapor pressures. Fairbanks and others (1985), for example, detected no volatilization of bis(2-ethylhexyl) phthalate applied to three sludge-amended soils. Finally, although no data were found on the photodecomposition of phthalate esters in aquatic systems, it is unlikely that they are degraded photolytically since they do not posses significant absorption maxima in the ultraviolet and visible regions of the electromagnetic spectrum (Callahan and others, 1979).

Environmental Distribution

Reported environmental levels of anthropogenically produced phthalate esters may be inaccurate because of the possible natural origins of these compounds and sample contamination by plastic sample containers. There is strong evidence to suggest that phthalate esters have natural as well as anthropogenic origins. Ortho-phthalic acid has been detected in wood, in the oxidation products of lignin, and as the product of the chemical and biological oxidation of compounds, such as naphthalene and its derivatives (Mathur, 1974). Phthalides also appear to be common constituents of plants, with phthalates serving as intermediates in biochemical pathways. Mathur (1974) has stated that, because phthalates and aliphatic alcohols are present in plants, it is reasonable to assume that phthalate esters are synthesized naturally in the environment. Additionally, phthalate esters in plastic sample containers can easily contaminate natural water, sediment, or biological samples. For example, phthalate esters have been found in extracts of the lining of plastic bags and in uncontaminated sand shaken in the bag (Mathur, 1974). As a result, reported environmental residues of phthalate esters may not simply reflect the anthropogenic origins of this group of compounds.

Peakall (1975) has ranked the uses of phthalate esters according to likelihood of escape into the environment. Nonplasticizer uses, such as pesticide carriers, insect repellent, cosmetics, fragrances, and oils, have the highest likelihood of escape, because the phthalate ester is not encased in a polymer matrix. Phthalate ester plasticizers used directly in contact with water pose the second-greatest risk of escaping to the environment, and include swimming-pool liners, garden hoses, and medical uses. Other plasticizer uses that only involve contact with air are the least likely to result in phthalate-ester loss to the environment. Additionally, phthalate esters have been reported in industrial discharges. Sheldon and Hites (1979) reported concentrations of dibutyl, butyl benzyl, and bis(2-ethylhexyl) phthalate in an industrial effluent of 50, 40, and 200 ppb, respectively.

Phthalate esters have been detected in numerous coastal and inland-water samples. Giam and others (1978) reported concentrations of di-n-butyl phthalate as high as 0.471 ppb and concentrations of bis(2-ethylhexyl) phthalate as high as 0.316 ppb in water samples collected from the Gulf of Mexico. Both these compounds also have been detected in the Tama River near Tokyo, Japan, with concentrations ranging from 0.4 to 6.8 ppb (Morita and others, 1974). Jungclaus and others (1978) reported even higher concentrations in a small, freshwater river. Concentrations of bis(2-ethyl hexyl) phthalate ranged from 1 to 50 ppb, and concentrations of di-n-octyl phthalate ranged from 1 to 20 ppb. Sheldon and Hites (1979) also reported the presence of aqueous phthalate esters, with concentrations in the Delaware River near Philadelphia as high as 0.6 ppb for butyl benzyl phthalate and 1.0 ppb for bis(2-ethylhexyl) phthalate. Similarly, maximum bis(2-ethyl hexyl) phthalate concentrations of 1.98 and 3.10 ppb were reported by Thuren (1986) in water samples taken from the Rivers Svartan and Ronnebyan, respectively, in southern Sweden.

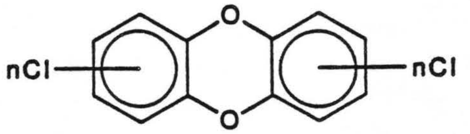
Sediment residues of phthalate esters also have been reported frequently, with detected concentrations usually ranging from a few parts-per-billion to a fraction of a part per million. In a study of the Chester River in Maryland, Peterson and Freeman (1984) reported maximum sediment residues of diethyl, diallyl, diisobutyl, dibutyl, dihexyl, bis(2-ethylhexyl), and di-n-octyl phthalate of 44, 5.5, 27.6, 900, 6.4, 4800, and 62 ppb, respectively. The maximum concentrations of dibutyl phthalate (69 ppb) and bis(2-ethylhexyl) phthalate (248 ppb) found in sediment samples collected from the Gulf coast and Mississippi delta were slightly lower (Giam and others, 1978). Much higher sediment concentrations were reported by Jungclaus and others (1978) and Van Luik (1984). The former study detected both bis(2-ethylhexyl) and di-n-octyl phthalate at concentrations ranging from 250 to 56,000 ppb in sediment samples collected downstream from a chemical manufacturing plant's discharge. The study by Van Luik (1984), which analyzed sediments from the Calumet-Sag channel, determined that the average sediment concentration of bis(2-ethylhexyl) phthalate was 29,800 ppb, with a high value of 63,770 ppb.

Laboratory studies have indicated that phthalate esters can bioaccumulate, and these results have been confirmed in field studies identifying significant residues of phthalate esters in aquatic organisms. Despite aqueous bis(2-ethylhexyl) phthalate concentrations of 0.316 ppb or less, biota from the Gulf of Mexico contained concentrations ranging from 1 to 135 ppb (Giam and others, 1978). DeVault (1985) detected high concentrations of both bis(2-ethylhexyl) and di-n-butyl phthalate in two fish samples taken from the Menominee and Kinnickinnic Rivers in Wisconsin. Unfortunately, no aqueous concentrations were reported. The ubiquity of phthalate esters is evidenced by the data of Stalling and others (1973), who detected residues of bis(2-ethylhexyl) phthalate in fish collected throughout the U.S. Concentrations ranged from 0.2 to 10 ppm and appeared highest near industrialized areas.

POLYCHLORINATED DIBENZO-P-DIOXINS

Uses, Production, and Properties

The polychlorinated dibenzo-p-dioxins (PCDDs) are characterized by the following structure:



Chlorination of the molecule can produce a total of 75 chlorinated species, ranging from monochlorodibenzo-p-dioxin to octachlorodibenzo-p-dioxin.

Although not deliberately manufactured and having no commercial use, PCDDs are produced inadvertently during the manufacture of 2,4,5-trichlorophenol from 1,2,4,5-tetrachlorobenzene (fig. 24). Because 2,4,5-trichlorophenol is used in the production of a variety of pesticides along with tetra- and pentachlorophenol, PCDDs have been found as contaminants in many of these compounds. Table 35 documents the detected residues of tetra-, hexa-, hepta-, and octachlorodibenzo-p-dioxin in several pesticides that were manufactured between 1950 and 1970. Although the extent of contamination is likely to vary with manufacturer, one company produced 2,4,5-T from 1966 to 1968 that typically contained 10 ppm of TCDD. Of 42 samples of 2,4,5-T tested, 23 contained detectable residues of PCDDs. One analyzed sample of pentachlorophenol contained nearly 1,000 ppm of both hepta- and octachlorodibenzo-p-dioxin (Helling and others, 1973). More recent commercial production of compounds such as 2,4,5-T has resulted in much lower residues, with TCDD concentrations usually less than 0.1 ppm (Isensee and Jones, 1975).

PCDDs are extremely toxic compounds. They were first identified as environmental contaminants in 1970 as a result of a report by the Office of Science and Technology noting that mice given a relatively large dose of the herbicide 2,4,5-T during early pregnancy produced an abnormally high number of deformed offspring (Helling and others, 1973). Analysis of the 2,4,5-T given to the mice revealed that it contained approximately 27 ppm of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Subsequent studies have shown that PCDDs have very high mammalian toxicities. Table 36 reports the single oral doses of some PCDDs required to kill 50 percent of the exposed animals (LD_{50}). TCDD appears to be the most toxic of the PCDDs, with an LD_{50} of just 2 μg/kg for guinea pigs. TCDD LD_{50} values of 10 μg/kg for rabbits and 0.6 μg/kg for guinea pigs have also been documented (Isensee and Jones, 1975).

Some of the less severe effects of PCDD exposure to humans include changes in skin color, skin rashes, excessive hair growth,

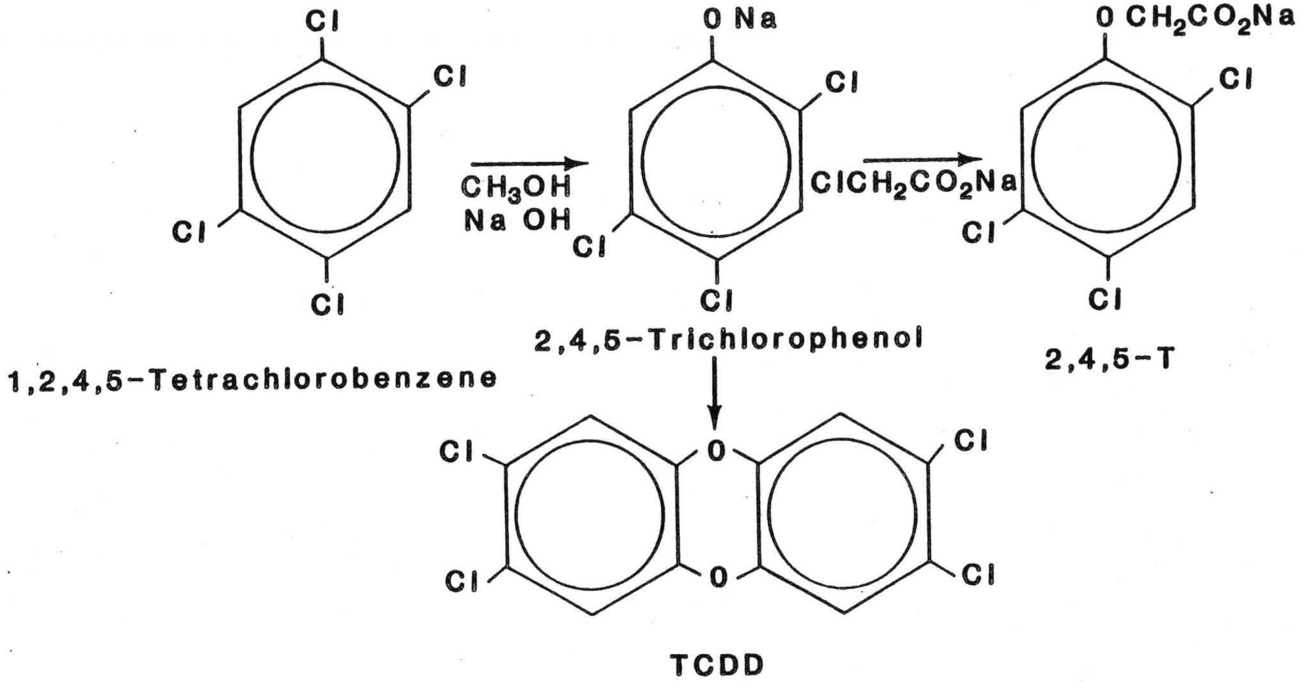


Figure 24. Formation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as a by-product in the synthesis of 2,4,5-T. [Reprinted with permission from Journal of Environmental Quality 7, 172 (1973). Copyright 1973 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America.]

Table 35. Chlorinated dibenzo-p-dioxin found in commercial pesticides. [From Helling and others, 1973]

	Chlorodibenzo-p-dioxin detected				Samples	
Pesticide	Tetra-	Hexa-	Hepta-	Octa-	Contaminated	Tested
2,4,5-T	**	**	-	-	23	42
Silvex	*	-	-	-	1	7
2,4-D	-	*	-	-	1	24
2,4-DB	-	-	-	-	0	3
2,4-DEP	-	-	-	-	0	2
Dichlorprop	-	-	-	-	0	1
Erbon	-	-	-	**	1	1
Sesone	-	*	-	-	1	1
Dicamba	-	-	-	-	0	8
Chlorophenols						
Tri-	-	*	*	*	4	6
Tetra-	-	**	**	**	3	3
Penta-	-	**	**	**	10	11
Others^	-	**	**	*	5	22

* Concentration of at least one sample was between 0.5 and 10 parts per million (ppm)

** Concentration of at least one sample was greater than 10 ppm

\- Concentration was less than the 0.5 ppm detection limit

^ DMPA, ronnel, and tetradifon had chlorodioxin residues; chloroneb, hexachlorophene, nematocide, and nitrofen had no detectable residues

Table 36. Single oral doses of dioxins necessary to kill 50 percent of the exposed animals (LD_{50}).
[µg/kg bw is micrograms per kilogram body weight; from Kriebel, 1981]

Dibenzo-p-dioxin	Animal	LD_{50} (µg/kg bw)
2,3,7,8-tetrachloro-	Guinea pig	2
	Rat (male)	22
	Rabbit	115
	Mouse	284
1,2,3,7,8-pentachloro-	Guinea pig	3
	Mouse	338
1,2,3,4,7,8-hexachloro-	Guinea pig	73
	Mouse	825

tingling and numbness of the arms and legs, and liver damage (Kriebel, 1981). TCDD exposure has also been linked to certain cases of birth defects. Pregnant women living near Alsea, Oregon experienced a significant increase in the number of spontaneous abortions during the months of June and July from 1972-77. From March to June of each of these years, herbicides including 2,4,5-T were routinely applied to nearby forests (Kriebel, 1981). Similarly, many Vietnam veterans claim that PCDDs in Agent Orange (approximately a 1:1 mixture of 2,4,5-T and 2,4-D) applied to Vietnamese forests have caused birth defects in their children (Kriebel, 1981). These examples indicate that even the low residues of PCDDs found in certain herbicides may cause adverse health effects owing to the high toxicity of the PCDDs.

Inasmuch as PCDDs are not deliberately manufactured, only gross estimates of production can be made. Based on a combined annual production figure of 30,000 metric tons for 2,4,5-T, and tri-, tetra-, and pentachlorophenol in the U.S., and assuming that the production of each kilogram of the technical grade formulation results in the production of 1 milligram of PCDD, then approximately 30 kilograms are produced each year from these sources. Similarly, more than 40,000 metric tons of Agent Orange were sprayed over the jungles of Southeast Asia, with the formulation having a mean TCDD concentration greater than 1.9 mg/kg (Crosby and Wong, 1977).

Although PCDDs are produced as byproducts in the manufacture of trichlorophenol, their properties and environmental behavior more closely resemble those of the chlorinated insecticides. As a group, they are sparingly soluble, lipophilic compounds of relatively long environmental persistence. Increased chlorination correlates with decreased solubility and increased lipophilicity. TCDD has been the subject of the majority of research on PCDDs and has a solubility of about 3 to 5 ppb (Biddinger and Gloss, 1984) and an octanol-water partition coefficient of 4.24×10^{6} (Marple and others, 1986).

Environmental Fate

Almost all the published fate data for the PCDDs are limited to TCDD. As a result, any conclusions about the environmental fate of the PCDDs are at best qualitative.

As a result of their relatively low solubilities, the PCDDs are likely to strongly sorb to sediments and bioaccumulate in aquatic organisms. Chemical and biological degradation processes appear very slow, making the PCDDs persistent environmental contaminants. Little data is available regarding the volatilization of PCDDs from surface-water systems.

Extremely low concentrations of PCDDs can cause significant residues in surface-water biota. By contaminating aquatic microcosms with TCDD sorbed to sediment, Isensee and Jones (1975) found that BCFs for a variety of organisms ranged from 1,000 to 63,300. After 30 days of exposure, equilibrium aqueous concentrations of TCDD as low as 50 pg/L (picograms per liter) caused TCDD concentrations in daphnids to be as great as 2.4 μg/L (corresponding to a BCF of 48,000). Other bioconcentration data from their study are summarized in table 37. Callahan and others (1979) have also reported that mosquito larvae bioaccumulated TCDD to concentrations 2,800 to 9,200 times greater than the aqueous concentration. BCFs determined for brine shrimp and silversides were 1600 and 54, respectively. Unfortunately, no bioaccumulation data were found for the other PCDDs, but, based on the strong tendency of TCDD to bioconcentrate, it is likely that other PCDDs of equal or greater chlorination will also be readily bioaccumulated.

Available data based on studies of TCDD indicate that the PCDDs strongly partition into sediment organic matter. The solubility of TCDD (3 to 5 ppb) is approximately equal to the solubility of p,p'-DDT, which has been documented as having sorption coefficients (K_d) greater than 10^4 and organic carbon/organic matter normalized sorption coefficients ($K_{oc/om}$) greater than 10^6 (table 7). Helling and others (1973) have noted that TCDD applied to fields coincident with 2,4,5-T application will not undergo significant leaching by runoff. Transport would only be likely to occur due to soil erosion. Ward and Matsumura (1978) confirmed the conclusions of Helling and others (1973) in a study employing anaerobic sediment-water microcosms dosed with radio-labelled TCDD. They typically found that from 93 to 96 percent of the recovered radioactivity was from the sediment, and speculated that much of the remaining TCDD was associated with dissolved organic matter. Similar results also were reported by Isensee and Jones (1975), who observed that from 85 to 99 percent of the TCDD originally added to a model ecosystem remained in the sediment after a 39-day period.

PCDDs appear to be highly resistant to both chemical and biological degradation. In a laboratory sediment-water system incubated under anaerobic conditions, the half life of TCDD was found to be approximately 600 days (Ward and Matsumura, 1978). Similarly, Helling and others (1973) reported that TCDD applied to moist soils exhibited half lives of approximately 1 year in the laboratory. TCDD half lives in soil greater than 10 years also have been documented (Moore and Ramamoorthy, 1984).

There is some evidence to indicate that the PCDDs can be chemically degraded by photolysis, however, photolytic decomposition rates will probably be unable to compete with sorption and bioaccumulation rates in surface-water systems. Crosby and Wong (1977) demonstrated that TCDD dissolved in organic solvents and exposed to natural sunlight on leaves and glass plates was rapidly photodegraded, with half-lives less than 6 hours. The organic solvent was believed to serve as a hydrogen donor, because, in its absence, photolytic degradation was greatly reduced. Longer half lives were observed for TCDD on soils, and this was attributed to upper-soil particles shading the lower-soil particles. The soil's protective effect against the

Table 37. Bioconcentration factors (BCFs) of 2,3,7,8-tetrachlorodibenzo-p-dioxin by a variety of aquatic organisms.
[From Isensee and Jones, 1975]

Organism	Exposure time, days	BCF
Algae	30	2,000-18,600
Duckweed	30	1,200-5,000
Snails	30	1,400-47,100
Daphnids	30	7,800-48,000
Mosquito fish	3	1,000-63,300
Catfish	6	2,000-27,900

photolytic degradation of TCDD also has been noted by Plimmer (1978). In surface-water systems, the rapid sorption of TCDD to sediments greatly reduces the amount of light reaching the TCDD molecules, thereby reducing the rate of photodecomposition. This is confirmed by the experiment of Ward and Matsumura (1978), who compared the degradation of TCDD in sediment-water microcosms incubated in the dark with identically prepared microcosms incubated in the light. After 39 days, the average recovery of TCDD from the 'dark' microcosms was 93.29 percent, whereas the average recovery of TCDD from the 'light' microcosm was 89.45 percent, indicating the lack of a significant photolytic influence. In aquatic systems, it is likely that PCDDs will be rapidly sorbed to sediments or bioaccumulated by aquatic organisms.

Environmental Distribution

Because PCDDs are byproducts of any manufacturing process that involves the production or use of trichlorophenol, they are commonly discharged to surface waters in effluents from chemical manufacturing plants, leather tanneries, kraft-pulp mills, wood-processing plants, or sewage-treatment plants (Moore and Ramamoorthy, 1984). For example, VanNess and others (1980) analyzed a series of industrial effluents and determined that 5 of the 20 samples contained detectable amounts of TCDD, with concentrations ranging up to 100 parts-per-trillion (ppt). PCDDs also enter the environment in conjunction with the application of pesticides, as discharges from chemical disposal sites, and from fly ash from municipal incinerators. Table 38 estimates the input of TCDDs into the Canadian environment from a variety of sources.

There is some evidence to indicate that PCDDs can be produced by the combustion of trichlorophenol or its derivatives. Small quantities of TCDD have been produced by burning 2,4,5-T under conditions simulating a forest fire (Kriebel, 1981), and it has been estimated that as much as 1 μg of PCDDs will be produced for every square meter of forest that is burned immediately after a herbicide treatment. Additionally, 2,4,6-trichlorophenol applied to dried leaves and allowed to burn resulted in a residual TCDD concentration of 2,100 ppm, about 100,000 times greater than the TCDD concentration in the original aliquot of trichlorophenol (Kriebel, 1981).

Upon entering surface-water systems, PCDDs strongly partition from water into sediments and biota. As a result, aqueous residues of PCDDs are generally below detectable limits, even with a significant input of PCDDs to the system. Despite low aqueous concentrations, sediment and biological residues of PCDDs have been reported in the parts-per-trillion to parts-per-billion range.

VanNess and others (1980) analyzed soil samples from a trichlorophenol-manufacturing plant. Eighty-five percent of the soil samples contained detectable residues of TCDD, with concentrations ranging from < 20 ppt to 600 ppb. O'Keefe and others (1984) detected a TCDD concentration of 10 ppt in a sediment sample collected from the

Table 38. Estimated annual inputs of polychlorinated dibenzo-p-dioxins to the Canadian environment from major sources.
[From Moore and Ramamoorthy, 1984]

	Annual inputs, in kilograms				
Source	British Columbia	Prairies	Ontario	Quebec	Maritimes
Pentachlorophenol usage	570	360	350	110	130
2,4-D usage	.3	8.9	< .1	< .1	< .1
Precipitated fly ash	< .1	< .1	1.6	5.1	< .1
Airborne fly ash	< .1	1.5	2.2	2.2	.6
Total	570	370	354	117	131

lower Hudson River. Two other samples taken from the lower Hudson, however, contained TCDD concentrations less than 7.3 ppt. Kriebel (1981) summarized the results of a study by Dow Chemical Company that reported PCDD residues in soils from a variety of locations in the U.S., including soil samples taken from one of their own chemical manufacturing plants. The ranges of the detectable concentrations are presented in table 39. The majority of the detectable concentrations were less than 3 ppb, with the exception of soil samples taken from the Dow plant, which were highly contaminated with isomers of tetra-, hexa-, hepta-, and octachlorodibenzo-p-dioxin. Based on this data, contaminated soils carried into surface waters by runoff can be a significant source of sediment TCDD residues.

Because of the high toxicity of PCDDs, and particularly TCDD, numerous researchers have documented biological residues of these compounds in edible fish. As a result of the heavy application of Agent Orange to South Vietnamese forests, carp and catfish sampled downstream from the sprayed areas contained average TCDD residues ranging from 70 to 810 ppt (Kriebel, 1981; Moore and Ramamoorthy, 1984). TCDD residues as high as 57 ppt have even been detected in the fat of some Vietnam veterans (Kriebel, 1981). Table 40 summarizes the detected residues of TCDD in a variety of fish taken from both fresh and marine waters. Although few studies have reported on the more highly chlorinated dioxins, they have also been detected in aquatic organisms. Concentrations as high as 388 (octa-), 304 (hepta-), 203 (hexa-), and 80 (penta-) ppt have been found in carp taken from the Niagara River (Moore and Ramamoorthy, 1984).

Table 39. Residues of chlorodibenzo-p-dioxins (micrograms per kilogram) in soil samples taken from various locations in the U.S. [From Kriebel, 1981]

	Range of detectable concentrations			
Location	Tetra-	Hexa-	Hepta-	Octa-
In and around Dow Chemical plant	1-120	7-280	70-3200	490-20,000
Metropolitan area	.005-.03	.03-.3	.1-3	.4-22
Urban area	nd	.03-1.2	.03-2	.05-2
Rural area	nd	nd	0.05	0.2

nd - no sample exceeded the limit of detection

Table 40. Mean and maximum concentrations of detected residues of 2,3,7,8-tetrachlorodibenzo-p-dioxin in a variety of freshwater and marine fish.
[ppt is part per trillion]

Locality	Aquatic organism	Mean (ppt)	Maximum (ppt)	Reference
Rhode Island coast	Striped bass	3.4	5.0	1
Little Neck Bay, Long Island, NY	Striped bass	16.3	39	1
Newark Bay, NJ	Striped bass	37.8	67	1
Lower Hudson River	Striped bass	61.4	120	1
Chesapeake Bay, MD	Striped bass	2.8	3.5	1
Great Lakes	Yellow perch	3.8	4.3	2
Great Lakes	Brown bullhead	6.0	8.6	2
Great Lakes	White sucker	3.0	4.0	2
Great Lakes	Channel catfish	15.5	17.7	2
Great Lakes	American eel	19.8	38.5	2
Great Lakes	Rainbow smelt	20.0	32.9	2
Lake Ontario	Lake trout	61.2	-	3
East coast of Canada	Ocean haddock	3.6	-	3
Lake Huron	Lake trout	30.4	-	3
Lake Ontario	Rainbow trout	32.3	-	3
Michigan rivers	Channel catfish	157	695	4
Michigan rivers	Carp	55	153	4
Michigan rivers	White sucker	11	21	4
Lake Ontario	Brown trout	14	162	4
Lake Ontario	Brown bullhead	4	5	4
Lake Erie	Coho salmon	1.4	1.9	4

1. O'Keefe and others (1984)
2. Ryan and others (1984)
3. Ryan and others (1983)
4. Moore and Ramamoorthy (1984)

POLYCYCLIC AROMATIC HYDROCARBONS

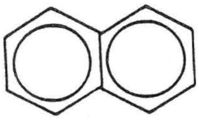
Uses, Production, and Properties

The polycyclic (or polynuclear) aromatic hydrocarbons (PAHs) are a large group of environmentally important compounds and, although little is known about their toxicities, several of the PAHs have been identified as carcinogens or mutagens. As a group, the PAHs are structurally characterized by two or more fused-ring compounds based upon benzene, with properties intermediate between benzene and olefinic hydrocarbons (Harrison and others, 1975). Two aromatic rings are considered to be fused when carbon atoms from each ring are shared. The environmentally significant PAHs have from two (naphthalene) to seven (coronene) rings. Structural diagrams of some of these compounds are given in figure 25.

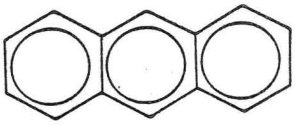
PAHs originate from both natural and anthropogenic sources; however, it is believed that their occurrence in aquatic systems is primarily due to anthropogenic inputs (Cossa and others, 1983). PAHs are produced mainly by high-temperature ($> 700^{0}$C) pyrolytic reactions such as municipal incineration or forest fires. Their residues also have been detected in fossil fuels and wood-preservative sludges (table 41).

A few of the simpler PAHs are produced commercially. Naphthalene is used in several chemical manufacturing processes to produce moth balls, pesticides, fungicides, dyes, wetting agents, synthetic resins, cutting fluids, solvents, and lubricants (Verschueren, 1983). Commercial production of petroleum naphthalene in the U.S. was 4.9×10^{4} metric tons in 1976, 4.7×10^{4} metric tons in 1980, and 6.5×10^{4} metric tons in 1981 (Moore and Ramamoorthy, 1984). The production of chloronaphthalenes (used in automobile capacitors and as oil additives for fabric dyeing and engine cleaning) is much less, with U.S. production probably below 270 metric tons per year (Moore and Ramamoorthy, 1984). Commercial uses of other PAHs such as anthracene, acenaphthene, and phenanthrene are small and limited primarily to dye and plastics manufacturing (Verschueren, 1983). Pyrolitic sources are probably the major input of PAHs to the environment. It has been estimated, based on data from 1966 to 1969, that the global emmision of benzo(a)pyrene from anthropogenic sources is about 4.6 million kilograms per year (Edwards, 1983). Table 42 lists the sources and approximate amounts of benzo(a)pyrene emitted to the atmosphere.

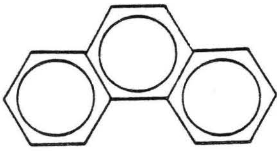
In general, the PAHs are compounds with relatively low solubilities and vapor pressures, and high octanol-water partition coefficients. These properties vary with the number of compound rings as indicated in table 43. As the number of rings increase, compound solubility and vapor pressure generally decrease, whereas the octanol-water partition coefficient increases. Acute toxicity is greatest for the low-molecular-weight PAHs, such as naphthalene, and increases with alkyl substitution (Van Luik, 1984). Benzo(a)pyrene is perhaps the



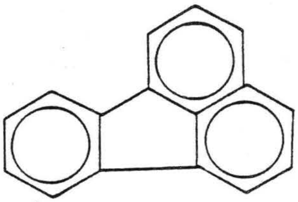
Naphthalene



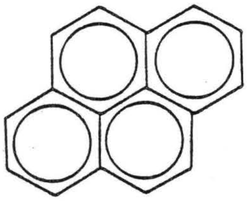
Anthracene



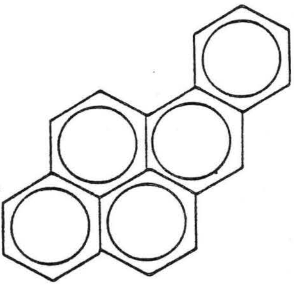
Phenanthrene



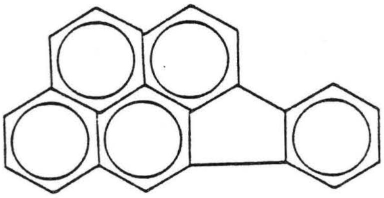
Fluoranthene



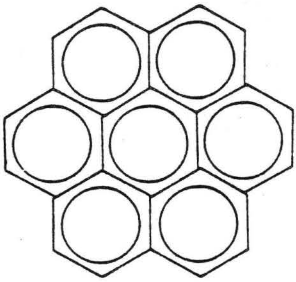
Pyrene



Benzo(a)pyrene



Indeno(1,2,3-cd)pyrene



Coronene

Figure 25. Structural diagrams of selected polycyclic aromatic hydrocarbons.

Table 41. Residues of polycyclic aromatic hydrocarbons (PAH) in oils, gasoline, bitumen, and sludge.
[From Verschueren, 1983]
[All PAH concentrations are part per million (ppm) except for wood preservative sludge which is grams per liter of raw sludge; km is kilometer; dash indicates no data available]

	Residue, in						
					Motor oil		
Compound	Gasoline	Crude oil	Bitumen	Wood preservative sludge	Fresh	Used (5,000 km)	Used (10,000 km)
Anthracene	1.55-2.59	-	-	-	-	-	-
Benzo(a)anthracene	0.04-0.27	1.7-2.3	0.13-0.86	5.18	-	-	-
Benzo(b)fluoranthene	0.16-3.9	<1.0	0.40-1.60	-	0.08	45-82	56-141
Benzo(j)fluoranthene	0.009	<1.0	-	0.31	-	-	-
Benzo(k)fluoranthene	0.009	<1.3	0.34-1.41	-	-	-	-
Benzo(g,h,i)perylene	0.32-9	<1.6	1.37-5.50	-	0.12	109-208	153-289
Benzo(a)pyrene	0.13-8.28	0.4-2.8	-	-	0.02-0.1	83.2-162	110-242
Chrysene	0.05-2.96	6.9-17.5	1.64-5.14	-	0.56	86-190	129-237
Coronene	0.06-1.9	-	-	-	0.00	25-37	28-63
Dibenz(a,h)anthracene	0.167	-	-	0.07	-	-	-
Fluoranthene	0.70-7.56	2.9-5.0	-	26.47	0.11	109-173	129-270
Fluorene	-	-	-	6.61	-	-	-
Indeno(1,2,3-cd)pyrene	0.04-2.88	-	-	-	0.03	34-59	47-83
Phenanthrene	15.7-20.5	26-70	-	-	-	-	-
Pyrene	1.55-17.1	3.5-4.5	0.17-0.80	24.2	0.29	286-450	330-700

Table 42. Estimated annual benzo(a)pyrene (BaP) emissions to the atmosphere. Values in parentheses are percentages of the total emission.
[From Edwards, 1983]

	Concentration (kg X 10^6)	
Sources	United States	Global
Heating and power	0.43 (36.8)*	2.36 (51.6)*
Industrial processes	.18 (15.4)**	.95 (20.8)**
Enclosed incineration	.03 (2.6)	.09 (2.0)
Coal refuse burning	.31 (26.5)	.62 (13.6)
Forest and agricultural fires	.13 (11.1)	.38 (8.3)
Other refuse burning	.07 (6.0)	.13 (2.8)
Trucks and buses	.01 (0.8)	.03 (0.7)
Automobiles	.01 (0.8)	.01 (0.2)
TOTAL	1.17	4.57

* 91 percent from coal and 8 percent from wood
** 99 percent from coke production

Table 43. Experimentally determined octanol-water partition coefficients, solubilities, and vapor pressures of selected polycyclic aromatic hydrocarbons (PAHs).
[mg/L is milligrams per liter; mm is millimeter; from Callahan and others, 1979]

PAH	Number of rings	Log K_{ow}	Solubility$_0$ (mg/L at 25 C)	Vapor pressure$_0$ (mm of Hg at 20 C)
Naphthalene	2	3.37	34.4	0.0492
Phenanthrene	3	4.46	1.00	6.8 X 10^{-4}
Anthracene	3	4.45	0.045	1.95 X 10^{-4}
Pyrene	4	nd	0.14	6.85 X 10^{-7}
Benzo(a)anthracene	4	5.61	0.014	5 X 10^{-9}
Benzo(k)fluoranthene	4	nd	nd	9.59 X 10^{-11}
Chrysene	4	5.61	0.002	nd
Benzo(a)pyrene	5	6.04	0.0038	5 X 10^{-9}*
Benzo(ghi)perylene	6	nd	0.00026	nd

* - vapor pressure determined at 25°C.
nd - no data available.

most highly carcinogenic compound of the group, but other compounds, such as benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(a)anthracene, chrysene, and indeno(1,2,3-cd)pyrene, also have been recognized as carcinogens (Harrison and others, 1975).

Environmental Fate

The PAHs are persistent surface-water contaminants. Due to their low solubilities and high octanol-water partition coefficients, they strongly partition from water into biota and particulate and dissolved organic matter. As a result, even low aqueous concentrations can result in environmentally significant sediment and biological residues. There is some evidence that PAHs can be photolytically degraded in the water column, but the importance of this process in natural systems is likely to be small because of the strong sorption of PAHs to sediments. The ultimate fate of the PAHs probably is sorption to sediments followed by slow biodegradation. Other transport/transformation processes, such as volatilization and hydrolysis, are not important fate processes.

Several laboratory studies have investigated the sorption of PAHs to sediments. Gardner and others (1979) exposed sand and salt marsh sediment to crude oil containing small amounts of anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene. Sorption of all four compounds was extensive, with the sediments having the highest organic-matter content sorbing the greatest amount of PAHs. PAH concentrations as high as 10 mg/kg also have been reported in rapid-sand-filter solids (Harrison and others, 1975). In a study comparing anthracene sorption to organic matter (yeast cells) and mineral particulate matter (powdered calcite), Herbes (1977) observed that the particulate organic matter rapidly sorbed the anthracene in solution, with equilibrium reached within minutes. In the presence of a 250 mg/L yeast-cell concentration, 72 percent of an initial anthracene concentration of 0.02 μg/L was sorbed by the organic matter. In constrast, the concentration of calcite required to sorb just 30 percent of the initial anthracene concentration was 300 g/L (grams per liter), indicating that anthracene is sorbed by partitioning into organic matter and that adsorption to mineral surfaces is relatively insignificant. Hassett and others (1980) also noted the importance of organic matter in the sorption of dibenzothiophene to several soils and sediments. Laboratory-measured sorption coefficients ranged from 5.8 to 388.

The sediment-water partition coefficients normalized for organic-carbon content for a variety of the PAHs can be calculated from solubility data using the empirical relation derived by Banwart and others (1982):

$$\log K_{oc} = -0.686 \log S + 4.273 ,$$

where S is the compound solubility in mg/L. The relation was developed from data from Karickhoff and others (1979) and Banwart and others

(1980), along with original sorption data for three nitrogen-heterocyclic compounds. Table 44 presents the calculated values of K_{oc} for some of the PAHs along with experimentally determined K_{oc} values for additional PAHs from Karickhoff and others (1979). The K_{oc} values indicate that a sediment sample with only 0.1 percent organic-carbon content may have an equilibrium benzo(a)pyrene concentration of $8.6 \times 10^5 \times 0.001$ or 860 times greater than the compound's concentration in the surrounding water. Means and others (1980, 1982) also determined K_{oc} values for several PAHs sorbed to 14 sediment and soil samples. Mean values for the 14 samples ranged from 517 (anthracene-9-carboxylic acid) to 1.8×10^6 (3-methylcholanthrene). These data indicate the strong tendency of benzo(a)pyrene and other PAHs of similarly low solubilities to partition into sediment organic matter.

In addition to their tendency to sorb to sediments, PAHs also accumulate in the lipid reservoirs of aquatic organisms, with BCFs generally increasing as compound solubility decreases. This observation is confirmed by the data of Southworth and others (1978a), who studied the bioaccumulation of seven PAHs by *Daphnia pulex*. They determined that the octanol-water partition coefficients of the PAHs were good estimators of BCFs, with laboratory-measured BCFs ranging from 100 for naphthalene to 10,000 for benz(a)anthracene. Casserly and others (1983) also found that BCFs increase with decreasing solubility. Exposure of the alga, *Selenastrum capricornutum*, to aqueous residues of naphthalene, phenanthrene, and pyrene resulted in BCFs of 12,600, 24,000, and 36,300, respectively. BCFs as great as 10,000 also have been documented for PAHs bioaccumulated by fish (Mackay, 1982b). Table 45 lists BCFs determined for a variety of PAHs. For a given compound, differences in BCFs determined for different organisms are at least partially attributable to differences in the lipid contents of the organisms. For a given compound, BCFs will increase with increasing lipid content of the aquatic organism.

In aqueous systems, PAHs are photodegraded by reactions with oxygen resulting in the formation of quinones (Smith and others, 1978). Although several laboratory experiments have documented short photolytic half lives for PAHs in distilled water samples, photodecomposition in natural systems may be relatively insignificant due to the strong partitioning of PAHs into particulate and dissolved organic matter. Smith and others (1978) measured photolysis half lives of several hours for benz(a)anthracene and benzo(a)pyrene in oxygen-saturated distilled water exposed to sunlight. However, when half-lives were similarly determined in natural waters or in distilled water containing dissolved humic acids, photolysis was significantly retarded. The low absorbance of the natural water used indicated that light screening alone probably was not responsible for the differences in photolysis rates. Partition of the two PAHs into the dissolved organic matter, however, may have altered the reactivity of the molecules and thereby reduced the photolysis rates. Photolytic degradation of PAHs may only be an important fate process when the

Table 44. Calculated and experimental sediment-water sorption coefficients normalized for organic carbon (K_{oc}) for a variety of polycyclic aromatic hydrocarbons (PAHs).

PAH	Solubility* (milligrams per liter)	K_{oc}
Naphthalene	34.4	1.3×10^3 (E)
Phenanthrene	1.00	2.3×10^4 (E)
Fluoranthene	.265	4.7×10^4 (C)
Pyrene	.14	8.4×10^4 (E)
Anthracene	.045	2.6×10^4 (E)
Benzo(a)anthracene	.014	3.5×10^5 (C)
Benzo(a)pyrene	.0038	8.6×10^5 (C)
Chrysene	.002	1.3×10^6 (C)
Benzo(ghi)perylene	.00026	5.4×10^6 (C)

C - Calculated according to Banwart and others (1982).

E - Experimental values are from Karickhoff and others (1979).

* - All solubility data are from Callahan and others (1979) except for fluoranthene, which is from Harrison and others (1975).

Table 45. Bioconcentration factors (BCFs) for selected polycyclic aromatic hydrocarbons.
[dash indicates no data are available]

Compound	Organism	Exposure time (days)	BCF	Reference
Naphthalene	*Daphnia pulex*	1	131	1
Naphthalene	*S. capricornutum*	1	12,500	2
Naphthalene	Fish	-	427	3
Chloronaphthalenes	Grass shrimp	3	50-300	4
Acenaphthene	Fish	-	389	3
Phenanthrene	*Daphnia pulex*	1	325	1
Phenanthrene	*S. capricornutum*	1	23,800	2
Phenanthrene	Fish	-	2,630	3
2-Chlorophenanthrene	Fish	-	4,266	3
2-Methylphenanthrene	Fish	-	3,020	3
Anthracene	*Daphnia pulex*	1	917	1
Anthracene	Fish	-	912	3
9-Methylanthracene	*Daphnia pulex*	1	4,583	1
9-Methylanthracene	Fish	-	4,571	3
Pyrene	*Daphnia pulex*	1	2,702	1
Pyrene	*S. capricornutum*	1	36,300	2
Pyrene	Fish	-	2,692	3
Fluorene	Fish	-	1,288	3
Benz(a)anthracene	*Daphnia pulex*	1	10,109	1
Benz(a)anthracene	Fish	-	10,000	3
Benzo(a)pyrene	Fish	-	22	4
Benzo(a)pyrene	Snail	-	3,000	4
Perylene	*Daphnia pulex*	1	7,191	1

1. Southworth and others (1978a)
2. Casserly and others (1983)
3. Mackay (1982b)
4. Biddinger and Gloss (1984)

PAHs are present in oil slicks or in shallow, low-turbidity waters with low dissolved-organic-matter content (Callahan and others, 1979).

Several studies have documented the biodegradation of PAHs. Low molecular weight PAHs, such as naphthalene, acenaphthene, and acenaphthylene, have been rapidly degraded in laboratory cultures, with greater than 90 percent degradation of initial concentrations of 5 to 10 mg/L occurring within 7 days (Tabak and others, 1981). PAHs of higher molecular weights such as fluoranthene, benz(a)anthracene, chrysene, benzo(a)pyrene, and anthracene, however, are much more resistant to biodegradation. For example, Smith and others (1978), were unable to develop a microbial culture capable of degrading benzo(a)pyrene or benz(a)anthracene when they were present as sole carbon sources. Figure 26 presents a proposed degradation pathway for phenanthrene by soil pseudomonads that is typical for three-ring PAHs (Harrison and others, 1975).

There is evidence to suggest that PAHs are slowly biodegraded after they have been sorbed to sediments. Gardner and others (1979) exposed fine sand, medium sand, and marsh sediment to crude oil enriched with benzo(a)pyrene, benz(a)anthracene, anthracene, and fluoranthene. Based on initial PAH concentrations ranging from 7.6 to 73.9 µg/g dry sediment, the percent degradation per week of the four PAHs ranged from 0.84 to 3.5 percent, with benzo(a)pyrene having the slowest degradation rate. The authors also noted that the presence of a polychaete worm, <u>Capitella capitata</u>, enhanced the degradation of the PAHs either by improving the sediment conditions for microbial degradation or by metabolically degrading the PAHs themselves. In a similar study, Varanasi and others (1985) determined that over a 4-week period, PAHs including benzo(a)pyrene present in sediments, were not significantly degraded. However, benzo(a)pyrene was metabolized by both shrimp and fish exposed to the contaminated sediment. These studies indicate that a possible fate of PAHs in surface-water systems is sorption to sediments followed by slow biodegradation.

Based on their relatively low vapor pressures (table 43), PAHs are not expected to volatilize from water at a significant rate, and this observation has been confirmed in laboratory studies. Southworth (1979) predicted the volatilization rates of several PAHs and determined that volatilization would not be a significant attenuation method in streams with depths greater than 1 m and average velocities less 1 m/s. In a stream 1.0 m deep at 25°C, predicted volatilization half lives of benz(a)anthracene and benzo(a)pyrene were greater than 100 hours for current and wind velocities up to 1 and 4 m/s, respectively. Similarly, volatilization half-lives of benzo(a)pyrene and benz(a)anthracene in aqueous solutions stirred at a fast rate have been determined to be 22 and 89 hours, respectively (Smith and others, 1978). The presence of sediments will likely increase these experimental half lives as a result of PAH sorption.

The stucture of PAHs, for the most part, prevents hydrolytic degradation, and this process is not expected to be an important fate process in surface-water systems (Callahan and others, 1979).

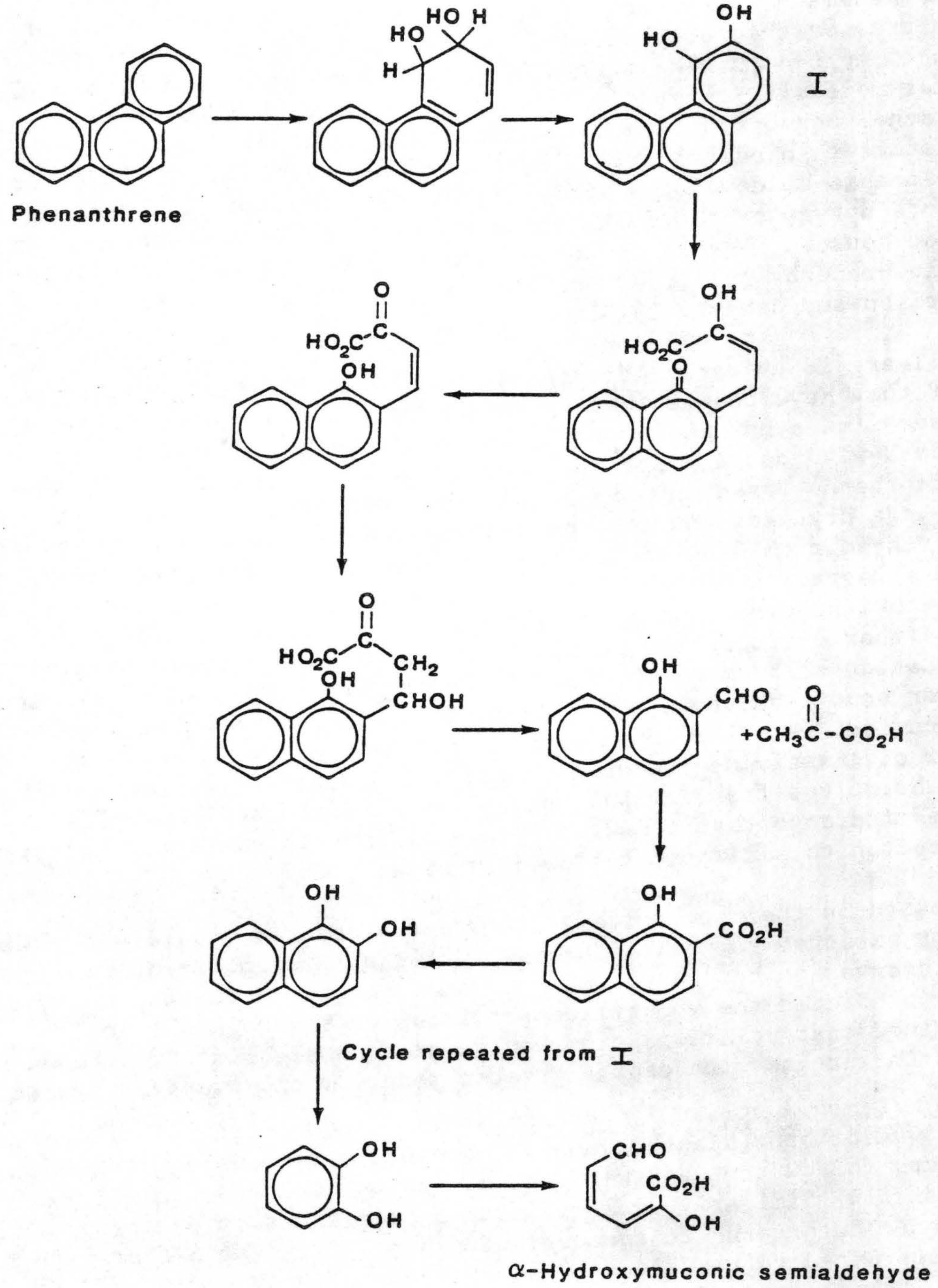


Figure 26. Proposed degradation pathway of phenanthrene by soil pseudomonads. [Reprinted with permission from Water Research **9**, 337 (1975). Copyright 1975 by Pergamon Press Ltd.]

Environmental Distribution

PAHs enter surface-water systems in a variety of ways, including atmospheric deposition, surface runoff and soil leaching, industrial discharges, and municipal wastewater effluents. Heit and others (1984) presented data indicating that fluoranthene is atmospherically deposited in remote lakes in Rocky Mountain National Park. Similarly, Heit (1985) determined that atmospheric deposition is the prime source of PAHs to Cayuga Lake, New York. Runoff into the Delaware estuary between Trenton and Philadelphia has been found to contain both particulate and dissolved quantities of petroleum hydrocarbons, many of which were identified as PAHs (Whipple and Hunter, 1979). Naphthalene concentrations ranging from 1 to 4 mg/L have been reported by Jungclaus and others (1978) in the wastewater of a specialty chemicals manufacturing plant. Barrick (1982) estimated that approximately 1 metric ton per year of 3 to 7 ring PAHs are discharged to Puget Sound from Seattle's primary municipal wastewater effluents. Likewise, Eganhouse and Kaplan (1982) determined that southern California's wastewater-treatment plants annually discharge more than 17,400 metric tons of aliphatic and aromatic hydrocarbons to coastal waters.

The origin of PAH residues in surface waters commonly can be determined by the ratio of the concentration of parent hydrocarbons to their methyl isomers. PAHs of petroleum origin consist of homologous series in which the methyl and higher alkyl-substituted isomers greatly outnumber the parent compounds (Pancirov and Brown, 1977). In contrast, PAHs of pyrolitic origin (such as the combustion of fossil fuel or wood) contain predominantly the parent hydrocarbons (Pancirov and Brown, 1977). Therefore, PAHs in a water, sediment, or biota sample having a high concentration of pyrene relative to methylpyrene are likely to be of pyrolytic origin, while PAHs in samples having a high methylpyrene concentration relative to pyrene are likely a result of direct contamination from petroleum or petroleum-derived products. The limitation of the above reasoning is the assumption that both the parent hydrocarbon and its methyl isomer have the same aquatic fates. If, for example, pyrene is biodegraded at a faster rate than methylpyrene, the initial parent/methyl isomer ratio will be upset.

Because of their relatively low solubilities, PAHs are usually only found at low aqueous concentrations in surface waters. Sheldon and Hites (1979), for example, measured aqueous methylnaphthalene concentrations of 0.02 and 0.2 μg/L at two locations in the Delaware estuary. Similarly, Stainken and Frank (1979) detected 2- to 5-ring PAHs at concentrations ranging from 2 to 20 μg/L in the bottom waters of Raritan Bay. Downstream of a chemical manufacturing plant's effluent, Jungclaus and others (1978) reported low concentrations of naphthalene (6 to 10 μg/L) in river water. Harrison and others (1975) have also reported low aqueous concentrations of PAHs. Their maximum reported concentration for any of the PAHs in several European rivers was only 0.76 μg/L.

As a result of their generally low aqueous solubilities and high octanol-water partition coefficients, PAHs will strongly partition into sediment-associated organic matter, and consequently, sediments act as a reservoir for PAHs. Although aqueous PAH concentrations in surface waters are typically in the part-per-trillion to low part-per-billion range, sediment PAH concentrations can be several orders of magnitude higher. For example, Jungclaus and others (1978) detected significant residues of phenanthrene (0.2 to 25 ppm), fluorene (2 to 10 ppm), acenaphthylene (0.2 to 5 ppm), and pyrene (0.5 to 75 ppm) in the sediment of a river downstream from a chemicals manufacturing plant's discharge. Aqueous residues of these same compounds, however, were not detected. Table 46 presents documented residues of a variety of PAHs in sediment samples collected from U.S. surface waters. Benzo(a)pyrene concentrations greater than 300 ppm have been detected in the sediments of Lake Hansen, Los Angeles, and numerous researchers have reported sediment PAH concentrations ranging from 10 ppb to 10 ppm.

In addition to strongly partitioning into sediment organic matter, PAHs also accumulate in the lipid reservoirs of aquatic organisms. Table 47 presents mean and maximum reported concentrations of PAHs in aquatic organisms and illustrates that residues greater than 400 ppb have been reported. The data in Table 47 from Brown and Pancirov (1979) are concentrations of PAH in fish from the Baltimore Canyon area off the coast of New Jersey and Delaware. Despite the lack of any oil or gas production in the area, biological residues of PAHs were still found at significant concentrations (up to 4.1 ppb), indicating their strong tendency to bioaccumulate.

Although no studies have addressed temporal contamination trends of PAHs in surface waters across the nation, several localized studies have reported data indicating that PAH residues in sediments have been increasing over time. In a study of two New York lakes, Heit and others (1981) analyzed sediment cores for a variety of PAHs. They determined that with the exception of perylene, anthropogenically derived PAH concentrations decreased with increasing sediment depth until a background concentration was reached at a sediment depth estimated to be about 30 years old. Hurtt and Quinn (1979) examined PAH residues in sediment cores collected from Narragansett Bay, Rhode Island, and also discovered that PAH residues steadily decreased with sediment core depth, with concentrations stabilizing at a depth of 20-25 cm. Likewise, Heit and others (1984) observed that the highest fluoranthene concentrations in Rocky Mountain National Park occurred in the surficial sediments of four lakes. Lower concentrations were observed in deeper sediments. Finally, Bates and others (1984) noted that PAH concentration changes in the sediments of the central main basin of Puget Sound, Washington paralleled the urbanization of Seattle.

Several studies have also investigated regional PAH contamination trends and determined that the highest PAH residues are typically found near highly-populated, industrialized areas. Larsen and others (1983) reported strongly regional PAH contamination trends in the sediments of Casco Bay, Maine. In general, total PAH concentrations in the bay's upper and middle sections were below 900 ppb. Sediment

Table 46. Sediment residues of polycyclic aromatic hydrocarbons.
[μg/kg is micrograms per kilogram; dash indicates no data available]

Compound	Locality	Mean (μg/kg)	Max. (μg/kg)	Reference
Benzo(a)pyrene	Adirondack acid lake region, NY	409	690	1
Benzo(a)pyrene	Western U.S. lakes	38,000	305,000	2
Benzo(a)pyrene	Lake George, NY	-	30	3
Benzo(a)pyrene	Casco Bay, ME	122	805	4
Phenanthrene	Adirondack acid lake region, NY	239	324	1
Phenanthrene	Lake George, NY	-	150	3
Pyrene	Lake George, NY	-	150	3
Pyrene	Calumet-Sag Channel	6,300	10,000	5
Fluoranthene	Lake George, NY	-	160	3
Fluoranthene	Rocky Mountain lakes	165	375	6
Perylene	Adirondack acid lake region, NY	443	605	1
Perylene	Lake George, NY	16	-	3
Perylene	Cayuga Lake, NY	207	510	7
Benzo(g,h,i)-perylene	Adirondack acid lake region, NY	830	1,356	1
Benzo(k)fluoranthene	Casco Bay, ME	77.8	193	4
Anthracene	Adirondack acid lake region, NY	27	32	1
Benz(a)anthracene	Lake George, NY	-	30	3
Dibenzo(a,c/a,h)-anthracene	Cayuga Lake, NY	54	120	7
Indeno(c,d)pyrene	Adirondack acid lake region, NY	805	1,294	1
Coronene	Adirondack acid lake region, NY	495	801	1
Acenaphthene	Casco Bay, ME	293	1,150	4
Chrysene/ triphenylene	Cayuga Lake, NY	176	605	7

1. Heit and others (1981)
2. Heit (1979)
3. Heit and others (1980)
4. Larsen and others (1983)
5. Van Luik (1984)
6. Heit and others (1984)
7. Heit (1985)

Table 47. Residues of polycyclic aromatic hydrocarbons in biota. [μg/kg is micrograms per kilogram; dash indicates no data available]

Compound	Locality	Aquatic organism	Mean (μg/kg)	Max. (μg/kg)	Reference
Pyrene	Baltimore Canyon	Summer flounder	2.7	4.1	1
Pyrene	Manhasset Neck, NY	Mussels	-	370	2
Pyrene	Lake George, NY	Mussels	-	90	3
Benzo(a)pyrene	Lake Erie	Fish stomachs	7.1	15.5	4
Benzo(a)pyrene	U.S. east coast	Shellfish	1.3	3.0	5
Methylpyrene	Baltimore Canyon	Summer flounder	1.9	2.7	1
Indeno(1,2,3-c,d)pyrene	Lake Erie	Fish stomachs	15	15	4
Fluoranthene	Biloxi, MS	Mussels	-	90	2
Fluoranthene	Lake George, NY	Mussels	-	60	3
Benz(a)-anthracene	Baltimore Canyon	Summer flounder	0.7	1.1	1
Benz(a)-anthracene	U.S. east coast	Shellfish	2.0	8.0	5
Dibenz(a,h)-anthracene	Lake Erie	Fish stomachs	2.3	4.1	4
Chrysene/benz-(a)anthracene	Kinnickinnic River, WI	Carp	-	460	6
Chrysene	Lake Erie	Fish stomachs	13.1	26.1	4
Naphthalene	Biloxi, MS	Mussels	-	120	2
Phenanthrene	Lake George, NY	Mussels	-	60	3
Perylene	Lake George, NY	Mussels	-	300	3
Fluorene	Lake Erie	Fish stomachs	15.4	15.4	4

1. Brown and Pancirov (1979)
2. Farrington and others (1983)
3. Heit and others (1980)
4. Maccubbin and others (1985)
5. Pancirov and Brown (1977)
6. DeVault (1985)

samples taken from stations near the metropolitan area of Portland, however, had total PAH concentrations in excess of 2,000 ppb. Heit (1979) noted similar results after collecting and analyzing sediment samples from a variety of western lakes for residues of benzo(a)pyrene. The highest concentrations of the carcinogenic PAH were found in Hansen Lake, which is located in the urban environment of Los Angeles. Farrington and others (1983) sampled mussels taken from 62 locations from the Atlantic and Pacific coasts of the U.S. and analyzed them for PAH residues. Again, mussels sampled from stations near urban areas had elevated PAH concentrations relative to mussels from stations near rural, sparsely populated areas.

SUMMARY

This report critically reviews the scientific literature with regard to the processes influencing the occurrence and distribution of manmade organic compounds in surface-water systems. The distribution and concentration of organic compounds in surface-water systems are affected by sorption, bioaccumulation, photolysis, hydrolysis, biodegradation, and volatilization.

In aqueous systems, nonionic organic compounds are sorbed by partitioning between water and the sediment-associated organic matter. Adsorption does not contribute significantly to sorption due to the competitive advantage polar water molecules have for surface adsorption sites. Sediments with high organic-matter contents exhibit the greatest sorption capacity for nonionic organic compounds, and compounds with low aqueous solubilities exhibit the strongest tendency to partition into sediment organic matter. Ionic organic compounds may be able to successfully compete with polar water molecules for surface adsorption sites, and therefore, may be sorbed by an adsorption process.

Organic compounds can similarly partition into the lipid reservoirs of aquatic organisms, and available data indicate that the extent of bioaccumulation is dependent primarily on an organism's lipid content rather than its position in the aquatic food chain. The popular concept of biomagnification in aqueous systems is not well supported by the scientific literature.

Photolysis, hydrolysis, and biodegradation act to reduce the concentration of an organic compound by either a chemical or biological transformation. Volatilization also reduces the solute's concentration in the surface-water system, but does so by physically partitioning the solute into the atmosphere. The rates of all four processes are commonly modeled by first-order kinetics, in which the rate of transformation/transport is proportional to the solute's concentration in the water. Both the compound and environmental parameters that influence these processes are discussed.

Data regarding production and use, environmental fate, and environmental distribution are presented for eight groups of anthropogenic organic compounds. Polychlorinated biphenyls and chlorinated insecticides, despite almost complete cessation of their production more than ten years ago, remain at significant concentrations in the sediments and biota of surface waters across the U.S. and around the globe. Their low solubilities cause them to strongly partition into particulate organic matter and biological lipid reservoirs. They are extremely persistent organic contaminants and are highly resistant to biodegradation, photolysis, and hydrolysis. Although their vapor pressures are relatively low, their unusually high activities in water permit them to be volatilized from solution and transported atmospherically. In natural systems, aqueous concentrations of PCBs and chlorinated insecticides are typically low (in the part-per-trillion range), but sediment and biological concentrations in the part-per-million range have been reported.

Regionally, the highest PCB residues are commonly found in waters near highly populated, industrial areas, while the highest chlorinated insecticide residues are often found in surface waters draining agricultural areas. Surface-water residues of PCBs and chlorinated insecticides in the U.S. appear to be slowing decreasing, and this is attributable to North American bans on production and use of most of these compounds.

Organophosphorous (OP) and carbamate insecticides have seen widespread use in recent years as replacements for many of the chlorinated insecticides. They are readily degraded by both chemical and biological processes, and as a result, they are among the least environmentally-persistent pesticides. Their generally high aqueous solubilities prevent significant partitioning into organic phases, and therefore, the OP and carbamate insecticides do not tend to accumulate in sediments or biota. When present in surface-water systems, their highest concentrations are typically found in aqueous samples, but these residues typically do not persist for prolonged periods.

Herbicides, characterized by high aqueous solubilities and low vapor pressures, have been increasingly applied to major crops in the U.S., with atrazine and 2,4-D being the most extensively used. Similar to the OP and carbamate insecticides, the herbicides are relatively nonpersistent environmental contaminants that are readily biodegraded or chemically attenuated by photolytic or hydrolytic reactions. Herbicide bioaccumulation and sorption to sediments is minor, with the possible exception of the dinitroaniline and bipyridylium herbicides. In natural systems, herbicide residues are generally found in the aqueous phase. Aquatic herbicides are applied directly to water bodies, and their residues are therefore greatest immediately following application. Terrestrial herbicides are transported to surface waters primarily in the dissolved phase of surface runoff, and consequently, residues of these herbicides are usually greatest if a heavy rain immediately follows the application of the herbicide. In view of the increasing use of herbicides in the U.S., it is unlikely that herbicide residues in surface waters will decrease in the near future.

Phenols are a widely used group of compounds manufactured primarily by the organic chemical and pesticide industries. As a group, the phenols are of generally high solubility. However, increasing chlorination of the molecule results in decreased solubility and increased octanol-water partition coefficients. Phenols are primarily attenuated by biodegradation and photolysis. Sorption to sediments is generally, minor, inasmuch as the relatively high solubility of phenols prevents substantial partitioning of the solute into sediment-associated organic matter and the negative charge of particle surfaces minimizes adsorption of phenolate anions. Sediments with high organic-matter content, however, have been observed to sorb appreciable amounts of the highly chlorinated phenols because of their lower solubilities. Similarly, phenols are not readily bioaccumulated, with the exception of the highly chlorinated phenols such as pentachlorophenol. Phenols commonly enter surface waters in industrial or municipal effluents, and chlorination of these effluents can convert phenol to mono-, di-, or even trichlorophenol isomers. Despite their large-scale production, phenolic residues in surface waters usually are not found at concentrations greater than 1 ppm.

Halogenated aliphatic and monocyclic aromatic hydrocarbons (MAHs) are industrial chemicals that have a variety of uses including solvent degreasers, refrigerants, and styrene and dye manufacturing. They are highly soluble in water, and their primary fate in natural waters is volatilization followed by atmospheric photolysis. While many of these compounds have been biologically and chemically degraded in the laboratory, the degradation rates are generally not fast enough to successfully compete with volatilization from the water body. Sorption to sediments and bioaccumulation are not important fate processes, with the possible exception of the chlorinated benzenes. Because of the large quantities of halogenated aliphatic and MAHs produced annually, they are ubiquitous surface-water contaminants. Sediment, biological, and aqueous environmental residues, however, rarely exceed the part-per-billion range. Spatially, halogenated aliphatic and MAHs are typically found near industrial and highly-populated areas. Temporally, there is some evidence to suggest that environmental residues have decreased slightly since the late 1970's, paralleling a similar decrease in production of these compounds in the U.S.

Phthalate esters represent a relatively new class of environmental pollutants. They are extensively used as plasticizers to produce useful products from polymers of vinyl chloride. As a result of their low solubilities and nonionic nature, they tend to strongly partition into particulate organic matter and biological lipid reservoirs. Therefore, aqueous residues that exceed 50 ppb rarely have been reported, whereas sediment and biological residues have been reported in excess of 1 ppm. Reported environmental levels of phthalate esters should be viewed with caution, however, because there is strong evidence indicating that they may be produced naturally. Additionally, environmental samples can be contaminated with phthalate esters by the use of plastic sampling containers. The ultimate fate of phthalate esters in surface waters appears to be biodegradation.

Although not deliberately manufactured and having no commercial use, polychlorinated dibenzo-p-dioxins (PCDDs) enter the environment as impurities in compounds whose production involves the use of 2,4,5-trichlorophenol. These compounds include many pesticides and both tetra- and pentachlorophenol. Although the quantity of PCDDs produced each year is probably very small, they are extremely persistent contaminants that have been shown to be highly toxic to laboratory animals (particularly 2,3,7,8-tetrachlorodibenzo-p-dioxin). PCDDs strongly sorb to sediments and soils, and erosion of soil treated with PCDD-contaminated pesticides is a likely input of PCDDs to surface-water systems. PCDDs also strongly partition into biological lipid reservoirs, and aqueous concentrations as low as 50 pg/L have resulted in biological concentrations as great as 2.4 μg/L. There is some evidence to indicate that PCDDs can be degraded photolytically; however, the majority of PCDDs in surface waters will probably be unavailable for photolysis due to rapid sorption to sediments. The highest PCDD residues in surface-water systems are found in the sediments and biota, with reported concentrations typically in the ppt to ppb range.

Polycyclic aromatic hydrocarbons (PAHs) are produced by high-temperature pyrolytic reactions, such as municipal incineration, forest fires, or fuel combustion. Their residues also have been detected in fossil fuels and wastewater sludges. Important environmental-fate processes include sorption and bioaccumulation, and the ultimate fate of PAHs in surface-water systems may be sorption to sediments followed by slow biodegradation. Photolytic degradation of PAHs has been demonstrated in laboratory studies, but, in natural systems, it is uncertain if photolysis is a significant fate process due to the rapid sorption of PAHs to sediments. Because of their low solubilities, aqueous residues of PAHs in natural systems are typically low relative to sediment and biological concentrations. Based on sediment core data, PAH residues in surface-water systems appear to be increasing with time, and concentrations seem to parallel industrialization both temporally and spatially.

SELECTED REFERENCES

Abdullah, M.I., and Ringstad, O., 1982, Polychlorinated biphenyls in the sediments of the Inner Oslofjord: Water, Air, and Soil Pollution, v. 18, p. 485-497.

Acree, J., Beroza, M., and Bowman, M.C., 1963, Codistillation of DDT with water: Journal of Agricultural Food Chemistry, v. 11, p. 278-283.

Adams, R.S., 1973, Factors influencing soil adsorption and bioactivity of pesticides: Residue Reviews, v. 47, p. 1-45.

Addison, R.F., Paterson, S., and Mackay, D., 1983, The predicted environmental distribution of some PCB replacements: Chemosphere, v. 12, no. 6, p. 827-834.

Agarwal, H.C., Mittal, P.K., Menon, K.B., and Pillai, M.K.K., 1986, DDT residues in the river Jamuna in Delhi, India: Water, Air, and Soil Pollution, v. 28, p. 89-104.

Agarwal, H.C., Saxena, D.M., and Lal, Rup, 1982, Accumulation and metabolism of DDT and its metabolites by Tetrahymena: Water, Air, and Soil Pollution, v. 18, p. 441-447.

Akhavein, A.A., and Linscott, D.L., 1968, The dipyridilium pesticides: paraquat and diquat: Residue Reviews, v. 23, p. 98-140.

Alexander, Martin, 1985, Biodegradation of organic chemicals: Environmental Science and Technology, v. 18, no. 2, p. 106-111.

Alexander, M., and Aleem, M.I.H., 1961, Effect of chemical structure on microbial decomposition of aromatic herbicides: Agricultural and Food Chemistry, v. 9, no. 1, p. 44-47.

Allison, L.E., 1965, Organic Carbon, in Black, C., Evans, D., White, J., Ensminger, L., and Clark, F., eds., Methods of soil analysis, part 2: Madison, Wisconsin, American Society of Agronomy, Inc., p. 1367-1378.

Almgren, Mats, Grieser, Franz, Powell, J.R., and Thomas, J.K., 1979, A correlation between the solubility of aromatic hydrocarbons in water and micellar solutions, with their normal boiling points: Journal of Chemical and Engineering Data, v. 24, no. 4, p. 285-287.

Al-Omar, M.A., Al-Ogaily, N.H., and Shebil, D., 1986, Residues of organochlorine insecticides in fish from polluted water: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 109-113.

Anderson, R.L., 1985, Environmental effects on metsulfuron and chlorsulfuron bioactivity in soil: Journal of Environmental Quality, v. 14, no. 4, p. 517-521.

Andrilenas, P.A., 1974, Farmers' use of pesticides in 1971 - Quantities: U.S. Department of Agriculture, Agricultural Economic Report 252, 56 p.

Anjum, F., and Qadri, S.S.H., 1986, In vivo metabolism of fenitrothion (o,o-dimethyl-o-(4-nitro-m-tolyl) phosphorothioate) in fresh water teleost (*Tilapia mossambica*): Bulletin of Environmental Contamination and Toxicology, v. 36, p. 140-145.

Ansari, G.A.S., James, G.P., Hu, L.A., and Reynolds, E.S., 1986, Organochlorine residues in adipose tissue of residents of the Texas Gulf Coast: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 311-316.

Arbuckle, W.B., 1983, Estimating activity coefficients for use in calculating environmental parameters: Environmental Science and Technology, v. 17, no. 9, p. 537-542.

Aslanzadeh, J., and Hedrick, H.G., 1985, Search for mirex-degrading soil microorganisms: Soil Science, v. 139, no. 4, p. 369-374.

Averitt, W.K., and Gangstad, E.O., 1976, Dissipation of residues of 2,4-D in static water: Journal of Environmental Quality, v. 5, no. 2, p. 145-147.

Avnimelech Y., Yamamato, M., and Menzel, R.G., 1983, Evaluating the release of soluble components from sediments: Journal of Environmental Quality, v. 12, no. 1, p. 86-91.

Bailey, G.W., and White, J.L., 1965, Herbicides: a compilation of their physical, chemical and biological properties: Residue Reviews, v. 10, p. 97-121.

Bailey, G.W., White, J.L., and Rothberg, T., 1968, Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate: Soil Science Society of America Proceedings, v. 32, p. 222-234.

Baird, R.B., Kuo, C.L., Shapiro, J.S., and Yanko, W.A., 1974, The fate of phenolics in wastewater determinations by direct injection GLC and Warburg Respirometry: Archives of Environmental Contamination and Toxicology, v. 6, p. 165-178.

Baker, E.T., and Feely, R.A., 1978, Chemistry of oceanic particulate matter and sediments: Science, v. 200, p. 533-535.

Baker, J.E., Eisenreich, S.J., Johnson, T.C., and Halfman, B.M., 1985, Chlorinated hydrocarbon cycling in the benthic nepheloid layer of Lake Superior: Environmental Science and Technology, v. 19, no. 9, p. 854-861.

Banerjee, Sujit, 1984, Solubility of organic mixtures in water: Environmental Science and Technology, v. 18, no. 8, p. 587-591.

Banerjee, Sujit, 1985, Calculation of water solubility of organic compounds with UNIFAC-derived parameters: Environmental Science and Technology, v. 19, no. 4, p. 369-370.

Banerjee, S., Howard, P.H., Rosenberg, A.M., Dombrowski, A.E., Sikka, H., and Tullis, D.L., 1984a, Development of a general kinetic model for biodegradation and its application to chlorophenols and related compounds: Environmental Science and Technology, v. 18, no. 6, p. 416-422.

Banerjee, S., Sugatt, R.H., and O'Grady, D.P., 1984b, A simple method for determining bioconcentration parameters of hydrophobic compounds: Environmental Science and Technology, v. 18, no. 2, p. 79-81.

Banerjee, S., Yalkowsky, S.H., and Valvani, S.C., 1980, Water solubility and octanol/water partition coefficients of organics; Limitations of the solubility-partition coefficient correlation: Environmental Science and Technology, v. 14, no. 10, p. 1227-1229.

Banwart, W.L., Hasset, J.J., Wood, S.G., and Means, J.C., 1982, Sorption of nitrogen-heterocyclic compounds by soils and sediments: Soil Science, v. 133, p. 42-47.

Banwart, W.L., Khan, A., and Hassett, J.J., 1980, Effect of sample pretreatment on sorption of acetophenone by soils and sediments: Journal of Environmental Science and Health, v. B15, p. 165-179.

Barber, R.T., and Warlen, S.M., 1979, Organochlorine insecticide residues in deep sea fish from 2500 m in the Atlantic Ocean: Environmental Science and Technology, v. 13, no. 9, p. 1146-1148.

Barbera, J.C., Lopez, F.J., Hernandez, F., Medina, J., and Pastor, A., 1986, Gas chromatographic determination of organochlorine pesticides; contamination of dicofol, fenson, and tetradifon in fish and natural waters of a wet area beside the Mediterranean Sea: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 211-218.

Barrick, R.C., 1982, Flux of aliphatic and polycyclic aromatic hydrocarbons to central Puget Sound for Seattle (Westpoint) primary sewage effluent: Environmental Science and Technology, v. 16, p. 682-692.

SELECTED REFERENCES--Continued

Barker, J.L., 1984, Organochlorine pesticide and polychlorinated biphenyl residues at four trophic levels in the Schuylkill River, Pennsylvania, in Meyer, E.L., ed., Selected papers in the hydrologic sciences: U.S. Geological Survey Water-Supply Paper 2262, p. 25-31.

Bates, T.S., Hamilton, S.E., and Cline, J.D., 1984, Vertical transport and sedimentation of hydrocarbons in the central main basin of Puget Sound, Washington: Environmental Science and Technology, v. 18, no. 5, p. 299-305.

Baum, S.J., 1982, Introduction to organic and biological chemistry: Macmillan Publishing Co., New York, 560 p.

Belluck, David, and Felsot, Allan, 1981, Bioconcentration of pesticides by egg masses of the caddisfly, Triaenodes tardus milne: Bulletin of Environmental Contamination and Toxicology, v. 26, p. 299-306.

Benefield, L.D., and Randall, C.W., 1980, Biological process design for wastewater treatment: Prentice-Hall, Englewood Cliffs, 515 p.

Berner, R.A., 1980, Early diagenesis: A theoretical approach: Princeton University Press, 241 p.

Bernhard, M., 1981, Heavy metals and chlorinated hydrocarbons in the Mediterranean: in Geyer, M., ed., Marine Environmental Pollution, part 2, Dumping and Mining, Elsevier Scientific Publishing Co., p. 143-192.

Bevenue, Arthur, 1976, The "bioconcentration" aspects of DDT in the environment: Residue Reviews, v. 61, p. 37-112.

Biddinger, G.R., and Gloss, S.P., 1984, The importance of trophic transfer in the bioaccumulation of chemical contaminants in aquatic ecosystems: Residue Reviews, v. 91, p. 103-145.

Bilby, R. E., and Likens, G. E., 1979, Effects of hydrologic fluctuations on the transport of fine particulate organic carbon in a small stream: Limnology and Oceanography, v. 24, no. 1, p. 69-75.

Birmingham, B C., and Colman, Brian, 1983, Potential phytotoxicity of diquat accumulated by aquatic plants and sediments, Water, Air, and Soil Pollution, v. 19, p. 123-131.

Blair, W.R., Olson, G.J., Brinckman, F.E., and Iverson, W.P., 1982, Accumulation and fate of tri-n-butyltin cation in estuarine bacteria: Microbial Ecology, v. 8, p. 241-251.

Bobra, A., Mackay, D., and Shiu, W.Y., 1979, Distribution of hydrocarbons among oil, water and vapor phases during oil dispersant toxicity tests: Bulletin of Environmental Contamination and Toxicology, v. 23, p. 558-565.

Boehm, P.D. , and Quinn, J.G., 1973, Solubilization of hydrocarbons by the dissolved organic matter in sea water: Geochimica et Cosmochimica Acta, v. 37, p. 2459-2477.

Bopp, R.F., Simpson, H.J., Olsen, C.R., and Kostyk, N., 1981, Polychlorinated biphenyls in sediments of the tidal Hudson River, New York: Environmental Science and Technology, v. 15, no. 2, p. 210-216.

Bopp, R.F., Simpson, H.J., Olsen, C.R., Trier, R.M., and Nostyk, N., 1982, Chlorinated hydrocarbons anbd radionuclide chronologies in sediments of the Hudson River and Estuary, New York: Environmental Science and Technology, v. 16, no. 10, p. 666-676.

Borighem, G., and Vereecken, J., 1978, Study of the biodegradation of phenol in river water: Ecological Modelling, v. 4, p. 51-59.

Bouchard, D.C., and Lavy, T.L., 1985, Hexazinone adsorption-desorption studies with soil and organic adsorbents: Journal of Environmental Quality, v. 14, no. 2, p. 181-186.

Bovey, R.W., Burnett, E., Richardson, C., Merkle, M.G., Baur, J.R., and Knisel, W.G., 1974, Occurrence of 2,4,5-T and picloram in surface runoff water in the blacklands of Texas: Journal of Environmental Quality, v. 3, no. 1, p. 61-64.

Bowman, B.T., and Sans, W.W., 1985a, Partitioning behavior of insecticides in soil-water systems: I. Adsorbent concentration effects: Journal of Environmental Quality, v. 14, no. 2, p. 265-269.

Bowman, B.T., and Sans, W.W., 1985b, Partitioning behavior of insecticides in soil-water systems: II. Desorption hysteresis effects: Journal of Environmental Quality, v. 14, no. 2, p. 270-273.

Boyle, E.A., Edmond, J.M., and Sholkovitz, E.R., 1977, The mechanism of iron removal in estuaries: Geochimica et Cosmochimica Acta, v. 41, p. 1313-1324.

Bradley, J.R., Sheets, T.J., and Jackson, M.D., 1972, DDT and toxaphene movement in surface water from cotton plots: Journal of Environmental Quality, v. 1, no. 1, p. 102-105.

Brooks, J.M., Wiesenburg, D.A., Burke, R.A., and Kennicutt, M.C., 1981, Gaseous and volatile hydrocarbon inputs from a subsurface oil spill in the Gulf of Mexico: Environmental Science and Technology, v. 15, no. 8, p. 951-959.

Brown, D.S., and Flagg, E.W., 1981, Empirical prediction of organic pollutant sorption in natural sediments: Journal of Environmental Quality, v. 10, no. 3, p. 382-386.

Brown, R.A., and Pancirov, R.J., 1979, Polynuclear aromatic hydrocarbons in Baltimore Canyon fish: Environmental Science and Technology, v. 13, no. 7, p. 878-879.

Brown, M.P., Werner, M.B., Sloan, R.J., and Simpson, K.W., 1985, Poly-chlorinated biphenyls in the Hudson River: Environmental Science and Technology, v. 19, no. 8, p. 656-661.

Buchel, K.H., 1983, Chemistry of pesticides: New York, John Wiley and Sons, Inc., 518 p.

Bunce, N.H., and Kumar, Y., 1978, An assessment of the impact of solar degradation of PCB's in the aquatic environment: Chemosphere, v. 2, p. 155-164.

Burkhard, L.P., Andren, A.W., and Armstrong, D.E., 1985, Estimation of vapor pressures for polychlorinated biphenyls: A comparison of eleven predictive methods: Environmental Science and Technology, v. 19, no. 6, p. 500-507.

Burns, N.M., and Rosa, F., 1980, In situ measurement of the settling velocity of organic carbon particles and 10 species of phytoplankton: Limnology and Oceanography, v. 25, no. 5, p. 855-864.

Buser, Hans-Rudolf, 1986, Polybrominated dibenzofurans and dibenzo-p-dioxins: Thermal reaction products of polybrominated diphenyl ether flame retardants: Environmental Science and Technology, v. 20, no. 4, p. 404-408.

Cadena, F., Eiceman, G.A., and Vandiver, V.J., 1984, Removal of volatile organic pollutants from rapid streams: Journal of the Water Pollution Control Federation, v. 56, no. 5, p. 460-463.

Call, D.J., Brooke, L.T., Kent, R.J., Poirier, S.H., Knuth, M.L., Shubat, P.J., and Slick, E.J., 1984, Toxicity, uptake, and elimination of the herbicides alachlor and dinoseb in freshwater fish: Journal of Environmental Quality, v. 13, no. 3, p. 493-498.

Callahan, M.A., Slimak, M.W., Gabel, N.W., May, I.P., Fowler, C.F., Freed, J.R., Jennings, P., Durfee, R.L., Whitmore, F.C., Maestri, B., Mabey, W.R., Holt, B.R., and Gould, C., 1979, Water-related environmental fate of 129 priority pollutants: U.S. Environmental Protection Agency, EPA-440/4-79-029a,b.

Campbell, J.R., and Luthy, R.G., 1985, Prediction of aromatic solute partition coefficients using the UNIFAC group contribution model: Environmental Science and Technology, v. 19, p. 980-985.

Campbell, J.R., Luthy, R.G., and Carrondo, M.J.T., 1983, Measurement and prediction of distribution coefficients for wastewater aromatic solutes: Environmental Science and Technology, v. 17, no. 10, 582-589.

Canton, J.H., Greve, P.A., Slooff, W., and van Esch, G.J., 1975, Toxicity, accumulation and elimination studies of hexachlorocyclohexane (HCH) with freshwater organisms of different trophic levels: Water Research, v. 9, p. 1163-1169.

Canton, J.H., van Esch, G.J., Greve, P.A., and van Hellemond, A.B.A.M., 1977, Accumulation and elimination of hexachlorocyclohexane (HCH) by the marine algae *Chlamydomonas* and *Dunaliella*: Water Research, v. 11, p. 111-115.

Carlson, D.J., 1983, Dissolved organic materials in surface microlayers: Temporal and spatial variability and relation to sea state: Limnology and Oceanography, v. 28, no. 3, p. 415-431.

Caron, G., Suffet, I.H., and Belton, T., 1985, Effect of dissolved organic carbon on the environmental distribution of nonpolar organic compounds: Chemosphere, v. 14, no. 8, p. 993-1000.

Carranza de Storani, M.M., Rosas, S.B., and Ghittoni, N.E., 1986, Alterations in lipid composition of membranes from *Rhizobium meliloti* exposed to parathion: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 267-270.

Carter, C.W., and Suffet, I.H., 1982, Binding of DDT to dissolved humic materials: Environmental Science and Technology, v. 16, no. 11, p. 735-740.

Casserly, D.M., Davis, E.M., Downs, T.D., and Guthrie, R.K., 1983, Sorption of organics by *Selenastrum capricornutum*: Water Research, v. 17, no. 11, p. 1591-1594.

Champion, D.R., and Olsen, S.R., 1971, Adsorption of DDT on solid particles: Soil Science Society of America Proceedings, v. 35, p. 887-891.

Chapman, B.M., 1982, Numerical simulation of the transport and speciation of nonconservative chemical reactants in rivers: Water Resources Research, v. 18, no. 1, p. 155-167.

Chase, R.R.P., 1979, Settling behavior of natural organic particulates: Limnology and Oceanography, v. 24, no. 3, p. 417-426.

Chau, A.S.Y., and Lee, H.B., 1980, Analytical Reference Materials. III. Preparation and homogeneity test of large quantities of wet and dry sediment reference materials for long term polychlorinated biphenyl quality control studies: Journal of the Official Association of Analytical Chemists, v. 63, no. 5, p. 947-951.

Chiou, C.T., 1981, Partition coefficient and water solubility in environmental chemistry: in Saxena, J., and Fisher, F. Eds., Hazard Assessment of Chemicals: Current Developments, New York Academic Press, v. 1, p. 117-153.

Chiou, C.T., 1985, Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors: Environmental Science and Technology, v. 19, no. 1, p. 57-62.

Chiou, C.T., and Freed, V.H., 1977, Environmental Science and Technology, v. 11, p. 1220.

Chiou, C.T., Freed, V.H., Peters, L.J., and Kohnert, R.L., 1980, Evaporation of solutes from water: Environment International, v. 3, p. 231-236.

Chiou, C.T., Freed, V.H., Schmedding, D.W., and Kohnert, R.L., 1977, Partition coefficient and bioaccumulation of selected organic chemicals: Environmental Science and Technology, v. 11, no. 5, p. 475-478.

Chiou, C.T., Kohnert, R.L., Freed, V.H., and Tonkyn, R.G., 1983a, Predictions of evaporative loss rates of solutes in stagnant and turbulent waters in relation to rates of reference materials: Environment International, v. 9, p. 13-17.

Chiou, C.T., Malcolm, R.L., Brinton, T.I., and Kile, D.E., 1986, Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids: Environmental Science and Technology, v. 20, no. 5, p. 502-508.

Chiou, C.T., and Manes, M., 1980, On the validity of the codistillation model for the evaporation of pesticides and other solutes from water solution: Environmental Science and Technology, v. 14, p. 1253-1254.

Chiou, C.T., Peters, L.J., and Freed, V.H., 1979, Physical concept of soil-water equilibria for nonionic organic compounds: Science, v. 206, p. 831-832.

Chiou, C.T., Peters, L.J., and Freed, V.H., 1981a, Science, v. 213, p. 684.

Chiou, C.T., Porter, P.E., and Schmedding, D.W., 1983b, Partition equilibria of nonionic organic compounds between soil organic matter and water: Environmental Science and Technology, v. 17, no. 4, p.227-231.

Chiou, C.T., Porter, P.E., and Shoup, T.D., 1984, Environmental Science and Technology, v. 18, no. 4, p. 295.

Chiou, C.T., Schmedding, D.W., and Block, J.H., 1981b, Correlation of water solubility with octanol-water partition coefficient: Journal of the Pharmaceutical Sciences, v. 70, no. 10, p. 1176-1177.

Chiou, C.T., Schmedding, D.W., Block, J.H., and Manes, M., 1982a, Substituent contribution to the partition coefficients of substituted benzenes in solvent-water mixtures: Journal of Pharmaceutical Sciences, v. 71, no. 11, p. 1307-1309.

Chiou, C.T., Schmedding, D.W., and Manes, M., 1982b, Partitioning of organic compounds in octanol-water systems: Environmental Science and Technology, v. 16, no. 1, p. 4-10.

Chiou, C.T., and Shoup, T.D., 1985, Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity: Environmental Science and Technology, v. 19, no. 12, p. 1196-1200.

Chiou, C.T., Shoup, T.D., and Porter, P.E., 1985, Mechanistic roles of soil humus and minerals in the sorption of nonionic organic compounds from aqueous and organic solutions: Organic Geochemistry, v. 8, no. 1, p. 9-14.

Choi, W.W., and Chen, K.Y., 1976, Association of chlorinated hydrocarbons with fine particles and humic substances in nearshore surficial sediments: Environmental Science and Technology, v. 10, no. 8, p. 782-786.

Christman, R.F., and Gjessing, E.T., 1983, Priorities in humic research, in Christman, R. and Gjessing, E., eds.: Aquatic and Terrestrial Humic Materials, Ann Arbor Science Publishers, p. 517-528.

Chu, J.P., and Kirsch, E.J., 1972, Metabolism of pentachlorophenol by an axenic bacterial culture: Applied Microbiology, v. 23, no. 5, p. 1033-1035.

Clark, J.R., Patrick, J.M., Moore, J.C., and Forester, J., 1986, Accumulation of sediment-bound PCBs by fiddler crabs: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 571-578.

Clayton, J.R., Pavlou, S.P., and Breitner, N. F., 1977, PCB's in coastal marine zooplankton; Bioaccumulation by equilibrium partitioning: Environmental Science and Technology, v. 11, no. 7, p. 676-682.

Coates, J.T., and Elzerman, A.W., 1986, Desorption kinetics for selected PCB congeners from river sediments: Journal of Contaminant Hydrology, v. 1, p. 191-210.

Cole, R.H., Frederick, R.E., Healy, R.P., and Rolan, R.G., 1984, Preliminary findings of the priority pollutant monitoring project of the nationwide urban runoff program: Journal of the Water Pollution Control Federation, v. 56, no. 7, p. 898-908.

Collier, T.K., Gruger, E.H., and Varanasi, Usha, 1985, Effect of Aroclor 1254 on the biological fate of 2,6-dimethylnaphthalene in Coho salmon (*Oncorhynchus kisutch*): Bulletin of Environmental Contamination and Toxicology, v. 34, p. 114-120.

Connolly, J.P., Armstrong, N.E., and Miksad, R.W., 1983, Adsorption of hydrophobic pollutants in estuaries: Journal of the Environmental Engineering Division, American Society of Civil Engineers, v. 109, no. EE1, p. 17-35.

Connor, M.S., 1984a, Fish/sediment concentration ratios for organic compounds: Environmental Science and Technology, v. 18, no. 1, p. 31-35.

Connor, M.S., 1984b, Comparison of the carcinogenic risks from fish vs. groundwater contamination by organic compounds: Environmental Science and Technology, v. 18, no. 8, p. 628-631.

Conrad, Ralf, and Seiler, Wolfgang, 1985, Characteristics of abiological carbon monoxide formation from soil organic matter, humic acids, and phenolic compounds: Environmental Science and Technology, v. 19, no. 12, p. 1165-1169.

Cossa, D., Picard-Berube, M., and Gouygou, J.P., 1983, Polynuclear aromatic hydrocarbons in mussels from the Estuary and northwestern Gulf of St. Lawrence, Canada: Bulletin of Environmental Contamination and Toxicology, v. 31, p. 41-47.

Criddle, C.S., McCarty, P.L., Elliott, M.C., and Barker, J.F., 1986, Reduction of hexachloroethane to tetrachloroethylene in groundwater: Journal of Contaminant Hydrology, v. 1, p. 133-142.

Crosby, D.G., and Wong, A.S., 1977, Environmental degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD): Science, vol. 195, p. 1337-1338.

Curl, R.L., and Keoleian, G.A., 1984, Implicit-adsorbate model for apparent anomalies with organic adsorption on natural adsorbents: Environmental Science and Technology, v. 18, no. 12, p. 916-922.

Czuczwa, J.M., McVeety, B.D., and Hites, R.A., 1984, Polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments from Siskiwit Lake, Isle Royale: Science, v. 226, no. 4674, p. 568-569.

Dahchour, A., Bitton, G., Coste, C.M., and Bastide, J., 1986, Degradation of the herbicide propanil in distilled water: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 556-562.

Dao, T.H., Lavy, T.L., and Dragun, J., 1983, Rationale of the solvent selection for soil extraction of pesticide residues: Residue Reviews, v. 87, p. 91-104.

Davani, B., Ingram, J., Gardea, J.L., and Eiceman, G.A., 1986, Organic compounds in soils and sediments from unlined waste disposal pits for natural gas production and processing: Water, Air, and Soil Pollution, v. 27, p. 267-276.

Davis, J.A., 1982, Adsorption of natural dissolved organic matter at the oxide/water interface: Geochimica et Cosmochimica Acta, v. 46, p. 2381-2393.

DeLaune, R.D., Gambrell, R.P., and Reddy, K.S., 1983, Fate of pentachlorophenol in estuarine sediment: Environmental Pollution (Series B), v. 6, p. 297-308.

DeLaune, R.D., and Salinas, L.M., 1985, Fate of 2,4-D entering a freshwater aquatic environment: Bulletin of Environmental Contamination and Toxicology, v. 35, p. 564-568.

Delfino, J.J., 1979, Toxic substances in the Great Lakes: Environmental Science and Technology, v. 13, no. 12, p. 1462-1468.

DePinto, J.V., Young, T.C., and Martin, S.C., 1980, Aquatic sediments: Journal of the Water Pollution Control Federation, v. 52, no. 6, p. 1656-1670.

DePinto, J.V., Young, T.C., and Martin, S.C., 1981, Aquatic sediments: Journal of the Water Pollution Control Federation, v. 53, no. 6, p. 999-1007.

DePinto, J.V., Young, T.C., and Martin, S.C., 1982, Aquatic sediments: Journal of the Water Pollution Control Federation, V. 54, no. 6, p. 855-862.

DePinto, J.V., Young, T.C., and Martin, S.C., 1983, Aquatic sediments: Journal of the Water Pollution Control Federation, v. 55, no. 6, p. 822-829.

DeVault, D.S., 1985, Contaminants in fish from Great Lakes harbors and tributary mouths: Archives of Environmental Contamination and Toxicology, v. 14, p. 587-594.

Dhamotharan, S., Gulliver, J.S., and Stefan, H.G., 1981, Unsteady one-dimensional settling of suspended sediment: Water Resources Research, v. 17, no. 4, p. 1125-1132.

Dietrich, A.M., Millington, D.S., and Christman, R.F., 1983, Specific identification of organic pollutants in Haw River water using gas chromatography/mass spectrometry: Raleigh, North Carolina, Water Resources Research Institute of the University of North Carolina, Report 206, 91 p.

Dietrich, W.E.,1982, Settling velocity of natural particles: Water Resources Research, v. 18, no. 6, p. 1615-1626.

Dilling, W.L., 1977, Interphase transfer processes. II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions: Environmental Science and Technology, v. 11, no. 4, p. 405-409.

Dilling, W.L., Bredeweg, C.J., and Tefertiller, N.B., 1976, Organic photochemistry: Simulated atmospheric photodecomposition rates of methylene chloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other compounds: Environmental Science and Technology, v. 10, no. 4, p. 351-356.

Dilling, W.L., Tefertiller, N.B., and Kallos, G.J., 1975, Evaporation rates and reactivities of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions: Environmental Science and Technology, v. 9, no. 9, p. 833-838.

Di Salvo, L.H., Guard, H.E., and Hunter, Leon, 1975, Tissue hydrocarbon burden of mussels as potential monitor of environmental hydrocarbon insult: Environmental Science and Technology, v. 9, no. 3, p. 247-251.

Di Toro, D.M., and Horzempa, L.M., 1982, Reversible and resistant components of PCB adsorption-desorption isotherms: Environmental Science and Technology, v. 16, no. 9, p. 592-602.

Di Toro, D. M., Horzempa, L. M., Casey, M. M., and Richardson, W., 1982, Reversible and resistant components of PCB adsorption-desorption; Adsorbent concentration effects: Journal of Great Lakes Research, v. 8, no. 2, p. 336-349.

Di Toro, D.M., Jeris, J.S., and Ciarcia, Daniel, 1985, Diffusion and partitioning of hexachlorobiphenyl in sediments: Environmental Science and Technology, v. 19, no. 12, p. 1169-1175.

Drake, E.H., and Motto, H.L., 1982, An analysis of the effect of clay and organic matter content on the cation exchange capacity of New Jersey soils: Soil Science, v. 133, no. 5, p. 281-288.

Drifmeyer, J.E., Rosenberg, C.L., and Heywood, M.A., 1980, Chlordecone (kepone) accumulation on estuarine plant detritus: Bulletin of Environmental Contamination and Toxicology, v. 24, p. 364-368.

Drivas, P.J., 1982, Calculation of evaporative emissions from multicomponent liquid spills: Environmental Science and Technology, v. 11, no. 4, p. 405-409.

Duce, R.A., Quinn, J.G., Olney, C.E., Piotrowicz, S.R., Ray, B.J., and Wade, T.L., 1972, Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island: Science, v. 176, p. 161-163.

Duinker, J.C., 1980, Suspended matter in estuaries: Adsorption and desorption processes, in Olausson, E. and Cato, I., eds.: Chemistry and Biochemistry of Estuaries, John Wiley and Sons, New York, p. 121-145.

Duinker, J.C., Hillebrand, M.T.J., Palmork, K.H., and Wilhelmsen, S., 1980, An evaluation of existing methods for quantitation of polychlorinated biphenyls in environmental samples and suggestions for an improved method based on measurement of individual components: Bulletin of Environmental Contamination and Toxicology, v. 25, p. 956-964.

Dyer, K.R., 1972, Sedimentation in estuaries, in Barnes, R., and Green, J., eds.: The Estuarine Environment, Applied Science Publishers, p. 10-33.

Dzombak, D.A., and Luthy, R.G., 1984, Estimating adsorption of polycyclic aromatic hydrocarbons on soils: Soil Science, v. 137, no. 5, p. 297.

Eberhardt, L.L., Gilbert, R.O., Hollister, H.L., and Thomas, J.M., 1976, Sampling for contaminants in ecological systems: Environmental Science and Technology, v. 10, no. 9, p. 917-925.

Eckert, J.M., and Sholkovitz, E.R., 1976, The flocculation of iron, aluminum and humates from river water by electrolytes: Geochimica et Cosmochimica Acta, v. 40, p. 847-848.

Edwards, N.T., 1983, Polycyclic aromatic hydrocarbons (PAHs) in the terrestrial environment- A review: Journal of Environmental Quality, v. 12, no. 4, p. 427-441.

Edzwald, J.K., Upchurch, J.B., and O'Melia, C.R., 1974, Coagulation in estuaries: Environmental Science and Technology, v. 8, no. 1, p. 58-63.

Eganhouse, R.P., and Kaplan, I.R., 1982, Extractable organic matter in municipal wastewaters. 1. Petroleum hydrocarbons: Temporal variations and mass emission rates to the ocean: Environmental Science and Technology, v. 16, no. 3, p. 180-186.

Eichers, T.R., Andrilenas, P.A., and Anderson, T.W., 1978, Farmers' use of pesticides in 1976: U.S. Department of Agriculture, Agricultural Economic Report 418, 58 p.

Eichers, T.R., Andrilenas, P.A., Blake, Helen, Jenkins, Robert, and Fox, A.S., 1970, Quantities of pesticides used by farmers in 1966: U.S. Department of Agriculture, Agricultural Economic Report 179, 61 p.

Eichholz, G.G., Craft, T.F., and Galli, A.N., 1967, Trace element fractionation by suspended matter in water: Geochimica et Cosmochimica Acta, v. 31, p. 737-745.

Eidt, D.C., Sosiak, A.J., and Mallet, V.N., 1984, Partitioning and short-term persistence of fenitrothion in New Brunswick (Canada) headwater streams: Archives of Environmental Contamination and Toxicology, v. 13, p. 43-52.

Eisenreich, S.J., Elzerman, A.W., and Armstrong, D.E., 1978, Enrichment of micronutrients, heavy metals, and chlorinated hydrocarbons in wind-generated lake foam: Environmental Science and Technology, v. 12, no. 4, p. 413-417.

Eisenreich, S.J., Hollod, G.J., and Johnson, T.C., 1979, Accumulation of PCBs in surficial Lake Superior sediments. Atmospheric deposition: Environmental Science and Technology, v. 13, no. 5, p. 569-573.

Eisenreich, S.J., Hollod, G.J., Johnson, T.C., and Evans, J., 1980, Polychlorinated biphenyl and other microcontaminant-sediment interactions in Lake Superior, in Baker, R., ed., Contaminants and sediments, Volume 1: Ann Arbor, Michigan, Ann Arbor Science Publishers, p. 67-94.

Eisma, D., 1981, Suspended matter as a carrier for pollutants in estuaries and the sea, in Geyer, R., ed., Marine Environmental Pollution, part 2 Dumping and Mining: Elsevier Scientific Publishing Co., p. 281-295.

Elder, D.L., and Bowden, S.W., 1977, Polychlorinated biphenyls: Penetration into the deep ocean by zooplankton fecal pellet transport: Science, v. 197, p. 459-461.

Elder, J.F. and Mattraw, H.C., Jr., 1984, Accumulation of trace elements, pesticides, and polychlorinated biphenyls in sediments and the clam *Corbicula manilensis* of the Apalachicola River, Florida: Archives of Environmental Contamination and Toxicology, v. 13, p. 453-469.

El-Dib, M.A., and Aly, O.A., 1976a, Persistence of some phenylamide pesticides in the aquatic environment - I. Hydrolysis: Water Research, v. 10, p. 1047-1050.

El-Dib, M.A., and Aly, O.A., 1976b, Persistence of some phenylamide pesticides in the aquatic environment - II. Adsorption on clay minerals: Water Research, v. 10, p. 1051-1053.

El-Dib, M.A., and Aly, O.A., 1976c, Persistence of some phenylamide pesticides in the aquatic environment - III. Biological Degradation: Water Research, v. 10, p. 1055-1059.

Engelhardt, G., and Wallnofer, P.R., 1975, The microbial metabolism of di-n-butyl phthalate and related dialkyl phthalates: Bulletin of Environmental Contamination and Toxicology, v. 13. no. 3, p. 342-347.

Environmental Protection Agency, 1978, Environmental pathways of selected chemicals in freshwater systems: Part II Laboratory studies: EPA-600/7-78-074, 404 p.

Environmental Protection Agency, 1979, Water related fate of 129 priority pollutants, volumes I and II: EPA-440/4-79-029a,b.

Environmental Protection Agency, 1981, Aquatic fate process data for organic priority pollutants: EPA-440/4-81-014, 432 p.

Environmental Protection Agency, 1982, Treatability manual: Volume I, Treatability Data: EPA-600/2-82-001a.

Ertel, J.R., and Hedges, J.I., 1983, Bulk chemical and spectroscopic properties of marine and terrestrial humic acids, melanoidins and catechol-based synthetic polymers: in Christman, R., and Gjessing, E., eds., Aquatic and Terrestrial Humic Materials: Ann Arbor Science Publishers, Ann Arbor, Michigan, p. 143-163.

Fairbanks, B.C., O'Connor, G.A., and Smith, S.E., 1985, Fate of di-2-(ethylhexyl)phthalate in three sludge-amended New Mexico soils: Journal of Environmental Quality, v. 14, no. 4, p. 479-483.

Farrington, J.W., Goldberg, E.D., Risebrough, R.W., Martin, J.H., and Bowen, V.T., 1983, U.S. "mussel watch" 1976-1978: An overview of the trace-metal, DDE, PCB, hydrocarbon, and artificial radionuclide data: Environmental Science and Technology, v. 17, no. 8, p. 490-496.

Faust, S.D., and Suffet, I.H., 1966, Recovery, separation, and identification of organic pesticides from natural and potable waters: Residue Reviews, v. 15, p. 45-111.

Feltz, H.R., 1980, Significance of bottom material data in evaluating water quality, in Baker, R., ed., Contaminants and sediments, Volume 1: Ann Arbor, Michigan, Ann Arbor Science Publishers, p. 271-287.

Feng, T.H., 1972, Bottom deposits: Journal of the Water Pollution Control Federation, v. 44, no. 6, p. 1092-1101.

Ferrario, J.B., Lawler, G.C., DeLeon, I.R., and Laseter, J.L., 1985, Volatile organic pollutants in biota and sediments of Lake Pontchartrain: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 246-255.

Fishel, D.K., 1984, Water-quality and chemical loads of the Susquehanna River at Harrisburg, Pennsylvania, April 1980 to March 1981: U. S. Geological Survey Water-Resources Investigations Report 83-4164, 90 p.

Fisher, J.S., Pickral, J., and Odum, W.E., 1979, Organic detritus particles: Initiation of motion criteria: Limnology and Oceanography, v. 24, no. 3, p. 529-532.

Foess, G.W. and Feng, T.H., 1971, Bottom deposits: Journal of the Water Pollution Control Federation, v. 43, no. 6, p. 1257-1266.

Forstner, U., and Wittman, G., 1979, Metal pollution in the aquatic environment: New York, Springer-Verlag, 486 p.

Fortner, A.R. and Sick, L.V., 1985, Simultaneous accumulations of naphthalene, a PCB mixture, and benzo(a)pyrene, by the oyster, *Crassostrea virginica*: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 256-264.

Fox, L.E., 1983a, The removal of dissolved humic acid during estuarine mixing: Estuarine, Coastal and Shelf Science, v. 16, p. 431-440.

Fox, L.E., 1983b, Geochemistry of humic acid during estuarine mixing, in Christman, R., and Gjessing, E., eds., Aquatic and Terrestrial Humic Materials: Ann Arbor Science Publishers, Ann Arbor, Michigan, p. 407-427.

Frank, R., Braun, H.E., Van Hove Holdrinet, M., Sirons, G.J., and Ripley, B.D., 1982, Agriculture and water quality in the Canadian Great Lakes basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977: Journal of Environmental Quality, v. 11, no. 3, p. 497-505.

Frank, R., Thomas, R.L., Braun, H.E., Gross, D.L., and Davies, T.T., 1981, Organochlorine insecticides and PCB in surficial sediments of Lake Michigan (1975): Journal of Great Lakes Research, v. 7, no. 1, p. 42-50.

Frank, R., Thomas, R.L., Braun, H.E., Rasper, J., and Dawson, R., 1980a, Organochlorine insecticides and PCB in the surficial sediments of Lake Superior (1973): Journal of Great Lakes Research, v. 6, no. 2, p. 113-120.

Frank, R., Thomas, R.L., Holdrinet, M., Kemp, A.L.W., and Braun, H.E., 1979, Organochlorine insecticides and PCB in surficial sediments (1968) and sediment cores (1976) from Lake Ontario: Journal of Great Lakes Research, v. 5, no. 1, p. 18-27.

Frank, R., Thomas, R.L., Holdrinet, M.V.H., and Damiani, V., 1980b, PCB residues in bottom sediments collected from the Bay of Quinte, Lake Ontario, 1972-73: Journal of Great Lakes Research, v. 6, no. 4, p. 371-376.

Fredenslund, A., Jones, R.L., and Prausnitz, J.M., 1975, Group-contribution estimation of activity coefficients in nonideal liquid mixtures: American Institute of Chemical Engineering Journal, v. 21, no. 6, p. 1086-1099.

Freeman, D.H., and Cheung, L.S., 1981, A gel partitioning model for organic desorption from a pond sediment: Science, v. 214, p. 790-792.

Frissel, M.J., and Bolt, G.H., 1962, Interaction between certain ionizable organic compounds (herbicides) and clay minerals: Soil Science, v. 94, p. 284-291.

Fu, Jaw-Kwei, and Luthy, R.G., 1986, Effect of organic solvent on sorption of aromatic solutes onto soils: Journal of Environmental Engineering, v. 112, no. 2, p. 346-366.

Fuhrer, G.J., 1984, Chemical analyses of elutriates, native water, and bottom material from the Chetco, Rogue, and Columbia Rivers in western Oregon: U. S. Geological Survey Open-File Report 84-133, 57 p.

Fuhrer, G.J., and Rinella, F.A., 1983, Analyses of elutriates, native water, and bottom material in selected rivers and estuaries in western Oregon and Washington: U.S. Geological Survey Open-File Report 82-922, 147 p.

Gambrell, R.P., Reddy, C.N., Collard, V., Green, G., and Patrick, W.H. Jr., 1984, The recovery of DDT, kepone, and permethrin added to soil and sediment suspensions incubated under controlled redox potential and pH conditions: Journal of the Water Pollution Control Federation, v. 56, no. 2, p. 174-182.

Gardner, W.S., Lee, R.F., Tenore, K.R., and Smith, L.W., 1979, Degradation of selected polycyclic aromatic hydrocarbons in coastal sediments: Importance of microbes and polychaete worms: Water, Air, and Soil Pollution, v. 11, p. 339-347.

Garten, C.T., and Trabalka, J.R., 1983, Evaluation of models for predicting terrestrial food chain behavior of xenobiotics: Environmental Science and Technology, v. 17, no. 10, p. 590-595.

Gauger, W.K., MacDonald, J.M., Adrian, N.R., Matthees, D.P., and Walgenbach, D.D., 1986, Characterization of a streptomycete growing on organophosphate and carbamate insecticides: Archives of Environmental Contamination and Toxicology, v. 15, p. 137-141.

Gay, F.B. and Frimpter, M.H., 1985, Distribution of polychlorinated biphenyls in the Housatonic River and adjacent aquifer, Massachusetts: U.S. Geological Survey Water-Supply Paper 2266, 26 p.

Giam, C.S., Chan, H.S., Neff, G.S., and Atlas, E.L., 1978, Phthalate ester plasticizers: A new class of marine pollutant: Science, v. 199, p. 419-421.

Gibbs, R.J., 1977, Clay mineral segregation in the marine environment: Journal of Sediment Petrology, v. 47, p. 237-243.

Gibson, W.P., and Burns, R.G., 1977, The breakdown of malathion in soil and soil components: Microbial Ecology, v. 3, p. 219-230.

Gillette, Robert, 1971, DDT: In field and courtroom a persistent pesticide lives on: Science, v. 174, p. 1108-1110.

Gilliom R.J., 1985, Pesticides in rivers of the United States; in National Water Summary 1984: U.S. Geological Survey Water Supply Paper 2275, p. 85-92.

Gilliom, R.J., Alexander, R.B., and Smith, R.A., 1985, Pesticides in the Nation's rivers, 1975-1980, and implications for future monitoring: U. S. Geological Survey Water-Supply Paper 2271, 26 p.

Given, C.J., and Dierberg, F.E., 1985, Effect of pH on the rate of aldicarb hydrolysis: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 627-633.

Glooschenko, W.A., Capocianco, J., Coburn, J., and Glooschenko, V., 1981, Geochemical distribution of trace metals and organchlorine contaminants of a Lake Ontario shoreline marsh: Water, Air, and Soil Pollution, v. 15, p. 197-213.

Glotfelty, D.E., Taylor, A.W., Isensee, A.R., Jersey, J., and Glenn, S., 1984, Atrazine and simazine movement to Wye River Estuary: Journal of Environmental Quality, v. 13, no. 1, p. 115-121.

Gmehling, Jurgen, Rasmussen, Peter, and Fredenslund, Aage, 1982, Vapor-liquid equilibria by UNIFAC group contribution. Revision and extension. 2: Industrial Engineering Chemical Process Design and Development, v. 21, p. 118-127.

Goerlitz, D.F., and Law, L.M., 1974a, Determination of chlorinated insecticides in suspended sediment and bottom material: Journal of the Association of Analytical Chemists, v. 57, no. 1, p. 176-181.

Goerlitz, D.F., and Law, L.M., 1974b, Distribution of chlorinated hydrocarbons in stream bottom material: Journal of Research U.S. Geological Survey, v. 2, no. 5, p. 541-543.

Gooch, J.A., and Hamdy, M.K., 1983, Uptake and concentration factor of Arochlor 1254 in aquatic organisms: Bulletin of Environmental Contamination and Toxicology, v. 31, p. 445-452.

Grant, B.F., 1976, Endrin toxicity and distribution in freshwater: A review: Bulletin of Environmental Contamination and Toxicology, v. 15, no. 3, p. 283-290.

Graveel, J.G., Sommers, L.E., and Nelson, D.W., 1986, Decomposition of benzidine, naphtylamine, and p-toluidine in soils: Journal of Environmental Quality, v. 15, no. 1, p. 53-59.

Green, R.E., Goswami, K.P., Mukhtar, M., and Young, H.Y., 1977, Herbicides from cropped watersheds in stream and estuarine sediments in Hawaii: Journal of Environmental Quality, v. 6, no. 2, p. 145-154.

Green, T., and Houk, D.F., 1979, The removal of organic surface films by rain: Limnology and Oceanography, v. 24, no. 5, p. 966-970.

Green, W.J., Lee, G.F., Jones, R.A., and Palit, T., 1983, Interaction of clay soils with water and organic solvents: Implications for the disposal of hazardous wastes: Environmental Science and Technology, v. 17, no. 5, p. 278-282.

Greenberg, M., Anderson, R., Keene, J., Kennedy, A., and Page, G., 1982, Empirical test of the association between gross contamination of wells with toxic substances and surrounding land use: Environmental Science and Technology, v. 16, no. 1, p. 14-19.

Greig, R.A., Schurman, S., Pereira, J., and Naples, P., 1983, Metals and PCB concentrations in windowpane flounder from Long Island Sound: Bulletin of Environmental Contamination and Toxicology, v. 31, p. 257-262.

Greig, R.A., and Sennefelder, G., 1985, Metals and PCB concentrations in mussels from Long Island Sound: Bulletin of Environmental Contamination and Toxicology, v. 35, p. 331-334.

Grimes, D.J., and Morrison, S.M., 1975, Bacterial bioconcentration of chlorinated hydrocarbon insecticides from aqueous systems: Microbial Ecology, v. 2, p. 43-59.

Grover, R., and Hance, R.J., 1970, Effect of ratio of soil to water on adsorption of linuron and atrazine: Soil Science, v. 109, no. 2, p. 136-138.

Gschwend, P.M., and Wu, S., 1985, On the constancy of sediment- water partition coefficients of hydrophobic organic pollutants: Environmental Science and Technology, v. 19, no. 1, p. 90-96.

Gunkel, G., and Streit, B., 1980, Mechanisms of bioaccumulation of a herbicide (atrazine, s-triazine) in a freshwater mollusc (Ancylus fluviatilis mull.) and a fish (Coregonus fera jurine): Water Research, v. 14, p. 1573-1584.

Guthrie, M.A., Kirsch, E.J., Wukasch, R.F., and Grady, C.P.L., 1984, Pentachlorophenol biodegradation - II: Water Research, v. 18, no. 4, p. 451-461.

Haines, T.A., 1983, Organochlorine residues in Brook Trout from remote lakes in the northeastern United States: Water, Air, and Soil Pollution, v. 20, p. 47-54.

Haley, T.J., 1984, Pentachlorobiphenyls: Dangerous properties of industrial materials report, v. 4, no. 6, p. 2-17.

Hamaker, J.W., 1975, The interpretation of soil leaching experiments, in Haque, R., and Freed, V., eds., Environmental Dynamics of Pesticides: Plenum Press Publishers, p. 115-133.

Hamaker, J.W., and Thompson, J.M., 1972, Adsorption, in Goring, C., and Hamaker, J., eds., Organic Chemicals in the Soil Environment: Marcel Dekker Inc., v. 1, p. 51-132.

Hamelink, J.L., Waybrant, R.C., and Ball, R.C., 1971, A proposal: Exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments: Transactions of the American Fisheries Society, v. 100, p. 207-211.

Hansch, C., Quinlan, J.E., and Lawrence, G.L., 1968, The linear free-energy relationship between partition coefficients and the aqueous solubility of organic liquids: Journal of Organic Chemistry, v. 33, no. 1, p. 347-350.

Haque, R., and Freed, V.H., 1974, Behavior of pesticides in the environment: Residue Reviews, v. 52, p. 89-111.

Haque, R., Schmedding, D.W., and Freed, V.H., 1974, Aqueous solubility, adsorption, and vapor behavior of polychlorinated biphenyl Aroclor 1254: Environmental Science and Technology, v. 8, no. 2, p. 139-142.

Harris, C.R., and Miles, J.R.W., 1975, Pesticide residues in the Great Lakes region of Canada: Residue Reviews, v. 57, p. 27-81.

Harrison, R.M., Perry, R., and Wellings, R.A., 1975, Polynuclear aromatic hydrocarbons in raw, potable and waste waters: Water Research, v. 9, p. 331-346.

Harrold, D.E., and Young, J.C., 1982, Extraction of priority pollutants from solids: Journal of the Environmental Engineering Division, American Society of Civil Engineers, v. 108, no. EE6, p. 1211-1227.

SELECTED REFERENCES--Continued

Hassett, J.J., 1980, Sorption properties of sediments and energy related pollutants: U.S. Environmental Protection Agency, EPA-600/3-80-041, 132 p.

Hassett, J.P., and Anderson, M.A., 1979, Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems: Environmental Science and Technology, v. 13, no. 12,, p. 1526-1529.

Hassett, J.P., and Anderson M.A., 1982, Effects of dissolved organic matter on adsorption of hydrophobic organic compounds by river- and sewage-borne particles: Water Research, v. 16, p. 681-686.

Hassett, J.J., Banwart, W.L., and Griffin, R.A., 1983, Correlation of compound properties with sorption characteristics of nonpolar compounds by soils and sediments: concepts and limitations, in Francis, C., and Auerbach, S., eds., Environment and Solid Wastes: Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, p. 161-178.

Hassett, J.P., Means, J.C., Banwart, W.L., Wood, S.G., Ali, S., and Khan, A., 1980, Sorption of dibenzothiophene by soils and sediments: Journal of Environmental Quality, v. 9, no. 2, p. 184-186.

Hattula, M.L., 1974, Some aspects of the recovery of chlorinated residues (DDT-type compounds and PCB) from fish tissue by using different extraction methods: Bulletin of Environmental Contamination and Toxicology, v. 12, no. 3, p. 301-307.

Hayes, M.H.B., Pick, M.E., and Toms, B.A., 1975, Interactions between clay minerals and bipyridylium herbicides: Residue Reviews, v. 57, p. 1-25.

Heit, Merrill, 1979, Concentrations of benzo(a)pyrene in the sediments of six Western United States lakes: Water, Air, and Soil Pollution, v. 11, p. 447-454.

Heit, Merrill, 1985, The relationship of a coal fired power plant to the levels of polycyclic aromatic hydrocarbons (PAH) in the sediment of Cayuga Lake: Water, Air, and Soil Pollution, v. 24, p. 41-61.

Heit, Merrill, Klusek, Catherine, and Baron, Jill, 1984, Evidence of deposition of anthropogenic pollutants in remote Rocky Mountain lakes: Water, Air, and Soil Pollution, v. 22, p. 403-416.

Heit, Merrill, Klusek, C.S., and Miller, K.M., 1980, Trace element, radionuclide, and polynuclear aromatic hydrocarbon concentrations in Unionidae mussels from northern Lake George: Environmental Science and Technology, v. 14, no. 4, p. 465-468.

Heit, M., Tan, Y., Klusek, C., and Burke, J.C., 1981, Anthropogenic trace elements and polycyclic aromatic hydrocarbon levels in sediment cores from two lakes in the Adirondack acid lake region: Water, Air, and Soil Pollution, v. 15, p. 441-464.

Helling, C.S., 1976, Dinitroaniline herbicides in soils: Journal of Environmental Quality, v. 5, no. 1, p. 1-15.

Helling, C.S., Isensee, A.R., Woolson, E.A., Ensor, P.D.J., Jones, G.E., Plimmer, J.R., and Kearney, P.C., 1973, Chlorodioxins in pesticides, soils, and plants: Journal of Environmental Quality, v. 2, no. 2, p. 171-178.

Helsel, D.R., 1986, A review of bottom materials techniques: U.S. Geological Survey, in review.

Helsel, D.R., and Koltun, G.F., 1986, An evaluation of size-distribution effects and laboratory precision in the analysis of bottom materials: U.S. Geological Survey Water-Supply Paper __, in review.

Helwig, D.D., and Hora, M.E., 1983, Polychlorinated biphenyl, mercury, and cadmium concentrations in Minnesota smapping turtles: Bulletin of Environmental Contamination and Toxicology, v. 30, p. 186-190.

Helz, G.R., and Hsu, R.Y., 1978, Volatile chloro- and bromocarbons in coastal waters: Limnology and Oceanography, v. 23, no. 5, p. 858-869.

Herbes, S.E., 1977, Partitioning of polycyclic aromatic hydrocarbons between dissolved and particulate phases in natural waters: Water Research, v. 11, p. 493-496.

Hermann, R.B., 1972, Theory of hydrophobic bonding. II. The correlation of hydrocarbon solubility in water with solvent cavity surface area: Journal of Physical Chemistry, v. 76, no. 19, p. 2754-2759.

Hesselberg, R.J., and Nicholson, L.W., 1981, Influence of PCBs in water on uptake and elimination of DDT and DDE by Lake Trout: Journal of Environmental Quality, v. 10, no. 3, p. 315-318.

Hickman, G.T., and Novak, J.T., 1984, Acclimation of activated sludge to pentachlorophenol: Journal of the Water Pollution Control Federation, v. 56, no. 4, p. 364-369.

Hildebrand, J.H., 1968, A criticism of the term "hydrophobic bond": Journal of Physical Chemistry, v. 72, no. 5, p. 1841-1842.

Hildebrand, J.H., 1979, Is there a "hydrophobic effect"?": Proceedings of the National Academy of Science, v. 76, no. 1, p. 194.

Hill, J., Kollig, H.P., Paris, D.F., Wolfe, N.L., and Zepp, R.G., 1976, Dynamic behavior of vinyl chloride in aquatic ecosystems: U.S. Environmental Protection Agency, EPA-600/3-76-001, 59 p.

Hill, N.P., McIntyre, A.E., Perry, R., and Lester, J.N., 1986, Behaviour of chlorophenoxy herbicides during the activated sludge treatment of municipal waste water: Water Research, v. 20, no. 1, p. 45-52.

Hiraizumi, Y., Takahashi, M., and Nishimura, H., 1979, Adsorption of PCBs onto sea bed sediment, marine plankton, and other adsorbing agents: Environmental Science and Technology, v. 13, no. 5, p. 580-584.

Hochreiter, J.J., 1982, Chemical-quality reconnaissance of the water and surficial bed material in the Delaware River estuary and adjacent New Jersey tributaries, 1980-81: U.S. Geological Survey Water-Resources Investigations Report 82-36, 41 p.

Hoeppel, R.E., and Westerdahl, H.E., 1983, Dissipation of 2,4-D DMA and BEE from water, mud, and fish at Lake Seminole, Georgia: Water Resources Bulletin, v. 19, no. 2, p. 197-204.

Horowitz, A.J., 1984, A primer on trace metal-sediment chemistry: U.S. Geological Survey Open-File Report 84-709, 82 p.

Horzempa, L.M.,and Di Toro, D.M., 1983a, PCB partitioning in sediment-water systems: The effect of sediment concentration: Journal of Environmental Quality, v. 12, no.3, p. 373-380.

Horzempa, L.M., and Di Toro, D.M., 1983b, The extent of reversibility of polychlorinated biphenyl adsorption: Water Research, v. 17, no. 8, p. 851-859.

Howells, D.H., and Zielinski, Paul, 1982, Control of water pollution from toxics: Southeast U.S.: Journal of the Environmental Engineering Division, American Society of Civil Engineers, v. 108, no. EE5, p. 1045-1061.

Huang, J.C., 1971, Effect of selected factors on pesticide sorption and desorption in the aquatic system: Journal of the Water Pollution Control Federation, v. 20, p. 1739-1748.

Huggett, R.J., Nichols, M.M., and Bender, M.E., 1980, Kepone contamination of the James River estuary, in Baker, R., ed., Contaminants and sediments, Volume 1: Ann Arbor, Michigan, Ann Arbor Science Publishers, p. 33-52.

Hunt, C.D., 1983, Incorporation and deposition of Mn and other trace metals by flocculent organic matter in a controlled marine ecosystem: Limnology and Oceanography, v. 28, no. 2, p. 302-308.

Hunt, J.R., 1982, Particle dynamics in seawater; Implications for predicting the fate of discharged particles: Environmental Science and Technology, v. 16, no. 6, p. 303-309.

Hunter, K.A., and Liss, P.S., 1982, Organic matter and the surface charge of suspended particles in estuarine waters: Limnology and Oceanography, v. 27, no. 2, p. 322-335.

Hunter, R.G., Randolph, J.C., and Carroll, J.H., 1980, Polychlorinated biphenyls in the sediments and fish of an Oklahoma stream: Environmental Pollution (Series B), v. 1, p. 233-240.

Hurtt, A.C., and Quinn, J.G., 1979, Distribution of hydrocarbons in Narragansett Bay sediment cores: Environmental Science and Technology, v. 13, no. 7, p. 829-836.

Hutzinger, S., Safe, S., and Zitko, V., 1974, The chemistry of PCBs: Boca Raton, Florida, CRC Press, 269 p.

Imberger, J. and others, 1983, The influence of water motion on the distribution and transport of materials in a salt marsh estuary: Limnology and Oceanography, v. 28, no. 2, p. 201-214.

Isaacson, P.J., 1985, Sorption of phenol vapors and influence of ring substitution: Soil Science, v. 140, no. 3, p. 189-193.

Isaacson, P.J., and Frink, C.R., 1984, Nonreversible sorption of phenolic compounds by sediment fractions: The role of sediment organic matter: Environmental Science and Technology, v. 18, no. 1, p. 43-48.

Isensee, A.R., and Jones, G.E., 1975, Distribution of 2,3,7,8,-tetrachloro-dibenzo-p-dioxin (TCDD) in aquatic model ecosystem: Environmental Science and Technology, v. 9, no. 7, p. 668-672.

Ishiwatari, Ryoshi, 1985, Geochemistry of humic substances in lake sediments, in Aiken, G., McKnight, D., Wershaw, R., and MacCarthy, P., eds., Humic substances in soil, sediment, and water: New York, New York, John Wiley and Sons, p. 147-180.

Jackson, T.A., 1975, Humic matter in natural waters and sediments: Soil Science, v. 119, no. 1, p. 56-64.

Jaffe, P.R., 1986, Modeling sorbing chemicals: Considering the nonsingular adsorption/desorption isotherm: Journal of Environmental Science and Health, v. A21, no. 1, p. 55-69.

Jaffe, P.R., Parker, F.L., and Wilson, D.J., 1982, Distribution of toxic substances in rivers: Journal of the Environmental Engineering Division, American Society of Civil Engineers, v. 108, no. EE4, p. 639-649.

Jan, J., and Malnersic, S., 1980, Chlorinated benzene residues in fish in Slovenia (Yugoslavia): Bulletin of Environmental Contamination and Toxicology, v. 24, p. 824-827.

Jensen, Soren, and Rosenberg, Rutger, 1975, Degradability of some chlorinated aliphatic hydrocarbons in sea water and sterilized water: Water Research, v. 9, p. 659-651.

Johnsen, R.E., 1976, DDT metabolism in microbial systems: Residue Reviews, v. 61, p. 1-28.

Jones, T.W., Kemp, W.M., Stevenson, J.C., and Means, J.C., 1982, Degradation of atrazine in estuarine water/sediment systems and soils: Journal of Environmental Quality, v. 11, no.4, p. 632-638.

Joschek, J.I., and Miller, S.I., 1966, Photooxidation of phenol, cresols, and dihydroxybenxenes: Journal of the American Chemical Society, v. 88, no. 14, p. 3273-3281.

Josephson, Julian, 1982, Humic substances: Environmental Science and Technology, v. 16, no. 1, p. 20A-24A.

Jungclaus, G.A., Lopez-Avila, V., and Hites, R.A., 1978, Organic compounds in an industrial wastewater: A case study of their environmental impact: Environmental Science and Technology, v. 12, no. 1, p. 88-96.

Juo, A.S.R., and Oginni, O.O., 1978, Adsorption and desorption of paraquat in acid tropical soils: Journal of Environmental Quality, v. 7, no. 1, p. 9-12.

Kaiser, K.L.E., 1978, The rise and fall of mirex: Environmental Science and Technology, v. 12, no. 5, p. 520-528.

Kane, J.E., 1967, Organic aggregates in surface waters of the Ligurian Sea: Limnology and Oceanography, v. 12, p. 287-294.

Karickhoff, S.W., 1980, Sorption kinetics of hydrophobic pollutants in natural sediments, in Baker, R., ed., Contaminants and sediments: Ann Arbor, Michigan, Ann Arbor Science Publishers, p. 193-205.

Karickhoff, S.W., 1981, Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils: Chemosphere, v. 10, no. 8, p. 833-846.

Karickhoff, S.W., 1984, Organic pollutant sorption in aquatic systems: Proceedings of the American Society of Civil Engineers, Journal of the Hydraulic Engineering Division, v. 110, no. 6, p. 707-735.

Karickhoff, S.W., and Brown, D.S., 1978, Paraquat sorption as a function of particle size in natural sediments: Journal of Environmental Quality, v. 7, no. 2, p. 246-252.

Karickhoff, S.W., and Brown, D.S., 1979, Determination of octanol/water distribution coefficients, water solubilities, and sediment/water partition coefficients for hydrophobic organic pollutants: U. S. Environmental Protection Agency, EPA-600/4-79-932.

Karickhoff, S.W., Brown, D.S., and Scott, T.A., 1979, Sorption of hydrophobic pollutants on natural sediments: Water Research, v. 13, p. 241-248.

Karydis, M., 1980, Uptake of hydrocarbons by the marine diatom Cyclotella cryptica: Microbial Ecology, v. 5, p. 287-293.

Kearney, P.C., Woolson, E.A., Plimmer, J.R., and Isensee, A.R., 1969, Decontamination of pesticides in soils: Residue Reviews, v. 29, p. 137-149.

Keith, L.H., and Telliard, W.A., 1979, Priority pollutants- I. A perspective view: Environmental Science and Technology, v. 13, no. 4, p. 416-423.

Kenaga, E.E., 1975a, Partitioning and uptake of pesticides in biological systems, in Haque, R., and Freed, V., eds., Environmental Dynamics of Pesticides: Plenum Press, p. 217-273.

Kenaga, E.E., 1975b, Guidelines for environmental study of pesticides: Determination of bioconcentration potential: Residue Reviews, v. 44, p. 73-114.

Kenaga, E.E., 1980, Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties: Environmental Science and Technology, v. 14, no. 5, p. 553-556.

Kenaga, E.E., and Goring, C.A.I., 1980, Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota, in Eaton, J.G., Parish, P.R., and Hendricks, A.C., eds., Aquatic toxicology: American Society for Testing and Materials, ASTM STP 707, p. 78-115.

Khan, S.U., 1972a, Adsorption of pesticide by humic substances. A review: Environmental Letters, v. 3, no. 1, p. 1-12.

Khan, S.U., 1972b, The retention of hydrophobic organic compounds by humic acid: Geochimica et Cosmochimica Acta, v. 36, p. 745-754.

Khan, S.U., 1974a, Humic substances reactions involving bipyridylium herbicides in soil and aquatic environments: Residue Reviews, v. 52, p. 1-26.

Khan, S.U., 1974b, Adsorption of 2,4-D from aqueous solution by fulvic acid-clay complex: Environmental Science and Technology, v. 8, no. 3, p. 236-238.

Khan, S.U., 1974c, Adsorption of bipyridylium herbicides by humic acid: Journal of Environmental Quality, v. 3, no. 3, p. 202-206.

Khan, S.U., 1978, The interaction of organic matter with pesticides, in Schnitzer, M. and Khan, S.U., eds., Soil organic matter: New York, New York, Elsevier Scientific Publishing Company, p. 137-171.

Khan, S.U., 1980, Role of humic substances in predicting fate and transport of pollutants in the environment, in Haque, R., ed., Dynamics, exposure, and hazard assessment of toxic chemicals: Ann Arbor, Michigan, Ann Arbor Scientific Publishers, p. 215-230.

Knackmuss, H.J., and Hellwig, M., 1978, Utilization and cooxidation of chlorinated phenols by Pseudomonas sp. B 13: Archives of Microbiology, v. 117, p. 1-7.

Knap, A.H., and Williams, P.J., 1982, Experimental studies to determine the fate of petroleum hydrocarbons from refinery effluent on an estuarine system: Environmental Science and Technology, v. 16, no. 1, p. 1-4.

Kim, C.J., and Maier, W.J., 1986, Acclimation and biodegradation of chlorinated organic compounds in the presence of alternate substrates: Journal of the Water Pollution Control Federation, v. 58, no. 2, p. 157-164.

Klauda, R.J., Peck, T.H., and Rice, G.K., 1981, Accumulation of polychlorinated biphenyls in Atlantic Tomcod (*Microgadus tomcod*) collected from the Hudson River estuary, New York, v. 27, p. 829-835.

Kobylinski, G.J., and Livingston, R.J., 1975, Movement of mirex from sediment and uptake by the hogchoker, *Trinectes maculatus*: Bulletin of Environmental Contamination and Toxicology, v. 14, no. 6, p. 692-698.

Konemann, Hans, and van Leeuwen, Kees, 1980, Toxikinetics in fish: Accumulation and elimination of six chlorobenzenes by guppies: Chemosphere, v. 9, p. 3-19.

Koskinen, W.C., and Cheng, H.H., 1983, Effects of experimental variables on 2,4,5-T adsorption-desorption in soil: Journal of Environmental Quality, v. 12, no. 3, p. 325-330.

Kozak, J., Weber J.B., and Sheets, T.J., 1983, Adsorption of prometryn and metolachlor by selected soil organic matter fractions: Soil Science, v. 136, no. 2, p. 94-101.

Kriebel, David, 1981, The dioxins: Toxic and still troublesome: Environment, v. 23, no. 1, p. 6-13.

Krom, M.D., and Sholkovitz, E.R., 1977, Nature and reactions of dissolved organic matter in the interstitial waters of marine sediments: Geochimica et Cosmochimica Acta, v. 41, p. 1565-1573.

Kuntz, K.W., and Warry, N.D., 1983, Chlorinated organic contaminants in water and suspended sediments of the lower Niagara River: Journal of Great Lakes Research, v. 9, no. 2, p. 241-248.

Kuehl, D.W., Durhan, E., Butterworth, B., and Linn, D., 1984, Identification of polychlorinated planar chemicals in fishes from major watersheds near the Great Lakes: Environment International, v. 10, no. 1, p. 45-49.

Kuznetsov, S.I., 1975, The role of microorganisms in the formation of lake bottom deposits and their diagenesis: Soil Science, v. 119, no. 1, p. 81-88.

Kyle, B.G., 1981, Science, v. 213, p. 683-684.

LaFleur, K.S., 1979, Sorption of pesticides by model soils and agronomic soils: Rates and equilibria: Soil Science, v. 127, no. 2, p. 94-101.

Lake, J.L., Rogerson, P.F., and Norwood, C.B., 1981, A polychlorinated dibenzofuran and related compounds in an estuarine ecosystem: Environmental Science and Technology, v. 15, no. 5, p. 549-553.

Lal, D., 1977, The oceanic microcosm of particles: Science, v. 198, no. 4321, p. 997-1009.

Landner, L., Lindstrom, K., Karlsson, M., Nordin, J., and Sorensen, L., 1977, Bioaccumulation in fish of chlorinated phenols from kraft pulp mill bleachery effluents: Bulletin of Environmental Contamination and Toxicology, v. 18, no. 6, p. 663-673.

Landrum, P.F., Nlhart, S.R., Eadle, B.J., and Gardner, W.S., 1984, Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters: Environmental Science and Technology, v. 18, no.3, p. 187-192.

Lappalainen, K.M., 1982, Convection in bottom sediments and its role in material exchange between water and sediments: Hydrobiologia, v. 86, no. 1/2, p. 105-108.

Larsen, P.F., Gadbois, D.F., Johnson, A.C., and Doggett, L.F., 1983, Distribution of polycyclic aromatic hydrocarbons in the surficial sediments of Casco Bay, Maine: Bulletin of Environmental Contamination and Toxicology, v. 30, p. 530-535.

Larsson, P., 1983, Transport of C-14 labelled PCB compounds from sediment to water and from water to air in laboratory model systems: Water Research, v. 17, no. 10, p. 1317-1326.

Laska, A.L., Bartell, C.K., and Laseter, J.L., 1976, Distribution of hexachlorobenzene and hexachlorobutadiene in water, soil, and selected aquatic organisms along the lower Mississippi River, Louisiana: Bulletin of Environmental Contamination and Toxicology, v. 15, no. 5, p. 535-542.

Leenheer, J.A., 1981, Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters: Environmental Science and Technology, v. 15, no. 5, p. 578-587.

Leenheer, J.A., and Huffman, E.W.D., 1976, Classification of organic solutes in water by using macroreticular resins: U.S. Geological Survey Journal of Research, v. 4, no. 6, p. 737-751.

Leenheer, J.A., and Stuber, H.A., 1981, Migration through soil of organic solutes in an oil-shale process water: Environmental Science and Technology, v. 15, no. 12, p. 1467-1475.

Leistra, M., Dekker, A., and van der Burg, A.M.M., 1984, Leaching of oxidation products of aldicarb from greenhouse soils to water courses: Archives of Environmental Contamination and Toxicology, v. 13, p. 327-334.

Leo, A., Hansch, C., and Elkins, D., 1971, Partition coefficients and their uses: Chemical Reviews, v. 71, no. 6, p. 525-516.

Lerman, A., Lal, D., and Dacey, M.F., 1974, Stokes' settling and chemical reactivity of suspended particles in natural waters, in Gibbs, R., ed., Suspended Solids in Water: Plenum Press, p. 17-47.

Leung, S.T., Bulkley, R.V., and Richard, J.J., 1982, Pesticide accumulation in a new impoundment in Iowa: Water Resources Bulletin, v. 18, no. 3, p. 485-493.

SELECTED REFERENCES--Continued

Li, G., and Felbeck, G.T., 1972, Atrazine hydrolysis as catalyzed by humic acids: Soil Science, v. 114, no. 3, p. 201-209.

Lietman, P.L., Ward, J.R., and Behrendt, T.E., 1983, Effects of specific land uses on nonpoint sources of suspended sediment, nutrients, and herbicides- Pequea Creek Basin, Pennsylvania 1979-1980: U.S. Geological Survey Water-Resources Investigations Report 83-4113, 88 p.

Lorenzen, C.J., Welschmeyer, N.A., Copping, A.E., and Vernet, M., 1983, Sinking rates of organic particles: Limnology and Oceanography, v. 28, no. 4, p. 766-769.

Lotse, E.G., Graetz, D.A., Chesters, G., Lee, G.B., and Newland, L.W., 1968, Lindane adsorption by lake sediments: Environmental Science and Technology, v. 2, no. 5, p. 353-357.

Lucas, D., and others, 1980, Recommendations for the national surface-water monitoring program - Report 2", Research Triangle Institute, U.S. Environmental Protection Agency, Report RTI/1864/14/01-01I, 148 p.

Lurry, D.L., 1983, Analyses of native water, bottom material, elutriate samples, and dredged material from selected southern Louisiana waterways and selected areas in the Gulf of Mexico, 1979-1981: U.S. Geological Survey Open-File Report 82-690, 105 p.

Lush, D.L., and Hynes, H.B.N., 1973, The formation of particles in freshwater leachates of dead leaves: Limnology and Oceanography, v. 18, p. 968-977.

Mabey, W.R., and Mill, T., 1978, Critical review of hydrolysis of organic compounds in water under environmental conditions: Journal of Physical and Chemical Reference Data, v. 7, p. 383.

Mabey, W.R., Smith, J.H., Podoll, R.T., Johnson, H.L., Mill, T., Chou, T.-W., Gates, J., Partridge, I.W., Jaber, H., and Vandenberg, D., 1982, Aquatic fate process data for organic priority pollutants: U.S. Environmental Protection Agency, EPA 440/4-81-014, 434 p.

Maccubbin, A.E., Black, P., Trzeciak, L., and Black, J.J., 1985, Evidence for polynuclear aromatic hydrocarbons in the diet of bottom-feeding fish: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 876-882.

MacIntyre, F., 1974, The top millimeter of the ocean: Scientific American, v. 203, p. 62-77.

MacIntyre, W.G., and Smith, C.L., 1984, Environmental Science and Technology, v. 18, no. 4, p. 295-297.

Mackay, Donald, 1977: Environmental Science and Technology, v. 13, no. 11, p. 1219.

Mackay, Donald, 1979, Finding fugacity feasible: Environmental Science and Technology, v. 13, no. 10, p. 1218-1223.

Mackay, Donald, 1982a, Effects of surface films on air-water exchange rates: Journal of Great Lakes Research, v. 8, no. 2, p. 299-306.

Mackay, Donald, 1982b, Correlation of bioconcentration factors: Environmental Science and Technology, v. 16, no. 5, p. 274-278.

Mackay, D.M., Ball, W.P., and Durant, M.G., 1986, Variability of aquifer sorption properties in a field experiment on groundwater transport of organic solutes: Methods and preliminary results: Journal of Contaminant Hydrology, v. 1, p. 119-132.

Mackay, D., Bobra, A., Chan, D.W., and Shiu, W.Y., 1982, Vapor pressure correlations for low-volatility environmental chemicals: Environmental Science and Technology, v. 16, no. 10, p. 645-649.

Mackay, D., Bobra, A., Shiu, W.Y., and Yalkowsky, S.H., 1980a, Relationships between aqueous solubility and octanol-water partition coefficients: Chemosphere, v. 9, p. 701-711.

Mackay, D., and Leinonen, P.J., 1975, Rate of evaporation of low-solubility contaminants from water bodies to atmosphere: Environmental Science and Technology, v. 9, no. 13, p. 1178-1180.

Mackay, D., Mascarenhas, R., Shiu, W.Y., Valvani, S.C., and Yalkowsky, S.H., 1980b, Aqueous solubility of polychlorinated biphenyls: Chemosphere, v. 9, p. 257-264.

Mackay, Donald and Paterson, Sally, 1981, Calculating fugacity: Environmental Science and Technology, v. 15, no. 9, p. 1006-1014.

Mackay, Donald and Paterson, Sally, 1982, Fugacity revisited: Environmental Science and Technology, v. 16, no. 12, p. 654A-660A.

Mackay, Donald and Paterson, Sally, 1983, Fugacity models of indoor exposure to volatile chemicals: Chemosphere, v. 12, no. 2, p. 143-154.

Mackay, Donald, Paterson, Sally, and Joy, Michael, 1983, A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in rivers: Chemosphere, v. 12, no. 9/10, p. 1193-1208.

Mackay, D., and Shiu, W.Y., 1977, Aqueous solubility of polynuclear aromatic hydrocarbons: Journal of Chemical and Engineering Data, v. 22, no. 4, p. 399-402.

Mackay, D., Shiu, W.Y., and Sutherland, R.J., 1979, Estimating volatilization and water column diffusion rates of hydrophobic contaminants, in Haque, R., ed., Dynamics, exposure and hazard assessment of toxic chemicals: Ann Arbor, Michigan, Ann Arbor Science Publishers, p. 127-142.

Mackay, D., and Wolkoff, A.W., 1973, Rate of evaporation of low-solubility contaminants from water bodies to atmosphere: Environmental Science and Technology, v. 7, no. 7, p. 611-614.

Mackay, D., and Yeun, A.T.K., 1983, Mass transfer coefficient correlations for volatilization of organic solutes from water: Environmental Science and Technology, v. 17, no. 4, p. 211-217.

Madhun, Y.A., Young, J.L., and Freed, V.H., 1986, Binding of herbicides by water-soluble organic materials from soil: Journal of Environmental Quality, v. 15, no. 1, p. 64-68.

Maier-Bode, H., and Hartel, K., 1981, Linuron and Monolinuron: Residue Reviews, v. 77, p. 1-294.

Malcolm, R.L., 1985, Geochemistry of stream fulvic and humic substances, in Aiken, G., McKnight, D., Wershaw, R., and MacCarthy, P., eds., Humic substances in soil, sediment, and water: New York, New York, John Wiley and Sons, p. 181-210.

Maqueda, C., Perez Rodriguez, J.L., Martin, F., and Hermosin, M.C., 1983, A study of the interaction between chlordimeform and humic acid from a typic chromoxerert soil: Soil Science, v. 136, no. 2, p. 75-81.

Marinucci, A.C., and Bartha, R., 1982, Accumulation of the polychlorinated biphenyl Arochlor 1242 from contaminated detritus and water by the saltmarsh detritivore, Uca pugnax: Bulletin of Environmental Contamination and Toxicology, v. 29, p. 326-333.

Marple, Leland, Berridge, Bernard, and Throop, Lewis, 1986, Measurement of the water-octanol partition coefficient of 2,3,7,8-tetrachlorodibenzo-p-dioxin: Environmental Science and Technology, v. 20, no. 4, p. 397-399.

Martel, J.M., Rickert, D.A., and Siegel, F.R., 1975, PCB's in suburban watershed, Reston, Va.: Environmental Science and Technology, v. 9, no. 9, p. 872-875.

Mathur, S.P., 1974, Phthalate esters in the environment: Pollutants of natural products?: Journal of Environmental Quality, v. 3, no. 3, p. 189-197.

Mathur, S.P., and Rouatt, J.W., 1975, Utilization of the pollutant di-2-ethylhexyl phthalate by a bacterium: Journal of Environmental Quality, v. 4, no. 2, p. 273-275.

Matsuda, Keiichiro, and Schnitzer, Morris, 1971, Reactions between fulvic acid, a soil humic material, and dialkyl phthalates: Bulletin of Environmental Contamination and Toxicology, v. 6, no. 3, p. 200-204.

Matsumoto, Genki, 1983, Comparative study on organic constituents in polluted and unpolluted inland aquatic environments - V - Organic carbons and hydrocarbons in sediments: Water Research, v. 17, no. 7, p. 823-830.

Matsumoto, Genki, and Hanya, Takahisha, 1981, Comparative study on organic constituents in polluted and unpolluted inland aquatic environments - I - Features of hydrocarbons for polluted and unpolluted waters: Water Research, v. 15, p. 217-224.

McCall, P.J., Laskowski, D.A, Swann, R.L., and Dishburger, H.J., 1983, Estimation of environmental partitioning of organic chemicals in model ecosystems: Residue Reviews, v. 85, p. 231-243.

McElroy, A.D., Chiu, S.Y., Nebgen, J.W., Aleti, A., and Vandegrift, A.E., 1975, Water pollution from nonpoint sources: Water Research, v. 9, p. 675-681.

McFall, J.A., Huang, W.Y., and Laseter, J.L., 1979, Organics at the air-water interface of Lake Pontchartrain, Bulletin of Environmental Contamination and Toxicology, v. 22, p. 80-87.

McMurtrey, K.D., Wildman, N.J., and Tai, Han, 1983, Pyrolysis gas chromatography-mass spectrometry of polychlorinated biphenyls on sediment: Bulletin of Environmental Contamination and Toxicology, v. 31, p. 734-737.

Means, J.C., and Wijayaratne, R., 1982, Role of natural colloids in the transport of hydrophobic pollutants: Science, v. 215, p. 968-970.

Means, J.C., Wood, S.G., Hassett, J.J., and Banwart, W.L., 1980, Sorption of polynuclear aromatic hydrocarbons by sediments and soils: Environmental Science and Technology, v. 14, no. 12, p. 1524-1528.

Means, J.C., Wood, S.G., Hassett, J.J., and Banwart, W.L., 1982, Sorption of amino- and carboxy-substituted polynuclear aromatic hydrocarbons by sediments and soils: Environmental Science and Technology, v. 16, no. 2, p. 93-98.

Metcalf, R.L., 1972, Agricultural chemicals in relation to environmental quality: Insecticides today and tomorrow: Journal of Environmental Quality, v. 1, no. 1, p. 10-14.

Metcalf, R.L., and Pitts, J.N., 1969, Outline of environmental sciences: Advances in Environmental Sciences, v. 1, p. 1-23.

Metcalf, R.L., Sanborn, J.R., Lu, P.Y., and Nye, D., 1975, Laboratory model ecosystem studies of the degradation and fate of radiolabeled tri-, tetra-, and pentachlorobiphenyl compared with DDE: Archives of Environmental Contamination and Toxicology, v. 3, no. 2, p. 151-165.

Meyers, P.A., Leenheer, M.J., Eadie, B.J., and Maule, S.J., 1984, Organic geochemistry of suspended and settling particulate matter in Lake Michigan: Geochimica et Cosmochimica Acta, v. 48, p. 443-452.

Michael, P.R., Adams, W.J., Werner, A.F., and Hicks, O., 1984, Surveillance of phthalate esters in surface waters and sediments of the United States: Environmental Toxicology and Chemistry, v. 3, p. 377-389.

Middleditch, B.S., and Basile, Brenda, 1980, Alkanes in benthic organisms from the Buccaneer oil field: Bulletin of Environmental Contamination and Toxicology, v. 24, p. 945-952.

Miles, J.R.W., 1976, Insecticide residues on stream sediments in Ontario, Canada: Pesticide Monitoring Journal, v. 10, no. 3, p. 87-91.

Miller, Stanton, 1983, Photochemistry of natural water systems: Environmental Science and Technology, v. 17, no. 12, p. 568a-570a.

Miller, R.W., and Faust, S.D., 1972, Sorption from aqueous solution by organo-clays: II. Thermodynamics of 2,4-D sorption by various organo-clays: Environmental Letters, v. 2, no. 4, p. 183-194.

Miller, M.M., Wasik, S.P., Huang, G., Shiu, W., and Mackay, D., 1985, Relationships between octanol-water partition coefficient and aqueous solubility: Environmental Science and Technology, v. 19, no. 6, p. 522-529.

Miller, C.T., and Weber, W.J., 1986, Sorption of hydrophobic organic pollutants in saturated soil systems: Journal of Contaminant Hydrology, v. 1, p. 243-261.

Milner, C.R., and Goulder, R., 1986, The abundance, heterotrophic activity and taxonomy of bacteria in a stream subject to pollution by chlorophenols, nitrophenols and phenoxyalkanoic acids: Water Research, v. 20, no. 1, p. 85-90.

Mingelgrin, U., and Gerstl, Z., 1983, Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils: Journal of Environmental Quality, v. 12, no. 1, p. 1-11.

Mix, M.C., and Schaffer, R.L., 1979, Benzo(a)pyrene concentrations in mussels (Mytilus edulis) from Yaquina Bay, Oregon during June 1976 - May 1978: Bulletin of Environmental Contamination and Toxicology, v. 23, p. 677-684.

Miyazaki, Tomoyuki, Yamagishi, Tatsunori, and Matsumoto, Masao, 1984, Residues of 4-chloro-1-(2,4-dichlorophenoxy)-2-methoxybenzene(triclosan methyl) in aquatic biota: Bulletin of Environmental Contamination and Toxicology, v. 32, p. 227-232.

Moore, N.W., 1975, A synopsis of the pesticide problem: Advances in Ecological Research, Academic Press, v. 4, p. 75-129.

Moore, R.M., Burton, J.D., Williams, P.J., and Young, M.L., 1979, The behavior of dissolved organic material, iron, and manganese in estuarine mixing: Geochimica et Cosmochimica Acta, v. 43, p. 919-926.

Moore, J.W., and Ramamoorthy, S., 1984, Organic chemicals in natural waters - Applied monitoring and impact assessment: New York, New York, Springer-Verlag, New York Inc., 289 p.

Morgan, R.P., and Sommer, S.E., 1979, Polychlorinated biphenyls in Baltimore Harbor sediments: Bulletin of Environmental Contamination and Toxicology, v. 22, p. 413-419.

Morin, R., Gaboury, G., and Mamarbachi, G., 1986, Fenitrothion and aminocarb residues in water and balsam fir foliage following spruce budworm spraying programs in Quebec, 1979 to 1982: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 622-628.

Morita, M., Nakamura, H., and Mimura, S., 1974, Phthalic acid esters in water: Water Research, v. 8, p. 781-788.

Morris, R.J., and Calvert, S.E., 1975, Fatty acid uptake by marine sediment particles: Geochimica et Cosmochimica, v. 39, p. 377-381.

SELECTED REFERENCES--Continued

Mount, M.E., and Oehme, F.W., 1981, Carbaryl: A literature review: Residue Reviews, v. 80, p. 1-65.

Mowrer, J., Calambokidis, J., Musgrove, N., Drager, B., Beug, M.W., and Herman, S.G., 1977, Polychlorinated biphenyls in cottids, mussels, and sediment in southern Puget Sound, Washington: Bulletin of Environmental Contamination and Toxicology, v. 18., no. 5, p. 588-594.

Muir, D.C.G., Grift, N.P., Blouw, A.P., and Lockhart, W.L., 1980, Persistence of fluridone in small ponds: Journal of Environmental Quality, v. 9, no. 1, p. 151-156.

Mulholland, P.J., 1981, Formation of particulate organic carbon in water from a southeastern swamp-stream: Limnology and Oceanography, v. 26, no. 4, p. 790-795.

Mulholland, P.J., and Kuenzler, E.J., 1979, Organic carbon export from upland and forested wetland watersheds: Limnology and Oceanography, v. 24, no. 5, p. 960-966.

Mulla, M.S., and Mian, L.S., 1981, Biological and environmental impacts of the insecticides malathion and parathion on nontarget biota in aquatic ecosystems: Residue Reviews, v. 78, p. 101-137.

Mulla, M.S., Mian, L.S., and Kawecki, J.A., 1981, Distribution, transport and fate of the insecticides malathion and parathion in the environment: Residue Reviews, v. 81, p. 1-172.

Mullin, M.M., 1965, Size fractionation of particulate organic carbon in the surface waters of the western Indian Ocean: Limnology and Oceanography, v. 10, p. 459-462.

Munson, T.O., 1976, A note on toxaphene in environmental samples from the Chesapeake Bay region: Bulletin of Environmental Contamination and Toxicology, v.16, no. 4, p. 491-494.

Murphy, P.G., 1971, The effect of size on the uptake of DDT from water by fish: Bulletin of Environmental Contamination and Toxicology, v. 6, no. 1, p. 20-23.

Murphy, T.J., and Rzeszutko, C.P., 1977, Precipitation inputs of PCBs to Lake Michigan: Journal of Great Lakes Research, v. 3, no. 3-4, p. 305-312.

Murthy, N.B.K., Kaufman, D.D., and Fries, G.F., 1979, Degradation of pentachlorophenol (PCP) in aerobic and anaerobic soil: Journal of Environmental Science and Health, v. B14, no. 1, p. 1-14.

Nadeau, R.J., and Davis, R.A., 1976, Polychlorinated biphenyls in the Hudson River (Hudson Falls-Fort Edward, New York state): Bulletin of Environmental Contamination and Toxicology, v.16, no. 4, p. 436-444.

Nagy, E., Mudroch, P., Mudroch, A., and Thomas, R.L., 1984, Hydrocarbons in the surficial sediments of Lakes St. Clair, Erie, and Ontario: Environmental Geology and Water Science, v. 6, no. 1, p. 31-37.

Narine, D.R., and Guy, R.D., 1982, Binding of diquat and paraquat to humic acid in aquatic environments: Soil Science, v. 133, no. 6, p. 356-363.

Nau-Ritter, G.M., and Wurster, C.F., 1983, Sorption of PCBs to clay particulates and effects of desorption on phytoplankton: Water Research, v. 17, no. 383-387.

Nau-Ritter, G.M., Wurster, C.F., and Rowland, R.G., 1982, Partitioning of PCB between water and particulates with various organic contents: Water Research, v. 16, p. 1615-1618.

Neely, W., Branson, D., and Blau, G., 1974, Partition coefficient to measure bioconcentration potential of organic chemicals in fish: Environmental Science and Technology, v. 8, no. 13, p. 1113-1115.

Neff, J.M., 1984, Bioaccumulation of organic micropollutants from sediments and suspended particulates by aquatic animals: Fresenius Z. Anal. Chem., v. 319, no. 2, p. 132-136.

Nelson, C.R., and Hites, R.A., 1980, Aromatic amines in and near the Buffalo River: Environmental Science and Technology, v. 14, no. 9, p. 1147-1149.

Nemethy, G., Scheraga, H.A., and Kauzmann, W., 1968, Journal of Physical Chemistry, v. 72, no. 5, p. 1842.

Nigg, H.N., Henry, J.A., and Stamper, J.H., 1983, Regional behavior of pesticide residues in the United States: Residue Reviews, v. 85, p. 257-276.

Niimi, A.J., 1979, Hexachlorobenzene (HCB) levels in Lake Ontario salmonids: Bulletin of Environmental Contamination and Toxicology, v. 23, p. 20-24.

Niimi, A.J., and Cho, C.Y., 1983, Laboratory and field analysis of pentachlorophenol (PCP) accumulation by salmonids: Water Research, v. 17, no. 12, p. 1791-1795.

Niimi, A.J., and McFadden, C.A., 1982, Uptake of sodium pentachlorophenate (NaPCP) from water by rainbow trout (Salmo gairdneri) exposed to concentrations in the ng/l range: Bulletin of Environmental Contamination and Toxicology, v. 28, p. 11-19.

Nkedi-Kizza, P., Rao, P.S.C., and Hornsby, A.G., 1985, Influence of organic cosolvents on sorption of hydrophobic organic chemicals by soils: Environmental Science and Technology, v. 19, no. 10, p. 975-979.

Nkedi-Kizza, P., Rao, P.S.C., and Johnson, J.W., 1983, Adsorption of Diuron and 2,4,5-T on soil particle-size separates: Journal of Environmental Quality, v. 12, no. 2, p. 195-197.

Norris, L.A., 1981, The movement, persistence, and fate of the phenoxy herbicides and TCDD in the forest: Residue Reviews, v. 80, p. 66-126.

Novak, J.T., 1974, Temperature-substrate interactions in biological treatment: Journal of Water Pollution Control Federation, v. 46, no. 8, p. 1984-1994.

Novotny, Vladimir, 1980, Delivery of suspended sediment and pollutants from nonpoint sources during overland flow: Water Resources Bulletin, v. 16, no. 6, p. 1057-1065.

O'Connor, D.J., and Connolly, J.P., 1980, The effect of concentration of adsorbing solids on the partition coefficient: Water Research, v. 14, p. 1517-1523.

O'Connor, D.J., Mueller, J.A., and Farley, K.J., 1983, Distribution of Kepone in the James River estuary: Journal of Environmental Engineering, v. 109, no. 2, p. 396-413.

Ogner, G., and Schnitzer, M., 1970, Humic substances: Fulvic acid-dialkyl phthalate complexes and their role in pollution: Science, v. 170, p. 317-318.

Ogram, A.V., Jessup, R.E., Ou, L.T., and Rao, P.S.C., 1985, Effects of sorption on biological degradation rates of 2,4-(dichlorophenoxy)acetic acid in soils: Applied and Environmental Microbiology, v. 49, no. 3, p. 582-587.

Ogura, N., 1970, On the presence of 0.1-0.5 micron dissolved organic matter in seawater: Limnology and Oceanography, v. 15, p. 476-478.

O'Keefe, P., Hilker, D., Meyer, C., Aldous, K., Shane, L., Donnelly, R., Smith, R., Sloan, R., Skinner, L., and Horn, E., 1984, Tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofurans in Atlantic coast striped bass and in selected Hudson River fish, waterfowl and sediments: Chemosphere, v. 13, no. 8, p. 849-860.

O'Keefe, P.W., Hilker, D.R., Smith, R.M., Aldous, K.M., Donnelly, R.J., Long, D., and Pope, D.H., 1986, Nonaccumulation of chlorinated dioxins and furans by goldfish exposed to contaminated sediment and flyash: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 452-459.

Oliver, B.G., and Charlton, M.N., 1984, Chlorinated organic contaminants on settling particulates in the Niagara River vicinity of Lake Ontario: Environmental Science and Technology, v. 18, no. 12, p. 903-908.

Oliver, B.G., and Nicol, K.D., 1982, Chlorobenzenes in sediments, water, and selected fish from Lakes Superior, Huron, Erie, and Ontario: Environmental Science and Technology, v. 16, no. 8, p. 532-536.

Oliver, B.G., and Niimi, A.J., 1983, Bioconcentration of chlorobenzenes from water by rainbow trout: Correlations with partition coefficients and environmental residues: Environmental Science and Technology, v. 17, no. 5, p. 287-291.

Oliver, B.G., and Niimi, A.J., 1985, Bioconcentration factors of some halogenated organics for rainbow trout: Limitations in their use for prediction of environmental residues: Environmental Science and Technology, v. 19, no. 9, p. 842-849.

Olsen, C.R., Cutshall, N.H. and Larsen, I.L., 1982, Pollutant-particle associations and dynamics in coastal marine environments: A review: Marine Chemistry, v. 11, p. 501-535.

O'Melia, C.R., 1980, Aquasols; The behavior of small particles in aquatic systems: Environmental Science and Technology, v. 14, no. 9, p. 1052-1060.

Oschwald, W.R., 1972, Sediment-water interactions: Journal of Environmental Quality, v. 1, no. 4, p. 360-366.

Page, G.W., 1981, Comparison of groundwater and surface water for patterns and levels of contamination by toxic substances: Environmental Science and Technology, v. 15, no. 12, p. 1475-1481.

Page, G.W., and Greenberg, Michael, 1982, Maximum contaminant levels for toxic substances in water: A statistical approach: Water Resources Bulletin, v. 18, no. 6, p. 955-963.

Pancirov, R.J., and Brown, R.A., 1977, Polynuclear aromatic hydrocarbons in marine tissues: Environmental Science and Technology, v. 11, no. 10, p. 989-992.

Parejko, Ronald, Johnston, Raymond, and Keller, Robert, 1975, Chlorohydrocarbons in Lake Superior lake trout (Salvelinus namaycush): Bulletin of Environmental Contamination and Toxicology, v. 14, no. 4, p. 480-488.

Parejko, Ronald, and Wu, C.J., 1977, Chlorohydrocarbons in Marquette Fish Hatchery lake trout (Salvelinus namaycush): Bulletin of Environmental Contamination and Toxicology, v. 17, no. 1, p. 90-97.

Paris, D.F., and Lewis, D.C., 1973, Chemical and microbial degradation of 10 selected pesticides in aquatic systems: Residue Reviews, v. 45, p. 96-114.

Paris, D.F., Lewis, D.L., and Barnett, J.T., 1977, Bioconcentration of toxaphene by microorganisms: Bulletin of Environmental Contamination and Toxicology, v. 17, no. 5, p. 564-572.

Parker, B.L., Brammer, J.D., Whalon, M.E., and Berry, W.O., 1976, Chronic oil contamination and aquatic organisms with emphasis on diptera: Status and bibliography: Water Resources Bulletin, v. 12, no. 2, p. 291-305.

Parris, G.E., 1980, Covalent binding of aromatic amines to humates; 1. Reactions with carbonyls and quinones: Environmental Science and Technology, v. 14, no. 9, p. 1099-1106.

Pavlou, S.P., and Dexter, R.N., 1979, Distribution of PCBs in estuarine ecosystems; Testing the concept of equilibrium partitioning in the marine environment: Environmental Science and Technology, v. 13, no. 1, p. 65-71.

Pavlou, S.P., Dexter, R.N., Anderson, D.E., Quinlan, E.A., and Hom, W., 1980, Release, distribution, and impacts of PCBs induced by dredged material disposal activities at a deepwater estuarine site: Proceedings of the Fifth Meeting on Management of Bottom Sediments Containing Toxic Substances, U. S. Environmental Protection Agency, EPA 600/9-80-044, p. 129-174.

Pavlou, S.P., and Hom, W., 1976, Interlaboratory calibration results from chlorinated hydrocarbon analyses in marine sediments: Marine Chemistry, v. 4, p. 155-163.

Peakall, D.B., 1975, Phthalate esters: Occurrence and biological effects: Residue Reviews, v. 54, p. 1-39.

Pearlman, R.S., Yalkowsky, S.H., and Banerjee, S., 1984, Water solubilities of polynuclear aromatic and heteroaromatic compounds: Journal of Physical and Chemical Reference Data, v. 13, no. 2, p. 555-562.

Peck, D.E., Corwin, D.L., and Farmer, W.J., 1980, Adsorption-desorption of diuron by freshwater sediments: Journal of Environmental Quality, v. 9, no. 1, p. 101-106.

Pepe, M.G., and Byrne, J.J., 1980, Adhesion binding of 2,2',4,4',5,5'- hexachlorobiphenyl to glass and plastic: A possible source of error for PCB analysis: Bulletin of Environmental Contamination and Toxicology, v. 25, p. 936-940.

Perez, J.A., Hernandez, M.A., Ruiz, R.A., and Brown, P.J., 1977, The utilization of the plasticizer dimethyl phthalate by an isolated strain of *Enterobacter aerogenes*: Bulletin of Environmental Contamination and Toxicology, v. 18, no. 1, p. 104-107.

Peterle, T.J., 1969, DDT in antarctic snow: Nature, v. 224, p. 620-622.

Peterson, J.C., and Freeman, D.H., 1984, Variations of phthalate ester concentrations in sediments from the Chester River, Maryland: International Journal of Environmental and Analytical Chemistry, v. 18, p. 237-252.

Petrocelli, S.R., Hanks, A.R., and Anderson, J., 1973, Uptake and accumulation of an organochlorine insecticide (dieldrin) by an estuarine mollusc, *Rangia cuneata*: Bulletin of Environmental Contamination and Toxicology, v. 10, no. 5, p. 315-320.

Pfaender, F.K., Shuman, M.S., Dempsey, Herbert, and Harden, C.W., 1977, Monitoring heavy metals and pesticides in the Cape Fear river basin of North Carolina: Water Resources Research Institute of the University of North Carolina, Report no. 126, 151 p.

Pfister, R.M., Dugan, P.R., and Frea, J.I., 1969, Microparticulates: Isolation from water and identification of associated chlorinated pesticides: Science, v. 172, p. 878-879.

Picer, N., Picer, M., and Strohal, P., 1977, The interaction of DDT with suspended particles in sea water: Water, Air, and Soil Pollution, v. 8, p. 429-440.

Pierce, R.H., Brent, C.R., Williams, H.P., and Reeves, S.G., 1977, Pentachlorophenol distribution in a freshwater ecosystem: Bulletin of Environmental Contamination and Toxicology, v. 18, p. 251-258.

Pierce, R.H., Olney, C.E., and Felbeck, G.T., 1974, p,p'-DDT adsorption to suspended particulate matter in sea water: Geochimica et Cosmochimica Acta, v. 38, p. 1061-1073.

Pierce, D.P., Williamson, K.J., and Nelson, P.O., 1981, Partitioning of trace organics in sediments: Proceedings of the American Society of Civil Engineers, Environmental Engineering Division, v. 107, no. EE5, p. 1100-1105.

Pionke, H.B., and Chesters, G., 1973, Pesticide-sediment-water interactions: Journal of Environmental Quality, v. 2, no. 1, p. 29-45.

SELECTED REFERENCES--Continued

Plimmer, J.R., 1978, Photolysis of TCDD and trifluralin on silica and soil: Bulletin of Environmental Contamination and Toxicology, v. 20, p. 87-92.

Poirrier, M.A., Bordelon, B.R., and Laseter, J., 1972, Adsorption and concentration of dissolved carbon-14 DDT by coloring colloids in surface waters: Environmental Science and Technology, v. 6, no. 12, p. 1033-1035.

Pollock, G.A., and Kilgore, W.W., 1978, Toxaphene: Residue Reviews, v. 69, p. 87-143.

Powers, C.F., Sanville, W.D., and Stay, F.S., 1976, Aquatic sediments: Journal of the Water Pollution Control Federation, v. 48, no. 6, p. 1433-1439.

Powers, C.F., Sanville, W.D., Stay, F.S., and Schuytema, G.S., 1977, Aquatic sediments: Journal of the Water Pollution Control Federation, v. 49, no. 6, p. 1307-1316.

Powers, C.F., Stay, F.S., and Sanville, W.D., 1975, Aquatic sediments: Journal of the Water Pollution Control Federation, v. 47, no. 6, p. 1611-1617.

Presley, B.J., and Trefry, J.H., 1980, Sediment-water interactions and the geochemistry of interstitial waters, in Olausson, E., and Cato, I., eds., Chemistry and Biogeochemistry of Estuaries: John Wiley and Sons, p. 187-226.

Preston, M.R., and Riley, J.P., 1982, The interactions of humic compounds with electrolytes and three clay minerals under simulated estuarine conditions: Estuarine, Coastal and Shelf Science, v. 14, p. 567-576.

Pritchard, P.H., 1984, Fate of environmental pollutants: Journal of the Water Pollution Control Federation, v. 56. no. 6, p. 718-725.

Puffer, Harold W., and Gossett, Richard W., 1983, PCB, DDT, and benzo(a)pyrene in raw and pan-fried white croaker (Genyonemus lineatus): Bulletin of Environmental Contamination and Toxicology, v. 30, p. 65-73.

Purdue, E.M., 1983, Association of organic pollutants with humic substances: Partitioning equilibria and hydrolysis kinetics, in Christman, R.F. and Gjessing, E.T., eds., Aquatic and terrestrial humic materials: Ann Arbor, Michigan, Ann Arbor Science Publishers, p. 441-460.

Purdue, E.M., 1985, Acidic functional groups of humic substances, in Aiken, G, McKnight, D., Wershaw, R., and MacCarthy, P., eds., Humic substances in soil, sediment, and water: New York, New York, John Wiley and Sons, p. 493-526.

Qasim, S.R., Armstrong, A.T., Corn, J., and Jordan, B.L., 1980, Quality of water and bottom sediments in the Trinity River: Water Resources Bulletin, v. 16, no. 3, p. 522-531.

Rajagopal, B.S., Brahmaprakash, G.P., Reddy, B.R., Singh, U.D., and Sethunathan, N., 1984, Effect and persistence of selected carbamate pesticides in soil: Residue Reviews, v. 93, p. 1-207.

Ramamoorthy, S., 1985, Competition of fate processes in the bioconcentration of lindane: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 349-358.

Rao, P.S.C., and Davidson, J.M., 1979, Adsorption and movement of selected pesticides at high concentrations in soils: Water Research, v. 13, p. 375-380.

Rao, P.S.C., Green, R.E., Balasubramanian, V., and Kanehiro, Y., 1974, Field study of solute movement in a highly aggregated oxisol with intermittent flooding: II. Picloram: Journal of Environmental Quality, v. 3, no. 3, p. 197-201.

Rao, P.S.C., Hornsby, A.G., Kilcrease, D.P., and Nkedi-Kizza, P., 1985, Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation: Journal of Environmental Quality, v. 14, no. 3, p. 376-383.

Rashid, M.A., and King, L.H., 1970, Major oxygen-containing functional groups present in humic and fulvic acid fractions isolated from contrasting marine environments: Geochimica et Cosmochimica Acta, v. 34, p. 193-201.

Rathbun, R.E., and Tai, D.Y., 1982, Volatilization of organic compounds from streams: Proceedings of the American Society of Civil Engineers, Journal of the Environmental Engineering Division, v. 108, no. EE5, p. 973-989.

Rathbun, R.E., and Tai, D.Y., 1984, Comparison of nonlinear least squares and log transformation procedures for calculating volatilization coefficients: Chemosphere, v. 13, no. 7, p. 715-730.

Ray, S., Jessop, B.M., Coffin, J., and Swetnam, D.A., 1984, Mercury and polychlorinated biphenyls in striped bass (Morone saxatilis) from two Nova Scotia rivers: Water, Air, and Soil Pollution, v. 21, p. 15-23.

Reinert, R.E., 1972, Journal of the Fisheries Resource Board of Canada, v. 27, p. 1413.

Reinert, K.H., and Rodgers, J.H. Jr., 1984, Influence of sediment types on the sorption of endothall: Bulletin of Environmental Contamination and Toxicology, v. 32, p. 557-564.

Reutergardh, L., 1980, Chlorinated hydrocarbons in estuaries, in Olausson, E. and Cato, E., eds., Chemistry and biogeochemistry of estuaries: New York, New York, John Wiley and Sons Ltd., p. 349-365.

Rhead, M.M., and Perkins, J.M., 1984, An evaluation of the relative importance of food and water as sources of p,p'-DDT to the goldfish, Carassius auratus (l.): Water Research, v. 18, no. 6, p. 719-725.

Ricci, E.D., Hubert, W.A., and Richard, J.J., 1983, Organochlorine residues in sediment cores of a midwestern reservoir: Journal of Environmental Quality, v. 12, no. 3, p. 418-421.

Rice, C.P., Eadie, B.J., and Erstfeld, K.M., 1982, Enrichment of PCBs in Lake Michigan surface films: Journal of Great Lakes Research, v. 8, no. 2, p. 265-270.

Richardson, E.M., and Epstein, E., 1971, Retention of three insecticides on different size soil particles suspended in water: Soil Science Society of America Proceedings, v. 35, p. 884-887.

Rihan, T.I., Mustafa, H.T., Caldwell, G. Jr., and Frazier, L., 1978, Chlorinated pesticides and heavy metals in streams and lakes of northern Mississippi water: Bulletin of Environmental Contamination and Toxicology, v. 20, p. 568-572.

Riley, G.A., 1963, Organic aggregates in seawater and the dynamics of their formation and utilization: Limnology and Oceanography, v. 8, p. 372-381.

Riley, G.A., 1970, Particulate organic matter in sea water: Advances in Marine Biology, v. 8, p. 1-118.

Roberts, A.E., Hill, D.R., and Tifft, E.C. Jr., 1982, Evaluation of New York Bight lobsters for PCBs, DDT, petroleum hydrocarbons, mercury, and cadmium: Bulletin of Environmental Contamination and Toxicology, v. 29, p. 711-718.

Rodgers, P.W., and Swain, W.R., 1983, Analysis of PCB loading trends in Lake Michigan: Journal of Great Lakes Research, v. 9, no. 4, p. 548-558.

Rosales, M.T.L., and Escalona, R.L., 1983, Organochlorine residues in organisms of two different lagoons of northwest Mexico: Bulletin of Environmental Contamination and Toxicology, v. 30, p. 456-463.

Rosales, M.T.L., Escalona, R.L., Alarcon, R.M., and Zamora, V., 1985, Organochlorine hydrocarbon residues in sediments of two different lagoons of Northwest Mexico: Bulletin of Environmental Contamination and Toxicology, v. 35, p. 322-330.

Rossmann, R., and Siebel, E., 1977, Surficial sediment redistribution by wave energy; Element-grain size relationships: Journal of Great Lakes Research, v. 3, no.3-4, p. 258-262.

Routh, J.D., 1972, DDT residues in Salinas River sediments: Bulletin of Environmental Contamination and Toxicology, v. 7, p. 168-176.

Rudling, Lars, 1970, Determination of pentachlorophenol in organic tissues and water: Water Research, v. 4, p. 533-537.

Ryan, J.J., Lau, P.Y., Pilon, J.C., Lewis, D., McLeod, H.A., and Gervals, A., 1984, Incidence and levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin in Lake Ontario commercial fish: Environmental Science and Technology, v. 18, no. 9, p. 719-721.

Ryan, J.J., Pilon, J.C., Conacher, H.B.S., and Firestone, David, 1983, Interlaboratory study on determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in fish: Journal of the Association of Official Analytical Chemists, v. 66, no. 3, p. 700-707.

Saar, R.A., and Weber, J.H., 1982, Fulvic acid: Modifier of metal-ion chemistry: Environmental Science and Technology, v. 16, no. 9, p. 510a-517a.

Sabljic, Aleksandar, and Protic, Miroslava, 1982, Relationship between molecular connectivity indices and soil sorption coefficients of polycyclic aromatic hydrocarbons: Bulletin of Environmental Contamination and Toxicology, v. 28, p. 162-165.

Sabourin, T.D., Stickle, W.B., Michot, T.C., Villars, C.E., Garton, D.W., and Mushinsky, H.R., 1984, Organochlorine residue levels in Mississippi River water snakes in southern Louisiana: Bulletin of Environmental Contamination and Toxicology, v. 32, p. 460-468.

Saeger, V.W., Hicks, O., Kaley, R.G., Michael, P.R., Mieure, J.P., and Tucker, E.S., 1979, Environmental fate of selected phosphate esters: Environmental Science and Technology, v. 13, no. 7, p. 840-844.

Salim, R., and Cooksey, B.G., 1981, The effect of centrifugation on the suspended particles of river waters: Water Research, v. 15, p. 835-839.

Sanborn, J.R., Metcalf, R.L., Yu, C., and Lu, P., 1975, Plasticizers in the environment: The fate of di-n-octyl phthalate (DOP) in two model ecosystems and upatke and metabolism of DOP by aquatic organisms: Archives of Environmental Contamination and Toxicology, v. 3, no. 2, p. 244-255.

Sanders, H.O., and Chandler, J.H., 1972, Biological magnification of a polychlorinated biphenyl (Aroclor 1254) from water by aquatic invertebrates: Bulletin of Environmental Contamination and Toxicology, v. 7, no. 5, p. 257-263.

Sanville, W.D., Lauer, W.L., Stay, F.S., Schuytema, G.S., and Powers, C.F., 1978, Aquatic sediments: Journal of the Water Pollution Control Federation, v. 50, no. 6, p. 1414-1424.

Sauer, T.C., 1980, Volatile liquid hydrocarbons in waters of the Gulf of Mexico and Caribbean Sea: Limnology and Oceanography, v. 25, no. 2, p. 338-351.

Sawhney, B.L., Frink, C.R., and Glowa, W., 1981, PCBs in the Housitanic River: Journal of Environmental Quality, v. 10, no. 4, p. 444-448.

Sayler, G.S., Shon, M., and Colwell, R.R., 1977, Growth of an estuarine Pseudomonas sp. on polychlorinated biphenyl: Microbial Ecology, v. 3, p. 241-255.

Schaefer, C.H., Dupras, E.F. Jr., Stewart, R.J., Davidson, L.W., and Colwell, A.E., 1979, The accumulation and elimination of diflubenzuron by fish: Bulletin of Environmental Contamination and Toxicology, v. 21, p. 249-254.

Schaeffer, D.J., and Janardan, K.G., 1980, Abundance of organic compounds in water: Bulletin of Environmental Contamination and Toxicology, v. 24, p. 211-216.

Schellenberg, K., Leuenberger, C., and Schwarzenbach, R.P., 1984, Sorption of chlorinated phenols by natural sediments and aquifer materials: Environmental Science and Technology, v. 18, no. 9, p. 652-657.

Schlagbauer, B.G.L., and Schlagbauer, A.W.J., 1972, The metabolism of carbamate pesticides - A literature analysis: Residue Reviews, v. 42, p. 1-91.

Schnitzer, M., and Khan, S.U., 1972, Humic substances in the environment: Marcel Dekker Inc., 317 p.

Schnoor, J.L., and McAvoy, D.C., 1981, Pesticide transport and bioconcentration model: Journal of the Environmental Engineering Division, American Society of Civil Engineers, v. 107, no. EE6, p. 1229-1246.

Schroeder, R.A., and Barnes, C.R., 1983a, Polychlorinated biphenyl concentrations in Hudson River water and treated drinking water at Waterford, New York: U. S. Geological Survey Water-Resources Investigations Report 83-4188, 13 p.

Schroeder, R.A., and Barnes, C.R., 1983b, Trends in polychlorinated biphenyl concentrations in Hudson River water five years after elimination of point sources: U. S. Geological Survey Water-Resources Investigations Report 83-4206, 28 p.

Schwarzenbach, R.P., Molnar-Kubica, E., Giger, W., and Wakeham, S.G., 1979, Distribution, residence time, and fluxes of tetrachloroethylene and 1,4-dichlorobenzene in Lake Zurich, Switzerland: Environmental Science and Technology, v. 13, no. 11, p. 1367-1373.

Schwarzenbach, R.P., and Westall, J., 1981, Transport of nonpolar organic compounds from surface water to groundwater; Laboratory sorption studies: Environmental Science and Technology, v. 15, no. 11, p. 1360-1367.

Scott, W.S., 1980, Analysis of bottom sediments in the vicinity of a proposed submarine cable: Bulletin of Environmental Contamination and Toxicology, v. 24, p. 766-773.

Scott, H.D., Wolf, D.C., and Lavy, T.L., 1982, Apparent adsorption and microbial degradation of phenol by soil: Journal of Environmental Quality, v. 11, no. 1, p. 107-112.

Seelye, J.G., Hesselberg, R.J., and Mac M.J., 1982, Accumulation by fish of contaminants released from dredged sediments: Environmental Science and Technology, v. 16, no. 8, p. 459-464.

Seguchi, Koichiro, and Asaka, Shiro, 1981, Intake and excretion of diazinon in freshwater fishes: Bulletin of Environmental Contamination and Toxicology, v. 27, p. 244-249.

Seidler, J.J., Landau, M., Dierberg, F.E., and Pierce, R.H., 1986, Persistence of pentachlorophenol in a wastewater-estuarine aquaculture system: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 101-108.

Senesi, N., and Testini, C., 1980, Adsorption of some nitrogenated herbicides by soil humic acids: Soil Science, v. 130, no. 6, p. 314-320.

Shackelford, W.M., and Keith, L.H., 1976, Frequency of organic compounds identified in water: U.S. Environmental Protection Agency, EPA 600/4-76-062.

Shannon, L.R., 1977, Accumulation and elimination of dieldrin in muscle tissue of channel catfish: Bulletin of Environmental Contamination and Toxicology, v. 17, no. 6, p. 637-644.

Sharom, M.S., Miles, J.R.W., Harris, C.R., and McEwen, F.L., 1980a, Persistence of 12 insecticides in water: Water Research, v. 14, p. 1089-1093.

Sharom, M.S., Miles, J.R.W., Harris, C.R., and McEwen, F.L., 1980b, Behaviour of 12 pesticides in soil and aqueous suspensions of soil and sediment: Water Research, v. 14, p. 1095-1100.

Sharp, J.H., 1973, Size classes of organic carbon in seawater: Limnology and Oceanography, v. 18, p. 441-447.

Sheldon, R.W., 1968, Sedimentation in the estuary of the River Crouch, Essex, England: Limnology and Oceanography, v. 13, p. 72-83.

Sheldon, L.S., 1979, Sources and movement of organic chemicals in the Delaware River: Environmental Science and Technology, v. 13, no. 5, p. 574-579.

Sheldon, R.W., Evelyn, T.P.T., and Parsons, T.R., 1967, On the occurrence and formation of small particles in seawater: Limnology and Oceanography, v. 12, p. 367-375.

Sheldon, L.S., and Hites, R.A., 1979, Organic compounds in the Delaware River: Environmental Science and Technology, v. 12, no. 10, p. 1188-1194.

Sheldon, R.W., Prakash, A., and Sutcliffe, W.H., 1972, The size distribution of particles in the ocean: Limnology and Oceanography, v. 17, p. 327-340.

Sheldon, R.W., Sutcliffe, W.H., and Prakash, A., 1973, The production of particles in the surface waters of the ocean with particular reference to the Sargasso Sea: Limnology and Oceanography, v. 18, no. 5, p. 719-733.

Sholkovitz, E.R., 1976, Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater: Geochimica et Cosmochimica Acta, v. 40, p. 831-845.

Sholkovitz, E.R., 1979, Chemical and physical processes controlling the chemical composition of suspended material in the River Tay Estuary: Estuarine and Coastal Marine Science, V. 8, p. 523-545.

Sholkovitz, E.R., Boyle, E.A., and Price, N.B., 1978, The removal of dissolved humic acids and iron during estuarine mixing: Earth and Planetary Science Letters, v. 40, p. 130-136.

Sholkovitz, E.R., and Copland, D., 1982, The chemistry of suspended matter in Esthwaite Water, a biologically productive lake with seasonally anoxic hypolimnion: Geochimica et Cosmochimica Acta, v. 46, p. 393-410.

Sigleo, A.C., and Helz, G.R., 1981, Composition of estuarine colloidal material; Major and trace elements: Geochimica et Cosmochimica Acta, v. 45, p. 2501-2509.

Sigleo, A.C., Helz, G.R., and Zoller, W.H., 1980, Organic-rich colloidal material in estuaries and its alteration by chlorination: Environmental Science and Technology, v. 14, no. 6, p. 673-679.

Sigleo, A.C., Hoering, T.C., and Helz, G.R., 1982, Composition of estuarine colloidal material; Organic components: Geochimica et Cosmochimica Acta, v. 46, p. 1619-1626.

Simkins, Stephen, and Alexander, Martin, 1984, Models for mineralization kinetics with the variables of substrate concentration and population density: Applied and Environmental Microbiology, v. 47, no. 6, p. 1299-1306.

Simmons, M.S., Bialosky, D.I., and Rossman, R., 1980, PCB contamination in surficial sediments of northeastern Lake Michigan: Journal of Great Lakes Research, v. 6, no. 2, p. 167-171.

Simmons, M.S., and Kotz, K.T., 1982, Association studies of polybrominated biphenyls in aquatic systems: Bulletin of Environmental Contamination and Toxicology, v. 29, p. 58-63.

Skea, J.C., Simonin, H.A., Dean, H.J., Colquhoun, J.R., Spagnoli, J.J., and Veith, G.D., 1979, Bioaccumulation of Aroclor 1016 in Hudson River fish: Bulletin of Environmental Contamination and Toxicology, v. 22, p. 332-336.

Skea, J.C., Simonin, H.J., Jackling, S., and Symula, J., 1981, Accumulation and retention of mirex by brook trout fed a contaminated diet: Bulletin of Environmental Contamination and Toxicology, v. 27, p. 79-83.

Sloan, R.J., Simpson, K.W., Schroeder, R.A., and Barnes, C.R., 1983, Temporal trends toward stability of Hudson River PCB contamination: Bulletin of Environmental Contamination and Toxicology, v. 31, p. 377-385.

Smith, A.E., 1985, Identification of 2,4-dichloroanisole and 2,4-dichlorophenol as soil degradation products of ring-labelled [^{14}C]2,4-D: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 150-157.

Smith, J.H., Bomberger, D.C., and Haynes, D.L., 1980, Prediction of the volatilization rates of high-volatility chemicals from natural water bodies: Environmental Science and Technology, v. 14, no. 11, p. 1332-1337.

Smith, J.H., Bomberger, D.C., and Haynes, D.L., 1981, Volatilization rates of intermediate and low volatility chemicals from water: Chemoshpere, v. 10, no. 3, p. 261-289.

Smith, J.H., Mabey, W.R., Bohonos, N., Holt, B.R., Lee, S.S., Chou, T.W., Bomberger, D.C., and Mill, T., 1978, Environmental pathways of selected chemicals in freshwater systems, part II: Laboratory studies: U.S. Environmental Protection Agency, EPA-600/7-78-074, 518 p.

Smith, J.H., Mackay, D., and Ng, C.W.K., 1983, Volatilization of pesticides from water: Residue Reviews, v. 85, p. 73-88.

Smith, J.A., Harte, P.T., and Hardy, M.A., 1987, Trace metal and organochlorine residues in sediments of the Upper Rockaway River, New Jersey: Bulletin of Environmental Contamination and Toxicology (accepted).

Smith, J.A., and Novak, J.T., 1987, Biodegradation of chlorophenols in subsurface soils: Water, Air, and Soil Pollution, v. 33, p. 29-42.

Smith, F.A., Sharma, R.P., Lynn, R.I., and Low, J.B., 1974, Mercury and selected pesticide levels in fish and wildlife of Utah: I. Levels of mercury, DDT, DDE, dieldrin and PCB in fish: Bulletin of Environmental Contamination and Toxicology, v. 12, no. 2, p. 218-223.

Southworth, G.R., 1979, The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments: Bulletin of Environmental Contamination and Toxicology, v. 21, p. 507-514.

Southworth, G.R., Beauchamp, J.J., and Schmieder, P.K., 1978a, Bioaccumulation potential of polycyclic aromatic hydrocarbons in Daphnia pulex: Water Research, v. 12, p. 973-977.

Southworth, G.R., Beauchamp, J.J., and Schmieder, P.K., 1978b, Bioaccumulation potential and acute toxicity of synthetic fuels effluents in freshwater biota: Azaarenes: Environmental Science and Technology, v. 12, no. 9, p. 1062-1066.

Southworth, G.R., Herbes, S.E., Franco, P.J., and Giddings, J.M., 1985, Persistence of phenols in aquatic microcosms receiving chronic inputs of coal-derived oil: Water, Air, and Soil Pollution, v. 24, p. 283-296.

Southworth, G.R., Keffer, C.C., and Beauchamp, J.J., 1980, Potential and realized bioconcentration. A comparison of observed and predicted bioconcentration of azaarenes in the fathead minnow (*Pimephales promelas*): Environmental Science and Technology, v. 14, no. 12, p. 1529-1531.

Southworth, G.R., and Keller, J.L., 1986, Hydrophobic sorption of polar organics by low organic carbon soils: Water, Air, and Soil Pollution, v. 28, p. 239-248.

Southworth, G.R., Parkhurst, B.R., and Beauchamp, J.J., 1979, Accumulation of acridine from water, food, and sediment by the fathead minnow, *Pimephales promelas*: Water, Air, and Soil Pollution, v. 12, p. 331-341.

Spehar, R.L., Veith, G.D., DeFoe, D.L., and Bergstedt, B.V., 1979, Toxicity and bioaccumulation of hexachlorocyclopentadiene, hexachloronorbornadiene and heptachloronorbornene in larval and early juvenile fathead minnows, *Pimephales promelas*: Bulletin of Environmental Contamination and Toxicology, v. 21, p. 576-583.

Spencer, W.F., Cliath, M.M., Farmer, W.J., and Shepherd, R.A., 1974, Volatility of DDT residues in soil as affected by flooding and organic matter applications: Journal of Environmental Quality, v. 3, no. 2, p. 126-129.

Spencer, W.F., Farmer, W.J., and Cliath, M.M., 1973, Pesticide volatilization: Residue Reviews, v. 49, p. 1-40.

Spigarelli, S.A., Thommes, M.M., and Prepejchal, William, 1983, Thermal and metabolic factors affecting PCB uptake by adult brown trout: Environmental Science and Technology, v. 17, no. 2, p. 88-94.

Stainken, Dennis, 1979, Occurrence of extractable hydrocarbons in sediments from Raritan Bay, New Jersey: Bulletin New Jersey Academy of Science, v. 24, no. 1, p. 6-11.

Stainken, Dennis, and Frank, Uwe, 1979, Analysis of Raritan Bay bottom sediments for polynuclear aromatic hydrocarbons: Bulletin of Environmental Contamination and Toxicology, v. 22, p. 480-487.

Stainken, Dennis, and Rollwagen, Janice, 1979, PCB residues in bivalves and sediments of Raritan Bay: Bulletin of Environmental Contamination and Toxicology, v. 23, p. 690-697.

Stalling, D.L., Hogan, J.W., and Johnson, J.L., 1973, Phthalate ester residues - their metabolism and analysis in fish: Environmental Health Perspectives, v. 3, p. 159-173.

Stamer, J.K., Yorke, T.H., and Pederson, G.L., 1985, Distribution and transport of trace substances in the Schuykill River basin from Berne to Philadelphia, Pennsylvania: U.S. Geological Survey Water-Supply Paper 2256-A, 45 p.

Stanlake, G.J., and Finn, R.K., 1982, Isolation and characterization of a pentachlorophenol-degrading bacterium: Applied and Environmental Microbiology, v. 44, no. 6, p. 1421-1427.

Staples, C.A., Werner, A.F., and Hoogheem, T.J., 1985, Assessment of priority pollutant concentrations in the United States using storet database: Environmental Toxicology and Chemistry, v. 4, p. 131-142.

Steelink, Cornelius, 1985, Implications of elemental characteristics of humic substances, in Aiken, G., McKnight, D., Wershaw, R., and MacCarthy, P., eds., Humic substances in soil, sediment, and water: New York, New York, John Wiley and Sons, p. 457-476.

Steen, W.C., and Karickhoff, S.W., 1981, Biosorption of hydrophobic organic pollutants by mixed microbial populations: Chemosphere, v. 10, p. 27-32.

Steen, W.C., Paris, D.F., and Baughman, G.L., 1978, Partitioning of selected polychlorinated biphenyls to natural sediments: Water Research, v. 12, p. 655-657.

Stojanovic, B.J., Kennedy, M.V., and Shuman, F.L., 1972, Edaphic aspects of the disposal of unused pesticides, pesticide wastes and pesticide containers: Journal of Environmental Quality, v. 1, no. 1, p. 54-62.

Stumm, Werner, 1977, Chemical interaction in particle separation: Environmental Science and Technology, v. 11, no. 12, p. 1066-1070.

Sudhakar-Barik, and Sethunathan, N., 1978, Biological hydrolysis of parathion in natural ecosystems: Journal of Environmental Quality, v. 7, no. 3, p. 346-348.

Sugiura, Katsura, Washino, Tohoru, Hattori, Mitsuo, Sato, Eiji, and Goto, Miki, 1979, Accumulation of organochlorine compounds in fishes. Difference of accumulation factors by fishes: Chemosphere, v. 8, p. 359-364.

Sullivan, J.R., Delfino, J.J., Buelow, C.R., and Sheffy, T.B., 1983, Polychlorinated biphenyls in the fish and sediment of the Lower Fox River, Wisconsin: Bulletin of Environmental Contamination and Technology, v. 30, p. 58-64.

Swann, R.L., Laskowski, D.A., McCall, P.J., Vander Kuy, K., and Dishburger, H.J., 1983, A rapid method for the estimation of the environmental parameters octanol/water partition coefficient, soil sorption constant, water to air ratio, and water solubility: Residue Reviews, v. 85, p. 17-28.

Swanson, R.A., and Dutt, G.R., 1973, Chemical and physical processes that affect atrazine and distribution in soil systems: Soil Science Society of America Proceedings, v. 37, p. 872-876.

Tabak, H.H., Chambers, C.W., and Kabler, P.W., 1964, Microbial metabolism of aromatic compounds - I. Decomposition of phenolic compounds and aromatic hydrocarbons by phenol-adapted bacteria: Journal of Bacteriology, v. 87, no. 4, p. 910-919.

Tabak, H.H., Quave, S.A., Mashni, C.I., and Barth, E.F., 1981, Biodegradability studies with organic priority pollutant compounds: Journal of the Water Pollution Control Federation, v. 53, no. 10, p. 1503-1518.

Tahoun, S.A., and Mortland, M.M., 1966, Complexes of montmorillonite with primary, secondary, and tertiary amides: I. Protonation of amides on the surface of montmorillonite: Soil Science, v. 102, no. 4, p. 248-254.

Thomann, R.V., and Di Toro, D.M., 1983, Physico-chemical model of toxic substances in the Great Lakes: Journal of Great Lakes Research, v. 9, no. 4, p. 474-496.

Thuren, A., 1986, Determination of phthalates in aquatic environments: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 33-40.

Thurman, E.M., 1984, Determination of aquatic humic substances in natural waters: U.S. Geological Survey Water-Supply Paper 2262 (Selected Papers in the Hydrologic Sciences), p. 47-52.

Tipping, E. and Woof, C., 1983, Seasonal variations in the concentration of humic substances in a soft-water lake: Limnology and Oceanography, v. 28, no. 1, p. 168-172.

Truhlar, J.F., and Reed, L.A., 1976, Occurrence of pesticide residues in four streams draining different land-use areas in Pennsylvania, 1969-71: Pesticides Monitoring Journal, v. 10, no. 3, p.101-110.

Tschirley, F.H., 1986, Dioxin: Scientific American, v. 254, no. 2, p. 29-35.

Turk, J.T., 1980, Applications of Hudson River basin PCB-transport studies, in Baker, R. A., ed., Contaminants and sediments, volume 1: Ann Arbor, Michigan, Ann Arbor Science Publishers, Inc., p. 171-183.

Turk, J.T., and Troutman, D.E., 1981, Polychlorinated biphenyl transport in the Hudson River, New York: U.S. Geological Survey Water-Resources Investigations Report 81-9, 11 p.

Turner, A.G., DiGiano, F.A., and DeRosa, P.M., 1984, A survey of potential population exposures to chemical contaminants present in unprotected surface water supplies in North Carolina: Raleigh, North Carolina, University of North Carolina Water Resources Research Institute Report 213, 72 p.

Uchrin, C.G., and Katz, J., 1985, Reversible and resistant components of hexachlorocyclohexane (lindane) sorption to New Jersey coastal plain aquifer solids: Journal of Environmental Science and Health, v. A20, no. 2, p. 205-218.

Uchrin, C.G., and Mangels, G., 1986, Chloroform sorption to New Jersey coastal plain ground water aquifer solids: Environmental Toxicology and Chemistry, v. 5, p. 339-343.

U.S. Department of Agriculture, 1983, Outlook and situation, October: U.S. Government Printing Office, 23 p.

U.S. Environmental Protection Agency, 1976, Criteria for water: Washington D.C., Office of Water Planning and Standards, 0.222-904, p. 193.

U.S. Environmental Protection Agency, 1977, Quality criteria for water, 1976: U.S. Government Printing Office, 256 p.

U.S. Environmental Protection Agency, 1980a, Water quality criteria documents; Availability: U.S. Federal Register, v. 45, no. 231, p. 79318-79379.

U.S. Environmental Protection Agency, 1980b, Ambient water quality criteria for phenol: EPA-440/5-80-066.

U.S. Environmental Protection Agency, 1982, Sampling protocols for collecting surface water, bed sediment, bivalves, and fish for priority pollutant analysis: Washington, D.C., Office of Water Regulations and Standards.

Van Hove Holdrinet, Micheline, 1979, Confirmation of mirex and cis-trans-chlordane in the presence of other organochlorine insecticides and polychlorinated biphenyls: Bulletin of Environmental Contamination and Toxicology, v. 21, p. 46-52.

Van Luik, A., 1984, Mined land reclamation using polluted urban navigable waterway sediments: II. Organics: Journal of Environmental Quality, v. 13, no. 3, p. 415-422.

Van Middelem, C.H., 1963, Parathion residues on leafy crops: Residue Reviews, v. 2, p. 77-95.

VanNess, G.F., Solch, J.G., Taylor, M.L., and Tiernan, T.O., 1980, Tetrachlorodibenzo-p-dioxins in chemical wastes, aqueous effluents and soils: Chemosphere, v. 9, p. 553-563.

Varanasi, U., Reichert, W.L., Stein, J.E., Brown, D.W., and Sanborn, H.R., 1985, Bioavailability and biotransformation of aromatic hydrocarbons in benthic organisms exposed to sediment from an urban estuary: Environmental Science and Technology, v. 19, no. 9, p. 836-841.

Veith, G.D., DeFoe, D.L., and Bergstedt, B.V., 1979, Journal of the Fish Resources Board of Canada, v. 36, p. 1040.

Verschueren, K., 1983, Handbook of environmental data on organic chemicals, 2nd edition: Van Nostrand Reinhold Co. Inc., 1310 p.

Visser, S.A., Lamontagne, G., Zoulalian, V., and Tessier, A., 1977, Bacteria active in the degradation of phenols in polluted waters of the St. Lawrence River: Arhcives of Environmental Contamination and Toxicology, v. 6, p. 455-469.

Voice, T.C., Rice, C.P., and Weber, W.J., Jr., 1983, Effects of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems: Environmental Science and Technology, v. 17, no. 9, p. 513-518.

Voice, T.C., and Weber, W.J., Jr., 1983, Sorption of hydrophobic compounds by sediments, soils, and suspended solids- I. Theory and background: Water Research, v. 17, no. 10, p. 1433-1441.

Voice, T.C., and Weber, W.J., 1985, Sorbent concentration effects in liquid/solid partitioning: Environmental Science and Technology, v. 19, no. 9, p. 789-796.

Wakeham, S.G., and Carpenter, Roy, 1976, Aliphatic hydrocarbons in sediments of Lake Washington: Limnology and Oceanography, v. 21, no. 5, p. 711-723.

Wakeman, S.G., Davis, A.C., and Karas, J.L., 1983, Mesocosm experiments to determine the fate and persistence of volatile organic compounds in coastal seawater: Environmental Science and Technology, v. 17, no. 10, p. 611-617.

Walker, W.W., 1976, Chemical and microbiological degradation of malathion and parathion in an estuarine environment: Journal of Environmental Quality, v. 5, no. 2, p. 210-216.

Walker, J.D., Colwell, R.R., Hamming, M.C., and Ford, H.T., 1975, Extraction of petroleum hydrocarbons from oil-contaminated sediments: Bulletin of Environmental Contamination and Toxicology, v. 13, no. 2, p. 245-248.

Wallace, G.T., and Duce, R.A., 1978, Transport of particulate organic matter by bubbles in marine waters: Limnology and Oceanography, v. 23, no. 6, p. 1155-1167.

Wang, Wun-Cheng, 1975, Determination of cation-exchange capacity of suspended sediment: Water Resources Bulletin, v. 11, no. 5, p. 1052-1057.

Wang, T., Lenahan, R., and Kanik, M., 1985, Impact of trichloroethylene contaminated groundwater discharged to the main canal and Indian River lagoon, Vero Beach, Florida: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 578-586.

Ward, C.T., and Matsumura, F., 1978, Fate of 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD) in a model aquatic environment: Archives of Environmental Contamination and Toxicology, v. 7, p. 349-357.

Wasik, S.P., Miller, M.M., Tewari, Y.B., May, W.E., Sonnefeld, W.J., DeVoe, H., and Zoller, W.H., 1983, Determination of the vapor pressure, aqueous solubility, and octanol/water partition coefficient of hydrophobic substances by coupled generator column/liquid chromatographic methods: Residue Reviews, v. 85, p. 29-42.

Watkins, J., and Yarbrough, J.D., 1975, Aldrin and dieldrin uptake in insecticide-resistant and susceptible mosquitofish (*Gambusia affinis*): Bulletin of Environmental Contamination and Toxicology, v. 14, no. 6, p. 442-448.

SELECTED REFERENCES--Continued

Wauchope, R.D., 1978, The pesticide content of surface waters draining from agricultural fields - A review: Journal of Environmental Quality, v. 7, no. 4, p. 459-472.

Wauchope, R.D., and Myers, R.S., 1985, Adsorption-desorption kinetics of atrazine and linuron in freshwater-sediment aqueous slurries: Journal of Environmental Quality, v. 14, no. 1, p. 132-136.

Weber, W.J., and Gould, J.P., 1966, Sorption of organic pesticides from aqueous solution, in Organic pesticides in the environment: American Chemical Society, Advances in Chemistry Series 60, p. 280-304.

Weber, J.B., Perry, P.W., and Upchurch, R.P., 1965, The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D, and prometone by clays, charcoal, and an anion-exchange resin: Soil Science Society of America Proceedings, v. 29, p. 678-688.

Weber, W.J., Sherrill, J.D., Pirbarazi, M., Uchrin, C.G., and Lo, T.Y., 1980, Transport and differential accumulation of toxic substances in river-harbor-lake systems, in Haque, R., ed., Dynamics, exposure, and hazard assessment of toxic chemicals: Ann Arbor, Michigan, Ann Arbor Science Publishers, p. 191-213.

Weber, W.J., Voice, T.C., Pirbazari, M., Hunt, G.E., and Ulanoff, D.M., 1983, Sorption of hydrophobic compounds by sediments, soils and suspended soils- II. Sorbent evaluation studies: Water Research, v. 17, no. 10, p. 1443-1452.

Wegman, R.C.C., and van den Broek, H.H., 1983, Chlorophenols in river sediment in the Netherlands: Water Research, v. 17, p. 227-230.

Weinberger, P., Greenhalgh, R., Moody, R.P., and Boulton, B., 1982, Fate of fenitrothion in aquatic microcosms and the role of aquatic plants: Environmental Science and Technology, v. 16, no. 8, p. 470-473.

Welch, K.J., Kuehl, D.W., Leonard, E.N., Veith, G.D., and Schoenthal, N.D., 1981, Background hydrocarbon residues in fishes from the great lakes and eastern Montana: Bulletin of Environmental Contamination and Toxicology, v. 26, p. 724-728.

Wershaw, R.L., 1986, A new model for humic materials and their interactions with hydrophobic organic chemicals in soil-water or sediment-water systems: Journal of Contaminant Hydrology, v. 1, p. 29-45.

Wershaw, R.L., Burcar, P.J., and Goldberg, M.C., 1969, Interaction of pesticides with natural organic material: Environmental Science and Technology, v. 3, no. 3, p. 271-273.

Wershaw, R.L., and Pinckney, D.J., 1973, Determination of the association and dissociation of humic acid fractions by small angle X-ray scattering: U.S. Geological Survey Journal of Research, v. 1, no. 6, p. 701-707.

Whipple, W., and Hunter, J.V., 1979, Petroleum hydrocarbons in urban runoff: Water Resources Bulletin, v. 15, no. 4, p. 1096-1105.

White, R.J., Kim, H.T., and Kim, J.S., 1985, PCBs in striped bass collected from the Hudson River, New York, during Fall, 1981: Bulletin of Environmental Contamination and Toxicology, v. 34, p. 883-889.

Whitman, W.G., 1923, Preliminary experimental confirmation of the two-film theory of gas absorption: Chemical and Metallurgical Engineering, v. 29, p. 146-154.

Wicklund, A., and Suffet, I.H., 1983, Boonton Reservoir study; Part I - Sampling and analysis of organic chemicals: Trenton, New Jersey, New Jersey Department of Environmental Protection, 120 p.

Wijayaratne, R.D., and Means, J.C., 1984, Affinity of hydrophobic pollutants for natural estuarine colloids in aquatic environments: Environmental Science and Technology, v. 18, no. 2, p. 121-123.

Wilbur, W.G. and Hunter, J.V., 1979, The impact of urbanization on the distribution of heavy metals in bottom sediments of the Saddle River: Water Resources Bulletin, v. 15, no. 3, p.790-800.

Wildish, D.J., Metcalfe, C.D., and McLeese, D.W., 1980, Flux of Aroclor 1254 between estuarine sediments and water: Bulletin of Environmental Contamination and Toxicology, v. 24, p. 20-26.

Wilson, A.J., and Forester, J., 1978, Persistence of Aroclor 1254 in a contaminated estuary: Bulletin of Environmental Contamination and Toxicology, v. 19, p. 637-640.

Wilson, J.T., Miller, G.D., Ghiorse, W.C., and Leach, F.R., 1986, Relationship between the ATP content of subsurface material and the rate of biodegradation of alkylbenzenes and chlorobenzene: Journal of Contaminant Hydrology, v. 1, p. 163-170.

Winger, P.V., and Andreasen, J.K., 1985, Contaminant residues in fish and sediments from lakes in the Atchafalaya River Basin (Louisiana): Archives of Environmental Contamination and Toxicology, v. 14, p. 579-586.

Witkowski, P.J., Smith, J.A., Fusillo, T.V., and Chiou, C.T., 1987, A review of surface-water sediment fractions and their interactions with persistent manmade organic compounds: U.S. Geological Survey Circular 993.

Wolfe, N.L., Zepp, R.G., Gordon, J.A., Baughman, G.L., and Cline, D.M., 1977, Kinetics of chemical degradation of malathion in water: Environmental Science and Technology, v. 11, no. 1, p. 88-93.

Wolfe, N.L., Zepp, R.G., and Paris, D.F., 1978, Use of structure- reactivity relationships to estimate hydrolytic persistence of carbamate pesticides: Water Research, v. 12, p. 561-563.

Wood, L.W., Jones, P.A., and Richards, A., 1986, Possible sediment scavenging of chlordane and contamination of the aquatic biota in Belmont Lake, New York: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 159-167.

Woodburn, K.B., Rao, P.S.C., Fukui, M., and Nkedi-Kizza, P., 1986, Solvophobic approach for predicting sorption of hydrophobic organic chemicals on synthetic sorbents and soils: Journal of Contaminant Hydrology, v. 1, p. 227-241.

Woodwell, G.M., Craig, P.P., and Johnson, H.A., 1971, DDT in the biosphere: Where does it go?: Science, v. 174, p. 1101-1107.

Wszolek, P.C., Lisk, D.J., Wachs, T., and Youngs, W.D., 1979, Persistence of polychlorinated biphenyls and 1,1-dichloro-2,2- bis(p-chlorophenyl)ethylene (p,p'-DDE) with age in lake trout after 8 years: Environmental Science and Technology, v. 13, no. 10, p. 1269-1271.

Wu, Shian-chee, and Gschwend, P.M., 1986, Sorption kinetics of hydrophobic organic compounds to natural sediments and soils: Environmental Science and Technology, v. 20, no. 7, p. 717-725.

Wu, T.L., Lambert, L., Hastings, D., and Banning, D., 1980, Enrichment of the agricultural herbicide atrazine in the microsurface water of an estuary: Bulletin of Environmental Contamination and Toxicology, v. 24, p. 411-414.

Yalkowsky, S.H., Valvani, S.C., and Mackay, D., 1983, Estimation of the aqueous solubility of some aromatic compounds: Residue Reviews, v. 85, p. 43-55.

Yamamoto, Yasuhiro, Suzuki, Manabu, Shimohara, Kenichi, and Akiyama, Takashi, 1980, Behaviour of HCH (1,2,3,4,5,6-hexachlorocyclohexane) residue in the aquatic environment: Water Research, v. 14, p. 247-251.

SELECTED REFERENCES--Continued

Yaron, Bruno, 1978, Some aspects of surface interactions of clays with organophosphorous pesticides: Soil Science, v. 125, no. 4, p. 210-216.

Yaron, Bruno, and Saltzman, Sarina, 1972, Influence of water and temperature on adsorption of parathion by soils: Soil Science Society of America Proceedings, v. 36, p. 583-586.

Yasuhara, A., Shiraishi, H., Tsujl, M., and Okuno, T., 1981, Analysis of organic substances in highly polluted river water by mass spectrometry: Environmental Science and Technology, v. 15, p. 570-573.

Yorke, T.H., Stamer, J.K., and Pederson, G.L., 1985, Effects of low-level dams on the distribution of sediment, trace metals, and organic substances in the lower Schuylkill River basin, Pennsylvania: U.S. Geological Survey Water-Supply Paper 2256-B, 53 p.

Zabawa, C.F., 1978, Microstructure of agglomerated suspended sediments in northern Chesapeake Bay estuary: Science, v. 202, p. 49-51.

Zafiriou, O.C., Joussot-Dubien, J., Zepp, R.G., and Zika, R.G., 1984, Photochemistry of natural waters: Environmental Science and Technology, v. 18, no. 12, p. 358a-371a.

Zepp, R.G., and Cline, D.M., 1977, Rates of direct photolysis in aquatic environment: Environmental Science and Technology, v. 11, no. 4, p. 359-366.

Zierath, D.L., Hassett, J.J., Banwart, W.L., Wood, S.G. and Means, J.C., 1980, Sorption of benzidine by sediments and soils: Soil Science, v. 129, no. 5, p. 277-281.

Zitko, V., 1971, Polychlorinated biphenyls and organochlorine pesticides in some freshwater and marine fishes: Bulletin of Environmental Contamination and Toxicology, v. 6, no. 5, p. 464-470.

Zsolnay, A., 1979, Coastal colloidal carbon: A study of its seasonal variation and the possibility of river input: Estuarine and Coastal Marine Science, v. 9, p. 559-567.