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A Review of Surface-Water Sediment Fractions and Their Interactions With Persistent Manmade Organic Compounds

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GLOSSARY

Activity. A dimensionless quantity expressing the escaping tendency of a component in a system relative to that in a pure state of the same component at the same temperature and total pressure. It is the ratio of the partial pressures (or more precisely, the fugacities) of the dissolved component in the system to that of the component at standard state.

Activity coefficient. A dimensionless quantity that corrects for the deviation of the partial pressure (or fugacity) of a component in solution from that value defined by Raoult's law. If the observed partial pressure is greater than that predicted by Raoult's law, the activity coefficient is greater than one; conversely, if the observed partial pressure is less than that predicted by Raoult's law, the activity coefficient is less than one. Most organic solutes in water show positive deviation from ideality, that is, the activity coefficient is greater than one. This term provides an approximation of how much interaction exists between molecules at higher concentrations.

Adsorption. The interphase accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases, such as liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being concentrated or adsorbed is the adsorbate, and the adsorbing phase is termed the adsorbent.

Anthropogenic compounds. Compounds that are produced as a result of the activities of humans as contrasted with compounds formed by the actions of natural forces and events.

Bedload. Sediment that is transported in a stream by rolling, sliding, or skipping along the bed and very close to it, that is, within the bedlayer.

Bedload layer. A thin layer through which the bedload discharges, commonly assumed to be only a few grain diameters thick.

Bioturbation. Mixing processes in sediment layer caused by the activity of biological organisms.

Coagulation. A process where charge neutralization of discrete colloids occurs through interactions with available counterions.

Colloids. Operationally defined as discrete particles with at least one characteristic dimension in the micrometer to nanometer range.

Diagenesis. The gradual and successive chemical and physical changes that take place in sediment previous to or during its consolidation.

Dissolved. Operationally defined as discrete particles less than 0.45 μm in their maximum dimension.

Flocculation. Aggregation of neutral discrete colloids into larger masses by the mixing action of water.

Fulvic acids. The fraction of organic matter that remains dissolved in solution after sequential extraction of the sample with alkali and then acid.

Humic acids. The fraction of organic matter that remains dissolved in solution after extraction with alkali but that precipitates from solution upon further extraction with acid.

Humins. The fraction of organic matter that is not soluble in either alkali or acid.

Lipophilic. The characteristic of solutes or solvents that are readily miscible in other organic solvents such as lipids. Lipids as a heterogeneous group of substances include fatty acids, neutral fats, phosphatides, glycolipids, aliphatic alcohols and waxes, terpenes, and steroids. Lipids are categorized by their extractability in nonpolar organic solvents such as chloroform, carbon tetrachloride, benzene, ether, carbon disulfide, and petroleum ether.

Miscible. The ability of two or more substances to mix and to form a single, homogeneous phase.

Particulate. Operationally defined as discrete particles greater than 0.45 μm in their maximum dimension.

Partition. The distribution of a compound between two different bulk phases, usually by a solubilization process.

Polarity. Local charge groupings occurring as a result of geometric asymmetries between atoms of a given molecule. This chemical characteristic can lead to incompatibilities between liquids of different polarities. The relative polarity of large macromolecules, such as the humic and fulvic acids, is measured by comparing the oxygen to carbon ratios of the molecules. The larger the magnitude of the ratio, the greater the relative polarity of the compound.

Sediment. Fragmented material that originates from the disintegration of rocks and is transported by, suspended in, or deposited by water or air or is accumulated in beds by other natural processes.

Solute. The compound dissolved in solution.

Sorption. General expression for a process in which a component moves from one phase to be accumulated in another. The material being sorbed is the sorbate, and the sorbing phase is termed the sorbent. Sorption is used when it is not certain if the accumulating mechanism is a partitioning, an adsorption, or an absorption process.

Surface microlayer. Upper, very thin layer of a surface-water body characterized by high surface tension and some physical and chemical properties distinguishable from the bulk solution.

Surficial sediment layer. Upper sediment layer with a thickness that fluctuates depending on the deposition rates of new sediment and the degree of resuspension generated by boundary layer turbulence. In this paper, the surficial sediment layer is always considered to be submerged.

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ABSTRACT

This paper reviews the suspended and surficial sediment fractions and their interactions with manmade organic compounds. The objective of this review is to isolate and describe those contaminant and sediment properties that contribute to the persistence of organic compounds in surface-water systems. Most persistent, nonionic organic contaminants, such as the chlorinated insecticides and polychlorinated biphenyls (PCBs), are characterized by low water solubilities and high octanol-water partition coefficients. Consequently, sorptive interactions are the primary transformation processes that control their environmental behavior. For nonionic organic compounds, sorption is primarily attributed to the partitioning of an organic contaminant between a water phase and an organic phase. Partitioning processes play a central role in the uptake and release of contaminants by sediment organic matter and in the bioconcentration of contaminants by aquatic organisms.

Chemically isolated sediment fractions show that organic matter is the primary determinant of the sorptive capacity exhibited by sediment. Humic substances, as dissolved organic matter, contribute a number of functions to the processes cycling organic contaminants. They alter the rate of transformation of contaminants, enhance apparent water solubility, and increase the carrying capacity of the water column beyond the solubility limits of the contaminant. As a component of sediment particles, humic substances, through sorptive interactions, serve as vectors for the hydrodynamic transport of organic contaminants. The capabilities of the humic substances stem in part from their polyfunctional chemical composition and also from their ability to exist in solution as dissolved species, flocculated aggregates, surface coatings, and colloidal organomineral and organometal complexes.

The transport properties of manmade organic compounds have been investigated by field studies and laboratory experiments that examine the sorption of contaminants by different sediment size fractions. Field studies indicate that organic contaminants tend to sorb more to fine-grained sediment, and this correlates significantly with sediment organic matter content. Laboratory experiments have extended the field studies to a wider spectrum of natural particulates and anthropogenic compounds. Quantitation of isotherm results allows the comparison of different sediment sorbents as well as the estimation of field partition coefficients from laboratory-measured sediment and contaminant properties. Detailed analyses made on the basis of particle-size classes show that all sediment fractions need to be considered in evaluating the fate and distribution of manmade organic compounds. This conclusion is based on observations from field studies and on the variety of natural organic sorbents that demonstrate sorptive capabilities in laboratory isotherm experiments.

INTRODUCTION

There is a growing need to monitor riverine, estuarine, and lake sediment to provide a more complete understanding of contaminant transport and transformations in surface waters. As contaminants move through a surface-water body, they interact with natural particles suspended in the water column and those deposited in the surficial sediment layer. Through sorptive processes, sediment particles interact with organic contaminants and can become vectors for their hydrodynamic transport. Sediment also functions as a reservoir for contaminants and has the ability to take up and release contaminants in response to concentration variations in the overlying water column. Understanding the interactions between the sediment and water-column compartments helps to reveal how specific contaminants are transformed and transported within the surface-water body.

PURPOSE AND SCOPE

The objective of this paper is to review the characteristics of suspended and surficial sediment fractions and their interactions with manmade organic compounds. The emphasis is on sorptive interactions between natural particles and persistent organic contaminants. Sorption is a general term used to describe the variety of possible contaminant-sorbent interactions

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when the exact nature of the particle-contaminant interaction is not known or when the interaction may involve more than one dominant mechanism. Sorptive interactions are considered because they are an important mechanism through which persistent manmade contaminants interact with sediment particles. The influence of sorptive interactions on contaminant distribution and fate is shown to extend to the processes controlling the transport and transformation of the organic compounds. Consequently, the scope of this paper is not limited to interactions within the surficial sediment layer; it also encompasses important water-column interactions that occur during the deposition and resuspension of sediment components.

This review examines sediment-contaminant interactions. The sections on (1) Manmade Organic Contaminants and (2) Suspended and Surficial Sediment Fractions examine contaminant and sediment properties, respectively. Manmade Organic Contaminants describes the physicochemical properties, transformation processes, and environmental behaviors that combine to determine the fate of an anthropogenic organic compound. Suspended and Surficial Sediment Fractions describes some properties and transformation processes characteristic of biological organisms, inorganic particles, and humic substances found suspended in the water column and within the surficial sediment layer. Together, these sections provide the background information necessary to understand the complex interactions between organic contaminants and sediment fractions discussed in the section on Interactions Between Sediment Fractions and Manmade Organic Compounds.

The section on interactions looks specifically at how the various fractions of the sediment influence the fate of organic contaminants. Humic substances, the decay products of terrestrial and aquatic organic matter, modify the chemical form, stability, and reactivity of contaminants in surface-water systems. Examples show how humic substances can change the apparent solubility and affect the sorptive interactions of persistent organic contaminants. Field studies are reviewed that seek patterns and trends in the sorption of organic compounds by sediment sorbents characterized on the basis of size and type. Laboratory studies are reviewed that seek to quantify more exactly the discernible trends and patterns observed in the field data.

The section on Transport of Sorbed Manmade Organic Compounds examines the hydrodynamic forces that control the transport of contaminants sorbed to different sediment fractions separated on the basis of size. Finally, the section on Estimation of the Field Distribution of Manmade Organic Compounds deals with the methods used in estimating the field sorption behavior and bioconcentration of contaminants from laboratory-measurable physical properties of the sediment and the anthropogenic organic compounds.

Overall, the review is designed to provide some indication of what happens to an organic contaminant when it is introduced into a surface-water system. To achieve this objective, it is important to have a basic understanding of the nature of the aqueous environment in conjunction with the properties of the anthropogenic compound.

APPROACH

In considering the sorptive interaction of anthropogenic organic compounds with sediment, interest lies in determining and understanding the physical and chemical factors that control the spatial distribution and temporal patterns observed in field investigations. Field behavior of organic compounds is largely determined by physical and chemical properties of a compound as manifested under a given set of environmental conditions. If an organic chemical interacts with a natural particulate, the behavior of the compound will be modified to an extent that depends on the physical and chemical attributes of the compound and the sediment particle. Understanding the influence of sediment, in terms of its properties, is achieved by examining different sediment fractions. The different components of the bulk sediment are defined on the basis of size and chemical extraction procedure. The way that different sediment fractions contribute to the interactions with different organic compounds and the way that this behavior can be accounted for in relation to what is observable on the bulk sediment level are the subject of this review.

MANMADE ORGANIC CONTAMINANTS

This section examines some of the physicochemical properties that are characteristic of different groups of anthropogenic organic compounds in aqueous systems. In addition, the section considers several transformation processes that influence the fate of anthropogenic organic compounds. Together, the physicochemical properties and the transformation processes determine the environmental persistence of certain anthropogenic organic compounds. The remainder of the review will focus on these compound and system

Table 1.—*Classification of manmade organic compounds by chemical source*

Groups	Common examples or subgroups
Petroleum- and coal-derived hydrocarbons	1. Crude oil (alkanes, cycloalkanes, and aromatics). 2. Refined petroleum products (petrol, kerosene, diesel, heating oils, and asphalts). 3. Combustion and conversion products (PAHs, carbon dioxide, synfuels, and byproducts).
Synthetic organics	1. Halogenated hydrocarbons (PCBs, DDTs, Kepone, Mirex, dieldrin, chlordane, industrial solvents, and other pesticides). 2. Phthalate esters (plasticizers such as polyvinyl chloride (PVC)). 3. Others (surface-active agents, organophosphate insecticides, carbamate insecticides, and many herbicides).
Municipal wastes	1. Sewage sludge, secondary effluents, and trihalomethanes (THMs). 2. Nutrients (phosphates, nitrogen, carbon, and silica).

Source: Olsen and others (1982).

characteristics to examine the interaction of persistent organic compounds with sediment fractions.

The number of existing anthropogenic compounds is large, and their environmental behavior is more readily reviewed from the standpoint of compound groups rather than of individual chemicals. Table 1 categorizes organic compounds by source, and table 2 categorizes them by a combination of chemical families and substance usage groups. These tables are intended to be representative of the more common anthropogenic organic compounds and do not include all those that might have an adverse impact on water quality.

PHYSICAL AND CHEMICAL PROPERTIES

Several common physicochemical properties of anthropogenic organic substances contribute to environmental persistence and toxicity. Table 3 lists typical ranges of molecular weights, vapor pressures, water solubilities, and octanol-water partition coefficients for the compound groups and some subgroups from table 2. The ranges are meant to be representative within each group (outliers certainly exist) and also to serve as benchmarks for comparisons among different groups.

From the simple breakdown employed in table 3, several distinct physicochemical characteristics are apparent. Water solubility is probably the most important property affecting the movement of compounds among the various environmental compartments, including air, the water column, aquatic biota, and sediment (Oschwald, 1972; Pionke and Chesters, 1973). Many of the organic compounds are highly water insoluble with solubilities in the low milligram per liter to microgram per liter range. Within specific chemical

groups, a decreasing trend in water solubility is discernible as the degree of halogen substitution increases (for example, insecticides, aliphatic hydrocarbons, monocyclic aromatics, and phenols). Similarly, within specific chemical groups, water solubility decreases as the number of aromatic and cyclic ring substitutions increases (for example, polynuclear aromatic hydrocarbons (PAHs), ethers, and nitrogen-substituted compounds). Much of the following discussion focuses on these low-solubility compounds because they are representative of many persistent organic contaminants.

In general, the low solubility of an organic contaminant in water is commonly reflected by its affinity for relatively nonpolar organic phases (solid and liquid). This lipophilic tendency is found in compounds possessing high octanol-water partition coefficients, where concentrations in the organic phase are 10^3 to 10^6 times greater than those in the water phase (for example, PAHs, polychlorinated biphenyls (PCBs), and phthalate esters). The octanol-water partition coefficient is a dimensionless concentration ratio whose magnitude expresses the distribution of a compound between equal volumes of two partially miscible solvents, n-octanol and water (Leo and others, 1971). The magnitude of the partition coefficient is a useful index of the tendency of an organic compound to partition from water into sediment organic matter and into aquatic organisms (bioconcentration). The greater the magnitude of the partition coefficient, the greater the relative solubility of the compound in the organic phase over that in the aqueous phase.

The partition behavior of a compound in a simple organic solvent-water system provides a useful estimate of the probable behavior of that compound in an aqueous environment (Haque and Freed, 1974; U.S. EPA, 1979a). The use of the partition coefficient to estimate the environmental distribution of a

Table 2.—*Classification of manmade organic compounds by chemical structure and chemical usage*

Groups	Common examples or subgroups
Halogenated aliphatic hydrocarbons	Chlorinated/brominated alkanes and chlorinated/brominated alkenes
Halogenated ethers	Chloroalkyl ethers and chlorophenylethers
Monocyclic aromatics	Chlorinated benzenes, alkyl benzenes, nitrotoluenes, and aminobenzenes
Phenols and cresols	Chlorinated phenols, nitrophenols, alkylphenols, and substituted cresols
Phthalate esters	Dialkyl phthalates
Polynuclear aromatic hydrocarbons	Naphthalene, anthracene, chrysene, and benzo(a)pyrene
Nitrogen substituted compounds	Alkylamines, nitrosamines, and halogenated benzidines
Polychlorinated biphenyls	Isomers and Aroclors (1016, 1221, 1232, 1242, 1248, 1254, and 1260)
Organochlorine insecticides	Aldrin, DDTs, endosulfan, heptachlor, chlordane, methoxychlor, and toxaphene
Organophosphorus insecticides	Parathion, malathion, and diazinon
Carbamate insecticides and herbicides	Carbaryl (Sevin), carbofuran, and aldicarb
Acid herbicides (phenoxy and benzoic)	2,4-D, silvex, 2,4,5-T, benzoic acid, and dicamba
Triazine herbicides	Atrazine, propazine, simazine, and prometryne
Substituted urea herbicides	Diuron, flometuron, and linuron
Other herbicides	Bipyridylium (diquat and paraquat)
	Dinitroanilines (trifluralin and profluralin)
	Others (alachlor, propachlor, and picloram)
Other pesticides	Nematicides (ethylene dibromide and methyl bromide)
	Miticides (kelthane, chlorobenzilate, and dichlore)
	Fungicides (captan, quinones, and dithiocarbamic acid derivatives)

compound is based on the recognition that much of the molecular driving force controlling distribution among water, sediment, and biota is analogous to that found in the octanol-water model system (Chiou, 1981). The use of octanol-water partition coefficients to estimate sediment-water partition coefficients and bioconcentration factors (BCF) is discussed in more detail in the section on Estimation of the Field Distribution of Manmade Organic Compounds.

The vapor pressure of an organic compound indicates the extent to which it will volatilize from solution. Although vapor pressure exerts an important influence on the volatility of a compound as a pure substance, volatilization from an environmental system also depends on other physical properties (for example, water solubility) and system variables (for example, temperature, wind speed, and water turbulence). Low-molecular-weight compounds (<200 amu) such as aliphatic hydrocarbons, monocyclic aromatics, and some nitrogen-substituted compounds possess relatively high vapor pressures and limited water solubilities that in conjunction with certain environmental conditions make volatilization an important environmental pathway (U.S. EPA, 1978, 1981).

Although water solubility and octanol-water partitioning are of primary importance in controlling the environmental distribution of anthropogenic organic compounds, other physicochemical properties also exert a significant influence on their overall distribution. These properties include polarity, ionization constant, molecular charge, molecular size, and molecu-

lar configuration (U.S. EPA, 1979a; Verschueren, 1983). The exact contribution of each of these properties is difficult to isolate because the effects are exerted primarily at the molecular level. However, some properties, such as the tendency to ionize in solution, determine which compounds respond to changes in pH (for example, acid and bipyridylium herbicides) and which are not sensitive to its variation (for example, chlorinated insecticides). The polarity of the organic compound influences its degree of chemical compatibility with polar solvents such as water and other less polar solvents such as sediment organic matter. Finally, fundamental properties such as molecular size and charge exert their influence on the behavior of a compound at all levels, from molecular interactions to the macroscopic scale of field processes.

The more environmentally persistent organic compounds (for example, PCBs, chlorinated insecticides, PAHs, phthalate esters, highly halogenated aliphatics, and aromatics) are generally characterized by low water solubility and high octanol-water partition coefficients (U.S. EPA, 1982). Most of these chemical groups represent nonionic compounds that were synthesized for industrial and (or) agricultural applications that require physical stability and specific properties (U.S. EPA, 1979b; Verschueren, 1983). On the basis of low solubility and high partition coefficients, the distribution and fate of these persistent compounds in the environment largely depend on sorptive interactions with natural particles. Yet, other physicochemical properties may become important under certain specific conditions, and therefore, environmental behavior must

Table 3.—*Physical and chemical properties of selected groups of manmade organic compounds*

[>, greater than; mg/L, milligrams per liter]

Groups	Subgroups	Number of compounds	Molecular weight range	Log vapor pressure in torr*	Log water solubility in mg/L	Log octanol-water partition coefficient	References
Halogenated aliphatic hydrocarbons	1–4 Cl/Br	28	50-200	2 to 3	2 to 4	1 to 3	1,2,3,4,5,6
	>5 Cl/Br	3	200-300	− 2 to −1	0 to 1	3 to 4	1,2,3,4,5,6
Halogenated ethers	Aliphatic	5	100-200	− 1 to 1	3 to 5	1 to 3	1,2,3,4,5,6
	Aromatic	2	200-250	− 3 to −2	0 to 1	4 to 5	1,2,3,4,5,6
Monocyclic aromatics		19	100-200	− 1 to 2	2 to 3	2 to 4	1,2,3,4,5,6
Phenols		12	100-200	− 1 to 0	3 to 5	1 to 4	1,2,3,4,5,6
Monocyclic aromatics and phenols	>5 Cl/Br	2	250-300	− 5 to −4	−3 to 1	5 to 6	1,2,3,4,5,6,12
Phthalate esters		6	200-400	− 3 to −1	0 to 4	2 to 9	1,2,3,4,5,6,16
Polynuclear aromatic hydrocarbons	2 benzene rings	4	100-150	− 3 to −2	0 to 2	3 to 5	1,2,3,4,5,6,11
	3 benzene rings	3	175-200	− 6 to −4	−2 to 0	4 to 6	1,2,3,4,5,6,11
	4 benzene rings	5	200-250	−11 to −6	−3 to −1	5 to 7	1,2,3,4,5,6,11
	>4 benzene rings	4	250-275	−11 to −9	−4 to −3	6 to 8	1,2,3,4,5,6,11
Nitrogen-substituted compounds	Aliphatic	10	30-125	1 to 3	>4	−1 to 1	1,2,3,4,5,6
	Aromatic	4	175-250		0 to 3	2 to 3	1,2,3,4,5,6
Polychlorinated biphenyls		9	200-375	− 5 to −3	−3 to 1	3 to 7	1,2,3,4,6,10,12
Organochlorine insecticides		13	300-400	− 7 to −4	−3 to 0	3 to 6	1,2,3,4,5,6,9,12
Organophosphorus insecticides		10	275-375	− 7 to −4	1 to 2		8,9
Carbamate insecticides and herbicides		8	175-275	− 5 to −1	1 to 5		7,8,9,14,15
Acid herbicides		11	175-250	− 7 to −3	2 to 4		7,8,9,12,15
Triazine herbicides		11	200-250		1 to 3		7,8,9,15
Substituted urea herbicides		7	150-275	− 7 to −4	2 to 3		7,9,15
Bipyridylium herbicides		2	250-350		miscible		7,9,10
Dinitroaniline herbicides		13	200-450	− 8 to −4	−3 to 1		7,9,13

* 760 torr = 1 atmosphere

(1) U.S. EPA (1979a)
(2) U.S. EPA (1981)
(3) U.S. EPA (1982)
(4) Verschueren (1983)
(5) U.S. EPA (1978)
(6) U.S. EPA (1979b)
(7) Bailey and White (1965)
(8) Paris and Lewis (1973)
(9) Wauchope (1978)
(10) Garten and Tralbalka (1983)
(11) Hassett and others (1983)
(12) Mackay and others (1980)
(13) Helling (1976)
(14) Schlagbauer and Schlagbauer (1972)
(15) Bailey and others (1968)
(16) Mathur (1974)

Note: Base 10 raised to the −1 power = 0.1
Base 10 raised to the 0 power = 1.0
Base 10 raised to the +1 power = 10

be studied in terms of as many compound properties and environmental variables as possible.

TRANSFORMATION PROCESSES

Although physicochemical properties are indicative of the potential behavior of a compound in a water system, environmental variables are also important. This section reviews some of the transformation processes that can play a role in determining the environmental fate of an organic compound. The last part of this section (Environmental Behavior) examines how the physicochemical properties couple with the environmental variables to determine the primary transformation processes contributing to the persistence of certain anthropogenic organic compounds.

During their movement through the water column and the surficial sediment layer, organic compounds participate in many interactions which determine their ultimate environmental fate. Table 4 lists and briefly defines some of the more important transformation processes and controlling factors. Table 5 presents some of the measurable characteristics frequently used to assess the degree to which the behavior of a given compound is determined by a particular transformation process. The relative importance of the competing processes to each compound depends on the physicochemical properties of the organic chemical as well as the prevailing environmental conditions in the water column and in the surficial sediment layer.

Volatilization, as a transformation process, illustrates some of the information presented in tables 4 and 5.

Table 4.—*Physical, chemical, and biological transformation processes that affect manmade organic compounds*

Process	Definition and controlling variables
Volatilization	1. Evaporative loss of a chemical. 2. Depends on vapor pressure and water solubility of the chemical and environmental variables like wind, water turbulence, and temperature. 3. Potentially important for compounds with high vapor pressures, low solubilities, and high activity coefficients.
Sorption	1. General term encompassing surface attraction (absorption) and partition (solubilization). 2. Depends on the hydrophilic and lipophilic properties of the chemical and the composition of the sorbent. 3. Indicative parameters are solubility, octanol-water partition coefficient, and sorbent organic carbon content.
Photolysis	1. Nonmetabolic degradation requiring light energy: chemical undergoes either a direct transformation reaction from the absorbed energy or an indirect change from a reaction— for example, oxidation, with an excited chemical species or free radical. 2. Depends on the chemical's absorption spectrum coefficient in the ultraviolet to visible range as well as the sunlight intensity distribution for a given time of day, season, latitude, depth in water, and ozone thickness. Also depends on the chemical's reaction quantum yield.
Chemical oxidation	1. Breaking down of the chemical bonds in organic compounds through a chemical reaction with photochemically derived oxidants (singlet oxygen or free radicals). 2. Depends on the number and types of possible reactive sites and on the presence of oxidants. 3. Rate constants either measured directly or estimated from structure-activity relations.
Hydrolysis	1. Reaction of a chemical with water, hydrogen, or hydroxide ion, commonly resulting in the introduction of a hydroxyl group in exchange for the removal of another functional group. 2. Depends on the presence and number of hydrolyzable functional groups at neutral pH plus the catalytic effect of the addition of acids and bases at other pHs.
Bioaccumulation	1. Uptake and retention of chemicals in the water column by aquatic organisms through intake from water or diet. 2. Depends on the nature of the chemical (lipophilic) and the organism's fat content, metabolic, and depuration rates.
Biotransformation and biodegradation	1. Enzyme catalyzed transformation of chemicals as a source of energy, carbon, and nutrients. 2. Depends on the refractory and toxic nature of the chemical, and the presence of an acclimated microbial population, and a host of environmental factors including pH, temperature, dissolved oxygen, available nutrients, and cometabolites.

It can be an important exchange process between a compound dissolved in solution and one vaporized in the atmosphere. Organic compounds with high vapor pressures, low water solubilities, and high activity coefficients are most susceptible to volatilization (for example, aliphatic hydrocarbons, monocyclic aromatics, and some nitrogen-substituted compounds). The magnitude of Henry's law constant is used as an indicator of the volatility of a compound from water because it takes into account the physical properties of water solubility and vapor pressure. Yet, alone it cannot be used as a quantitative measure of the volatility of a compound, because volatilization also depends on environmental variables such as wind velocity, water turbulence, and temperature (U.S. EPA, 1978, 1979a). The balance of these environmental variables and physicochemical properties determines which groups of organic compounds are susceptible to volatilization and to what degree the exchange will alter the water column concentrations.

Photolysis is another example of a transformation process that depends on both the properties of a compound and the environmental conditions. The degree of photolysis depends on the amount of light a particular chemical can absorb (absorption spectrum coefficient) and the efficiency with which it uses that energy (reaction quantum yield). Given these properties of the organic compound, the actual degree of photolysis depends on climatic and meteorologic conditions such as sunlight intensity, cloud cover, time of day, season, latitude, and even ozone thickness (U.S. EPA, 1979a, 1981). In addition, the water turbidity determines the amount of incident sunlight that actually penetrates the water column to the depth of the organic

Table 5.—*Physical and chemical characteristics used to assess the distribution and fate of manmade organic compounds*

Characteristics	Definitions
Water solubility	Indicative of a chemical's hydrophobic/hydrophilic nature, the limiting load in water, and its potential behavior in solution. Units: mass per volume.
Vapor pressure	The partial pressure of vapor that is in equilibrium with a substance in pure state at a specified temperature. Relative or qualitative measure of the volatility of the chemical in its pure state. Units: torr.
Henry's law constant	Relative equilibrium concentration of a compound in air and water at standard temperature and pressure. Ratio of the vapor pressure divided by the chemical's water solubility; indicative of the compound's volatility. Units: torr per molar.
Reaeration rate ratio	Ratio of the first-order rate constant for loss of a chemical from aqueous solution divided by the rate constant for oxygen uptake by the same solution. Unitless. Estimate of the volatility of compounds with Henry's constants $>3,500$ torr per molar for which the volatilization rate constant is limited by diffusion through the liquid-phase boundary layer.
Partition coefficient	Equilibrium distribution of a compound solubilized between two immiscible solvents. Unitless.
Octanol-water partition coefficient	Equilibrium distribution of a compound between water and n-octanol. Indicative characteristic of the bioconcentration potential of compounds. Unitless.
Soil/sediment partition coefficient	Equilibrium distribution of a compound between water and a sediment/soil substrate. Mass of chemical per mass of sediment divided by the dissolved mass of chemical in solution per mass of solution volume. Unitless.
Soil/sediment partition constant	Soil/sediment partition coefficient divided by the sediment/soil percent organic carbon content. Normalizes the partition coefficient to a sediment/soil substrate that is 100 percent organic carbon, permitting comparison of partition coefficients between substrates of differing carbon content.
Absorption spectrum coefficient	Quantity of light absorbed by the chemical at a particular wavelength in the ultraviolet-visible range of the electromagnetic spectrum.
Reaction quantum yield	Efficiency of light utilization by a chemical. Ratio of the number of moles of the chemical transformed to the quantity (flux) of light absorbed. Unitless.
Photolysis rate constant	First-order rate constant for direct photolysis. Units: reciprocal time.
Oxidation rate constant	Sum of the rate constants for each individual type of reactive site in the compound. Units: reciprocal time.
Hydrolysis rate constant	First-order rate constant at pH of 7 and the second-order rate constants for acid- and base-promoted hydrolysis. Units: reciprocal time.
Bioconcentration factor	Concentration of a chemical in tissue on a dry-weight basis divided by the concentration in water. Also the ratio of the uptake to depuration rates for a compound in a given organism. Unitless.
Biotransformation rate constant	Second-order rate constant dependent on the chemical concentration and the microbial biomass. Units: reciprocal time.

compound. As a result of the large number of physico-chemical properties and environmental variables that determine photolysis, the rate of photolysis for a given compound is commonly expressed by an overall parameter such as the photolysis rate constant. This parameter lumps most of the important factors into one measure, and it is useful for relative comparisons of photolysis rates between different organic compounds measured under similar conditions.

A closer examination of the important transformation processes for anthropogenic organic compounds shown in table 4 indicates that different processes are spatially distributed throughout the water column and sediment layers. The distribution of different transformation processes reflects preferences dictated by the driving forces for each process (Pionke and Chesters, 1973; Haque and Freed, 1974). At the air-water interface, energy supplied by light, wind, or surface tension effects is important. Volatilization, photolysis, and surface microlayer concentration of organic compounds are the most influential processes near the air-water interface. In the bulk solution, factors such as pH, ionic strength, dissolved oxygen, and the polarity of the chemical relative to water control the behavior of compounds. Other processes, such as the biological and chemical transformations and sorptive interactions

depend more on the interaction of the bulk solution with natural particles and consequently can occur throughout the water column and surficial sediment layers (Olsen and others, 1982). At the sediment-water interface, the increase in organic matter, microbial populations, and other sediment components forces diagenetic reactions to take precedence (Oschwald, 1972). A brief description of these transformation processes follows, with the greatest detail given to those processes which are most important in controlling the behavior of persistent anthropogenic organic compounds (sorption and bioconcentration).

Atmospheric influence is most pronounced at the air-water interface, where volatilization provides an exchange mechanism for compounds in solution that have relatively high air-water partition coefficients (Henry's law constants). Input of light energy into the water column is also highest near the air-water interface. Consequently, the importance of photolysis as a degradative process for certain organic compounds decreases with depth as light radiation decreases. Some compounds may be concentrated within the surface microlayer (top 1 mm of the water column) to levels much greater than those found in the bulk solution (MacIntyre, 1974; Rice and others, 1982). This surface-excess effect is manifested at the air-water interface and results from the low affinity of highly nonpolar organic compounds for polar water molecules. Despite available exchange pathways and low water solubilites, many organic compounds still enter into aqueous solution at environmentally significant concentrations.

Once in the water column, organic compounds are subject to chemical and biological transformations or interactions with other sorbents. Reactions such as solvation, hydrolysis, oxidation, and ionization may affect the chemical speciation of certain organic molecules in a manner consistent with the oxidation-reduction potential (Eh), pH, and ionic strength of the bulk solution. Microbiologically mediated reactions mineralize parent organic molecules into more fundamental functional groups useful as nutrient and energy sources. Most of these reactions either transform the organic contaminant, sometimes to a more toxic form (for example, aldrin to dieldrin), or remove it from the water column to another environmental compartment such as the atmosphere, sediment, or biota.

Many of the processes that occur in the water column continue across the sediment-water interface and into the interstitial fluid of the bed sediment (Presley and Trefry, 1980). Broadly classified as diagenetic interactions, these physical, chemical, and biological processes include deposition, accumulation, com-

paction, mineralization, and decomposition of settled particulate matter along with its associated contaminant content (Krom and Sholkovitz, 1977; Baker and Feely, 1978). In the surficial sediment layer, chemical and microbial processes continue the degradation reactions that began in the water column. Biopolymers (proteins, lipids, and carbohydrates) are converted to monomers (amino acids, fatty acids, and sugars) and eventually to simple molecular components for recycling into solution by diffusion (Kuznetsov, 1975). Commonly these reactions are incomplete because new sediment is deposited or resuspension results from turbulent eddies or biological activity (bioturbation). Anthropogenic organic compounds, because of their sorptive interactions with natural organic materials, are incorporated into this biogeochemical cycling of elements. Consequently, diagenetic interactions provide another mechanism for exchange of anthropogenic organic compounds between the surficial sediment and the water column.

SORPTION AND BIOCONCENTRATION

Two other transformation processes—sorption and bioconcentration—are of particular importance to the fate of anthropogenic organic compounds. Sorptive interactions within the water column increase the carrying capacity of the bulk solution beyond the solubility limit of the contaminant. Sorptive interactions within the surficial sediment layer provide the sediment with a mechanism for accumulating and releasing organic contaminants. Together, sorptive interactions in the water column and in the surficial sediment layer can significantly affect the transport and cycling of contaminants (Eisma, 1981; Means and Wijayaratne, 1982; Olsen and others, 1982).

In a similar manner, the bioconcentration of organic compounds by biological organisms, in the water column and sediment, can affect the distribution and fate of contaminants. Biological organisms can progressively concentrate organic contaminants, and this can directly impact humans because of consumption within the food chain. In addition, because biological organisms do not necessarily move with the average flow of surface waters (many species are independently motile), contaminants stored within the organisms may differ in their transport characteristics from those in the bulk solution. Finally, because biological organisms play an integral role in the exchange of matter between the water column and sediment (for example, bioturbation), they can alter the distribution of contaminants by

exchanging organic compounds with the water column or the sediment (Kenaga, 1975a, b).

For sorptive processes, the exact nature of the particle-organic-compound interaction is a subject of practical importance in understanding the environmental behavior of organic contaminants. Current attention has focused on whether the sorption of organic contaminants results from a surface adsorption process or from a partitioning process between water and an organic sorbent (Chiou and others, 1979, 1983, 1984; Pavlou and Dexter, 1979; Mingelgrin and Gerstl, 1983). The advocates of a partition model believe that the sediment organic matter functions as an immobilized amorphous organic phase capable of partitioning nonionic organic compounds from the bulk aqueous solution in a manner similar to the solubilization taking place with a conventional polymer. The surface sorption concept treats the same results as adsorption wherein the mineral and organic fractions of the sediment have different adsorptive capacities. For metal ions and ionic organic solutes it is logical that surface adsorption by different colloidal particles can take place as a result of electrostatic attraction, covalent bonding, and hydrogen bonding (Weber, 1972; Stumm and Morgan, 1981). For nonionic organic solutes, available data indicate that sorption by soil/sediment particles is more effectively accounted for by the partition mechanism of the solutes with the soil/sediment organic phase.

This review deals primarily with nonionic organics (for example, chlorinated insecticides, PCBs, and PAHs), and therefore, it is pertinent to present evidence supporting the partition model. In addition to the recognized dependence of sorption on the soil/sediment organic content, Chiou and others (1979, 1983) show that the sediment concentration of nonionic organic solutes increases linearly with aqueous solute concentration up to the solubility limit of the solute. A nonlinear relation would be expected in a surface adsorptive process because the available adsorption sites eventually become saturated as solute concentrations approach solubility. In experiments using binary solutes, Chiou and others (1983) found that the sorption relation showed no competitive effects between different solutes and that the magnitudes of the sorptive capacities were similar to those for the single-solute cases. In a surface-adsorption model, solutes compete for a fixed number of adsorption sites, and the overall sorptive capacities per contaminant are generally lower than those in single-solute cases. Thermodynamically, the heats of sorption were found by Chiou and others (1983) to be small and less exothermic than the heats of solute condensation from water; this is in contrast to the large exothermic heats of adsorption characteristic of surface adsorptive processes. Chiou and others (1985) suggest that the inorganic fraction of the soil/sediment is relatively inert to nonionic organic compounds in the presence of water, presumably because water is preferentially adsorbed over the nonionic organic solutes. The role of organic matter and other sediment fractions in sorptive processes is discussed more thoroughly in the section on Suspended and Surficial Fractions.

Just as nonionic organic compounds partition into soil/sediment organic matter, bioconcentration can be viewed as a transformation process in which organic compounds partition into the lipid fraction of aquatic organisms. Bioconcentration is the accumulated concentration of a given compound over that in the surrounding medium (water) by a particular aquatic organism resulting from its diet or from intake of contaminated water during respiration (Kenaga, 1975a, b). This process generates a reservoir of contaminants within the organisms that may enter the food chain. Biomagnification is commonly associated with bioconcentration; it is the progressive increase in the concentration of a compound moving from one trophic level to the next higher trophic level of the food chain. This discussion is limited to bioconcentration because biomagnification studies lack a consistent reference point for comparison among different trophic levels, especially aquatic as opposed to terrestrial organisms. Biomagnification has yet to be rigorously defined in a manner that accounts for the physiologic differences between species and that provides an unequivocal reference concentration for each organic contaminant. Once a reference standard is established, it should compensate for the different compositions and amounts of organic solvents present in the bodily fluids of each species of aquatic organism.

Chiou (1985) has demonstrated that the bioconcentration of nonionic organics by aquatic organisms results from the partitioning of compounds into the lipid fraction of the organism. Those compounds that are strongly bioconcentrated generally have a low water solubility and a relatively high affinity for organic phases, as is indicated by a high octanol-water partition coefficient. These properties are characteristic of many pesticides whose original function was to penetrate the cellular structure of the organism and disrupt the life-sustaining processes of the plants and insects. Once within the organism, these compounds may exhibit improved stability against decomposition and transformation.

From a mass balance standpoint, bioconcentration and biomagnification cycle contaminants as well as

vital elements such as carbon. From a toxicological standpoint, these processes are important because of the physiologic effects promoted by elevated concentrations of persistent contaminants. In general, by the time most pesticides run off into surface waters, concentration levels are sufficiently low that the acute toxicity of the compound is low and frequently unnoticed (Neely and others, 1974). Bioconcentration raises the potential for chronic effects because it increases the residence time of contaminants within the biological reservoir. For these reasons, estimates of the bioconcentration potential of synthetic compounds are important in order to assess their possible impact prior to their widespread use and environmental release.

For the persistent manmade organic compounds, several physicochemical properties and transformation processes play important roles in their environmental distribution. Low water solubilities and high octanol-water partition coefficients are common characteristics. These properties lead to sorptive interactions and bioconcentration as the primary processes controlling environmental distribution. They are not solely responsible for the distribution of anthropogenic organics, but because their relative contribution is greater than that of other transformation processes, sorptive processes are the focus of the next discussion of interactions between organic compounds and sediment fractions. But first, the next part considers the contribution of environmental variables in determining the dominance of certain transformation processes under a given set of environmental conditions.

ENVIRONMENTAL BEHAVIOR

The specific behavior of organic compounds in the environment is primarily a manifestation of the interaction between the physical and chemical properties of the compound and the sorbent. The effect of these inherent properties in the water column and sediment may be subject to changes by environmental variables such as pH, Eh, dissolved oxygen, dissolved solids, temperature, water hydrodynamics, and atmospheric forcings. Table 6 presents some important reaction mechanisms controlling the transformation and removal processes for the different organic compound groups. For some groups, such as halogenated aliphatic hydrocarbons, a single property dominates the transformation mechanism. For others, apparent physicochemical properties can be masked because they are more dependent on environmental conditions. For example, the extent of hydrolysis of the carbamates and phenoxy herbicides is largely a function of pH.

The physicochemical properties of a compound alone may not adequately indicate its probable field behavior without also considering the effect of environmental variables. Physical and chemical characteristics are measured under controlled conditions, whereas in nature the behavior of organic compounds may be influenced by other physicochemical factors not identified in simple laboratory systems. This is especially true for periods before a steady-state condition is reached. For example, insecticides and herbicides may be applied in different modes such as water solutions, emulsions, gases, wettable powders, and granular pellets. The form of introduction of the compound certainly affects its residence time and transient behavior in the different environmental compartments. For instance, compounds that are sufficiently volatile in water, such as hexachlorobutadiene, are less likely to volatilize if they are initially sorbed to some soil or sediment particle. Nevertheless, the physicochemical properties of the compound and the sorbent provide an important criterion for predicting and evaluating the initial distribution tendency of a compound between different sorbent phases. Hence, the physicochemical properties provide a useful initial assessment of the ultimate fate of organic contaminants.

The fate of many organic compound groups is characterized by competing processes mediated by the properties of the compounds and the prevailing environmental conditions. For example, monocyclic aromatics are susceptible to either volatilization followed by atmospheric photolysis or sorption followed by bioaccumulation (U.S. EPA, 1979a, b). The pair of transformation processes that control the behavior of the compound may vary with environmental factors such as wind speed, wave turbulence, temperature, and the availability of particulates for sorption in the water column. The reactivity of other organic groups, such as the substituted phenols, likewise depends on the location of the compounds in the water column. Near the air-water interface, photolysis is the primary reaction mechanism, whereas closer to the sediment-water interface, photolysis is greatly reduced and biodegradation reactions predominate. For other compounds that readily undergo enzymatically catalyzed microbial degradation (for example, phenols, phenoxy herbicides, and triazine herbicides), environmental fate strongly depends on the presence of a sufficiently large and acclimated microbial population.

Organic compound groups such as the organophosphorus insecticides (for example, parathion and malathion) undergo rapid transformation to different chemical forms (paraoxon and malaoxon), which

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are more persistent and sometimes more toxic than the parent compounds. The dissipation of the parent compounds may appear to be deceptively rapid from an environmental standpoint, but their effect is manifested primarily through other reaction intermediates. Some other compounds (for example, halogenated ethers) may persist in an aqueous medium despite dissipation by hydrolysis primarily because of their very high solubilities in aqueous solution. In other words, consideration of the physical and chemical properties of a compound should indicate its tendency for transport and partitioning, whereas the environmental fate of the chemical may depend on other system conditions.

The combination of the properties of a compound and available field data give a good indication of its potential persistence in the water column and sediment system. Table 7 presents estimates of different pesticide half-life ranges based on data collected from different ecosystems (rivers, lakes, soils, and estuaries). Information on the industrial organic compounds is less readily available, and consequently these compounds are not included in the list. For industrial compounds, some estimates can be made on the basis of properties and environmental behaviors that are similar to those of the pesticides.

SUSPENDED AND SURFICIAL SEDIMENT FRACTIONS

This section examines the physical and chemical characteristics of various suspended and surficial sediment fractions. These sediment fractions are discussed to illustrate how their component particles interact with organic contaminants. It is recognized that certain components of sediment (for example, humic substances) do not exist as particles per se, and consequently, use of the term "particle" is not intended to imply a specific physical or geometric form but rather to differentiate fractions, some of which behave as discrete entities (for example, sand and colloids) when transported. Indeed, at the submicron end of the particle-size spectrum, the distinction between what is and what is not a particle becomes more unclear as the scale of observation approaches the limits between "particulate" and "dissolved." In general, 0.45 μm is the operationally defined demarcation between particulate and dissolved matter. Nevertheless, colloids are treated as discrete particles (Edzwald and others, 1974) even when their dimensions fall below the 0.45-μm mark.

As a result of the wide variety of particle types that comprise suspended and surficial sediment, their physical and chemical properties are not as readily measured as are those of pure anthropogenic organic compounds. Sediment varies widely in mineral composition, ultimate analysis, and organic matter content. Consequently, much of the description of suspended and surficial sediment remains qualitative, and the few measures that have been developed only partially characterize the different sediment fractions on the basis of physical size and chemical fractions.

The properties of suspended and surficial sediment are differentiated here in terms of three categories: biological particles, inorganic particles, and humic substances. Although these categories do not include all sediment components, they include those components currently thought to be most important in influencing the behavior of anthropogenic organic compounds.

BIOLOGICAL PARTICLES

Many biological organisms present in the water column influence the movement and transformation of dissolved and sorbed organic contaminants. They include bacteria, protozoans, phytoplankton, zooplankton, and other higher trophic species (fig. 1). Although these different biological species are not strictly considered suspended sediment, they are included here because they are suspended in the water column, participate in the transformation and transport of organic contaminants, and eventually (after they die, start to decay, and settle) become part of what is collectively considered surficial sediment. In addition, as dead aquatic organisms, they combine with terrestrial organic decay products to form detritus, and thus they become an integral component of the material cycle of elements between the water column and surficial sediment (Sigleo and others, 1980, 1982).

The ways that biological organisms transform organic contaminants are diverse. By exchanging water across their cellular membranes, bacteria, protozoans, plankton, and lower vertebrates can bioconcentrate dissolved contaminants within themselves (Lush and Hynes, 1973; Steen and Karickhoff, 1981). Some filter feeders, such as zooplankton, ingest lower trophic organisms and colloidal size particles and either bioaccumulate the contaminants within their bodies or excrete them with fecal pellets (Sheldon and others, 1973). The fecal pellets are denser and settle faster than the ingested colloids or organisms (Meyers and others, 1984). Consequently, as has been demonstrated for the oceanic distribution of PCBs, the pelletization process can provide a significant contribution to the

Table 6.—*Environmental fate processes for selected groups of manmade organic compounds*

Chemical group	Primary mechanism	Secondary mechanism	Comments	References
1. Halogenated aliphatic hydrocarbons	Volatilization		Compounds with more than five chlorine atoms are sorptive and have a potential for bioaccumulation.	1,2,4
2. Halogenated ethers aliphatic - - - - - - - →	Hydrolysis- - - →	Volatilization and photo-oxidation in atmosphere	Some persistence due to high solubility. Also persistence potential due to lipophilicity.	1,2,4
aromatic - - - - - - - →	Sorption - - - - - →	Bioaccumulation and biodegradation		
3. Monocyclic aromatics	Volatilization- - - →	Atmospheric oxidation/photolysis	Volatilization/sorption are competing reactions with environmental conditions determining dominance of one reaction. Some persistence from high solubility.	1,2,4
	Sorption and - - - → bioaccumulation	Slow biodegradation (especially nitrogen compounds)		
4. Phenols	Photolysis- - - - - - → Biodegradation- - →	(near air-water surface) (near water sediment if sufficient microbes)	No accumulation/persistence except for nitrophenols which sorb readily to clays.	1,2,4
5. Monocyclic aromatics and phenols with 5 or more chlorines	Sorption Bioaccumulation		Chlorine content dominates compound behavior.	1,2,4
6. Phthalate esters	Sorption	Bioaccumulation Biotransformation Biodegradation	Biologically reactive in metabolic processes. Because of sorption, transport depends on hydrogeologic conditions.	1,2,4
7. Polynuclear aromatic hydrocarbons	Sorption Bioaccumulation Biodegradation Volatilization	Photolysis (for compounds with low ring numbers)	Bioaccumulation short-term because readily metabolized. Sorption increases and biodegradation decreases with increasing number of benzene rings.	1,2,3,4
8. Nitrogen compounds aliphatic - - - - - - →	Photolysis		Mainly hydrospheric photolysis due to high solubility but also atmospheric.	1,2,4
aromatic - - - - - - →	Sorption - - - - - →	Biodegradation		
9. Organochlorine insecticides and PCBs	Sorption Bioaccumulation Biotransformation Acid pH - stable	Volatilization (if chemical is not immediately sorbed) Photo-oxidation	High degree of chlorination giving low solubility, high lipophilicity, and significant environmental persistence. Generally short half-lives.	1,2,3,4,5,
10. Organophosphorus insecticides	Alkaline pH - rapid chemical-microbial hydrolysis	Biological oxidation some sorption slows down hydrolysis	Oxidation byproducts (e.g., malaoxon and paraoxon) may be more persistent than the parent compounds.	3,5,7,8,9,10
11. Carbamate insecticides and herbicides	Chemical/microbial Hydrolysis -- - - → Photo-oxidation	pH sensitive Some sorption to sediments	Relatively short stability (weeks) with harmless decomposition byproducts.	5,6,11
12. Phenoxy acid herbicides	Photolytic decomp under ultraviolet light Hydrolysis (pH sensitive)	Slow microbial degradation Sorption more pronounced for esters than for acids	Low bioaccumulation potential due to low lipophilicity and high depuration rates.	5,6,7
13. Triazine herbicides	Hydrolysis (acid and base catalyzed)	Microbial degradation		5
14. Substituted urea herbicides	Sorption Degradation- - - →	Microbial, chemical, photo-chemical— slow (months)	Chemical reactions like oxidation, hydrolysis, etc., play minor role compared to enzymatically mediated degradation reactions.	12

Chemical group	Primary mechanism	Secondary mechanism	Comments	References
15. Bipyridylium herbicides	Sorption (clays)- - - -→ Sorption - - - → (humic substances)	Essentially irreversibly sorbed under field conditions. Strongly sorbed but unlike clays can undergo some microbial degradation.		13,14
16. Dinitroaniline herbicides	Highly sorptive		Not persistent because of photodecomposition, biodegradation, and high depuration rates.	15

Sources: (1) U.S. EPA (1979a)   (6) Norris (1981)   (11) Schlagbauer and Schlagbauer (1972)
(2) U.S. EPA (1981)   (7) Faust and Suffet (1966)   (12) Maier-Bode and Hartel (1981)
(3) U.S. EPA (1978)   (8) Van Middelem (1963)   (13) Akhavein and Linscott (1968)
(4) U.S. EPA (1982)   (9) Mulla and Mian (1981)   (14) Hayes and others (1975)
(5) Paris and Lewis (1973)   (10) Mulla and others (1981)   (15) Helling (1976)

vertical transport of organic compounds through the water column (Elder and Fowler, 1977). Finally, some biological organisms which are resident in the surficial sediment layer (for example, benthic macroinvertebrates) are capable of ingesting and resuspending (bioturbation) sediment particles along with their sorbed contaminants (Berner, 1980).

INORGANIC PARTICLES

The most commonly identified sediment components are the mineral particles of clay, silt, sand, and gravel (see fig. 1). These particles comprise the bulk of the transportable sediment on a mass basis. The clay, silt, sand, and gravel fractions are separated on the basis of size by sieving, settling, or centrifugation methods. Size is used as the distinguishing criterion because of its relation to the transport and settling properties of the various particle types. Unfortunately, the names assigned to the particle-size classes (sand, silt, and clay) also imply certain compositional properties. Although the implications are partially accurate, many particles falling within the sand-sized class may be composed of organic matter (shells, seeds, and detritus) rather than, say, quartz. Other particles falling within the clay-sized class may be metal precipitates (for example, iron and manganese oxides and hydroxides) rather than particles of clay mineral composition.

Mixed within the various size classes of sand, silt, and clay are other less readily identifiable mineral fragments. They occur in various stages of mineralization and dissolution and include the opaline and calcareous exoskeletons of dead organisms. Although the sorptive capacity of these mineral particles for nonionic organic compounds in water is small relative to the sorptive capacity of organic matter (Chiou and others,

1985), it is not negligible. The mineral particles are commonly coated with organic sheaths that provide a microscale organic medium for sorption (partition) of nonionic organic solutes. Commonly, this partitioning capacity is mistakenly attributed to the mineral grains.

Organic matter and metal oxides are two groups of surface-active substances capable of altering the electrochemical properties of suspended mineral particles in surface waters. Acting individually or together, these groups are abundant enough to affect the interfacial properties of transported sediment matter (Hunter and Liss, 1982). Surface-active substances are sufficiently strong to remove the intrinsic differences in the laboratory-measured stability of clay minerals (Gibbs, 1977). Hunter and Liss (1982) found that the charge distribution on suspended particle samples collected from four estuaries was highly uniform despite the mixed composition of the suspended matter particles. They attributed the homogeneous electrical properties to both the sorbed organic matter and the metal oxides.

Even though the percentage by weight of dissolved organic matter sorbed on suspended particles in lakes, rivers, and marine waters may be small, the extent of surface coverage by adsorbed organic matter can be large (table 8). Davis (1982) found that within the typical pH range of natural waters, almost complete surface coverage by dissolved organic matter can be expected for hydrous aluminum oxides, hydrous iron oxides, and edge sites of aluminosilicates. The natural organic matter is characterized by weak, acidic functional groups that form surface complexes with the relatively basic surface hydroxyls of the mineral and metal oxides (Davis, 1982). Other mineral types (for example, silica) have relatively acidic surface hydroxyls that form weaker complexes that under natural

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Table 7.—*Estimates of environmental persistence of selected groups of manmade organic compounds*

Groups	Estimated half-lives
Lead, arsenic, copper, and mercury pesticides	10 – 30 years
Organochlorine insecticides and PCBs	2 – >4 years
Bipyridylium herbicides	>2 years
Triazine herbicides	6 months – 2 years
Substituted urea herbicides and picloram	4 months – 1 year
Benzoic acid, dinitroaniline, and amide herbicides	3 months – 1 year
Phenoxy and toluidine herbicides	1 month – 6 months
Carbamates and aliphatic acid herbicides	2 weeks – 3 months
Organophosphorus insecticides	1 week – 2 months

Sources: Metcalf and Pitts (1969)
Wauchope (1978)
Stojanovic and others (1972)
Maier-Bode and Hartel (1981)
Metcalf (1972)
Paris and Lewis (1973)

conditions may not be sufficiently energetic to cause complete surface coverage. The extent of coverage of the oxide-water interface also depends on the pH, the availability of surface area sites and sorbable organics, the nature of the solid surface, and the inorganic electrolyte strength and composition of the bulk solution. Organic coatings may play a major role in the surface chemistry of some particulate-sized matter, especially for nonionic organic solutes; they are geochemically important in the interfacial processes of coagulation, sedimentation, and sorption.

Many inorganic particles fall within the colloidal range of the particle-size spectrum. They include clay mineral colloids as well as oxides and hydroxides of iron and manganese. Colloidal size, organic content, and composition give the clay particles cation-exchange capabilities for ionic species (for example, metal ions) and a micro-organic environment for sorption of nonionic organic solutes. Some expansive clays, like montmorillonite, allow interlamellar penetration and entrapment of cationic organic species, such as paraquat (Adams, 1973). Because of the presence of organic matter in the form of organomineral colloids, the sorptive capacities measured for clay-sized samples are commonly much larger than those expected solely on the basis of a pure mineral sorbent.

Depending on water pH and redox potential, trace metals such as iron and manganese are present in suspension in precipitated forms. The oxides and hydroxides of iron and manganese occur as "dissolved" colloids, organometal colloids, or aggregated particles
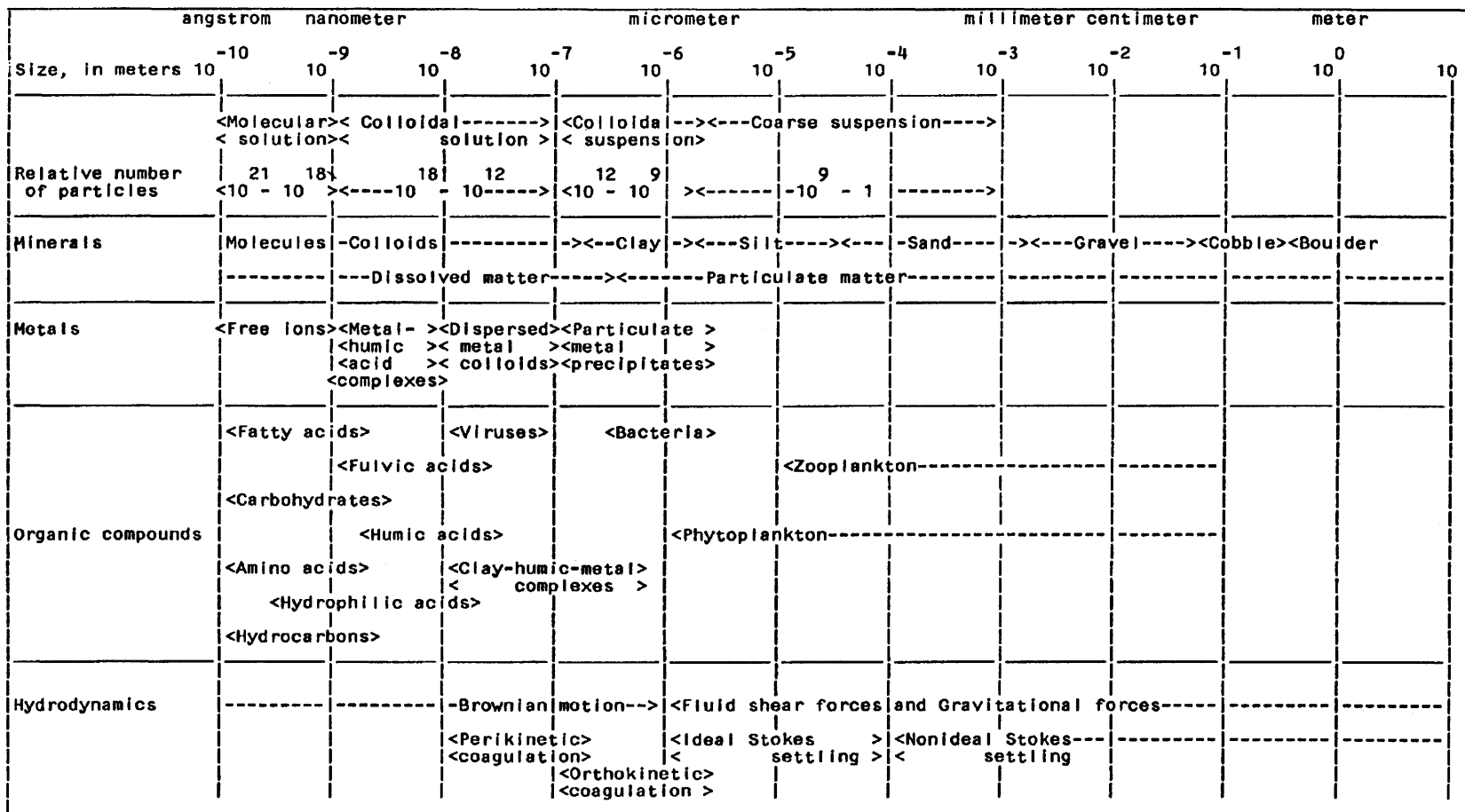
(Sigleo and Helz, 1981). In conjunction with humic materials, the metals coat the mineral particles that serve as nucleating surfaces for their precipitation reactions (Sholkovitz, 1976). The sorptive and scavenging ability of the metals is attributable to surface properties and is more pronounced for freshly precipitated flocs than for aged aggregates (Duinker, 1980). Sorption of ionic pesticides by iron and aluminum oxides has been hard to verify in field situations because of the difficulties in sampling the particle aggregates without altering or destroying them (Olsen and others, 1982).

HUMIC SUBSTANCES

Based on earlier work indicating the importance of organic matter in soil-pesticide interactions (Hamaker and Thompson, 1972; Hamaker, 1975; Schnitzer, 1978a, b; Chiou and others, 1979, 1983), similar procedures have been employed to isolate and study the organic matter in sediment. Chemical fractionation, as used here, refers to the various methods of extracting the organic matter from the inorganic matrix of the bulk sediment sample on the basis of solubility in different solvents. As used in this paper, chemical fractionation excludes the methodologies employed to separate organic contaminants from bulk sediment samples or their fractions even though the extraction principles and solvents used for organic contaminant and organic matter may be the same. Because most of the investigations described in the literature use the humic substance extraction method, this review of interactions between chemical fractions of the sediment and organic contaminants deals almost exclusively with the characteristics of the different classes of humic substances.

The most commonly used extraction method for organic matter was borrowed from the soil literature. It employs sequential isolation in dilute alkali and mineral acid to separate the humic substance fractions from the sediment. Other solvent extraction methodologies, which include inorganic solvents such as aqueous solutions of neutral salts (for example, sodium pyrophosphates or oxalate salts) and various organic solvents (for example, hexane, ethers, carbon tetrachloride, alcohol, or benzene), are less commonly used. These procedures are superior to acid and alkali methods because they are more selective to specific groups of organics (for example, waxes, lipids, fats, or celluloses) and they minimize the hydrolysis, decarboxylation, and oxidation of the organic matter that may result from the use of a stronger alkaline solution. More comprehensive

Figure 1.—Size spectrum of natural particulates and the hydrodynamic forces affecting their settling.

```
              angstrom    nanometer                    micrometer                      millimeter centimeter          meter
             -10        -9           -8          -7          -6          -5          -4          -3          -2          -1          0
Size, in meters 10      10           10          10          10          10          10          10          10          10          10          10

             <Molecular>< Colloidal------->|<Colloida|--><----Coarse suspension---->|
             < solution><          solution >|< suspension>
Relative number   21    18|           18|   12          12   9                  9
 of particles  <10 - 10  ><----10  - 10----->|<10 - 10  | ><------|-10  - 1 |-------->|

Minerals     |Molecules|-Colloids|--------- ->|<--Clay|-><---Silt---->|<----|-Sand----|-><---Gravel---->|<Cobble><Boulder
             |-------- -|---Dissolved matter---->|<--------Particulate matter--------|----------|----------|----------|----------|

Metals       <Free ions><Metal- ><Dispersed><Particulate >
                       |<humic  >< metal   ><metal   |   >
                       |<acid   >< colloids><precipitates>
                       <complexes>

             <Fatty acids>        <Viruses>|      <Bacteria>
                       |<Fulvic acids>                      |<Zooplankton----------------|---------->
             <Carbohydrates>
Organic compounds        <Humic acids>              <Phytoplankton----------------------|---------->
             <Amino acids>        <Clay-humic-metal>
                       <Hydrophilic acids>    complexes   >
             <Hydrocarbons>

Hydrodynamics |--------- |--------- -Brownian|motion-->|<Fluid shear forces|and Gravitational forces-----|----------|----------|
                       |<Perikinetic>        |<Ideal Stokes     >|<Nonideal Stokes---|----------|----------|
                       |<coagulation>        |<        settling >|<        settling
                                 |<Orthokinetic>
                                 |<coagulation >
```

Sources: Thurman (1985)   Sheldon and others (1972)
           Stumm   (1977)   Eisma (1981)
           O'Mella (1980)

Table 8.—*Colloids, aggregates, and their characteristics*

Particle groups	Cation-exchange capacity in meq/100g*	Surface area in m²/g	Dominant surface groups	Surface charge
Kaolinite	3 – 15	7 – 30	Oxygen/hydroxyl	(−)
Illite	10 – 40	65 – 100	Oxygen	(−)
Chlorite	20 – 50			(−)
Montmorillonite	80 – 120	600 – 800	Oxygen	(−)
Smectites	80 – 150			(−)
Vermiculite	120 – 200	600 – 800	Oxygen	(−)
Allophane	40 – 70	200 – 400+	Oxygen/hydroxyl	(+,−)
Iron hydroxides	10 – 25	100 – 800	Oxygen/hydroxyl	(+,o,−)
Manganese oxide	200 – 300		Oxygen/hydroxyl	(+,o,−)

Source: Horowitz (1984)
Note: * meq = milliequivalents

extraction techniques available for use on dissolved organic matter are capable of isolating hydrophilic (acid, base, and neutral) and hydrophobic (acid, base, and neutral) organic classes and subclasses (Leenheer, 1981). It is recognized, however, that all extraction procedures are incomplete in removing all organic carbon because different compounds have different solubilities in extractants. A tradeoff is necessary between the extent of removal from the sediment and the ability to maintain the chemical integrity and characteristics of the organic matter fraction of interest.

The importance of humic substances is reflected by the large quantity of recent research focused on the transport and fate of aquatic and terrestrial humic materials (Christman and Gjessing, 1983a, b; Aiken and others, 1985). As compounds from diverse origins and of complex chemical composition, humic substances can function in sediment and water chemistry as buffers, ion exchangers, surfactants, sorbents, and chelating agents (Kononova, 1966; Jackson, 1975). Research also indicates that humic substances interact with metal ions and their hydrous oxides, clay minerals, and organic pesticides and also serve as precursors to halogenated hydrocarbon formation following water-supply chlorination (Josephsen, 1982). A significant effect of the sorptive capacity of humic substances is the ability to concentrate toxic substances in solution to levels above their normal solubilities (Wershaw and others, 1969; Poirrier and others, 1972; Schnitzer and Khan, 1972; Carter and Suffet, 1982; Chiou and others, 1986).

The humic substances have been broadly defined as amorphous, brown or black, polydisperse substances with polar and acidic functional groups whose molecular weight ranges from several hundred to several million (Schnitzer, 1978a). This general definition does not describe the diverse physical forms humic substances take on in response to variations in pH and aqueous ionic strength. In solution, humic substances

may be in the form of dissolved species, dispersed colloids, precipitated flocs or in association with mineral and hydrous metal aggregates.

Research has shown that the characteristics of a humic substance are strongly dependent on its origin. Differences have been distinguished between humic substances derived from terrigenous plants and planktonic algal sources (Josephsen, 1982). Functional group content analyses indicate that terrigenous humic substances have a higher percentage of aromatics (for example, phenols) that are characteristic of lignin breakdown products derived from vascular plants (Plechanov and others, 1983). Planktonic humic substances are more aliphatic and are characterized by protein and carbohydrate residues (Ertel and Hedges, 1983). Terrigenous humic substances have higher carbon to nitrogen ratios than do planktonic ones, because of the higher content of nitrogen-poor, lignin- and cellulose-derived compounds (Meyers and others, 1984). Also, chemical fingerprinting has demonstrated that aquatic humic substances can be formed in situ, entirely from degradation of plankton and without any contribution from terrigenous sources (Khan, 1980).

The categorization and chemical characterization of humic substances are difficult because they represent organic matter from diverse origins that react degradatively to form an even wider spectrum of breakdown compounds. Consequently, most of the analytical research conducted has been aimed at elucidating the gross structural features and major functional moieties active in the different groups of degradative reactions (Christman and Gjessing, 1983a, b). The most commonly used classification of humic substances is operationally defined and founded on the basis of solubility in different extraction solvents. The three classes identified on the basis of solubility/insolubility in acid and dilute alkali are fulvic acids, humic acids, and humins (fig. 2). Further fractionation of the humic acids into hymatomelanic acid (alcohol soluble), gray humic acid
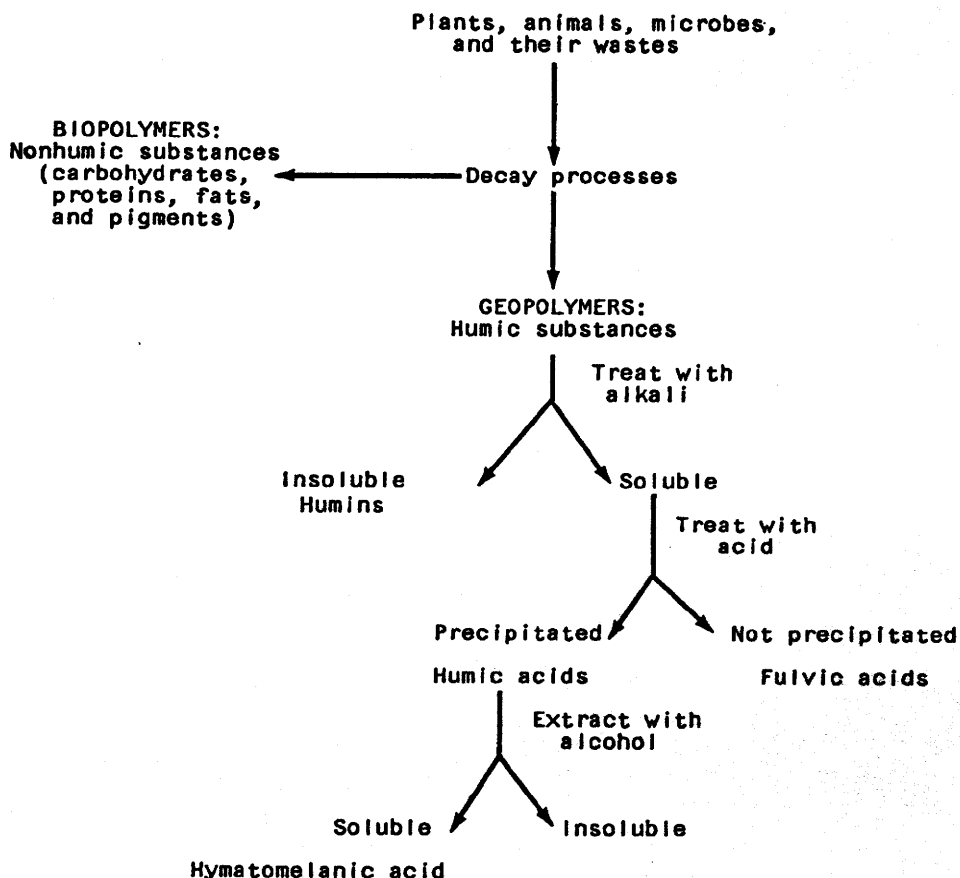
Plants, animals, microbes,
and their wastes

BIOPOLYMERS:
Nonhumic substances
(carbohydrates, ◄──────── Decay processes
proteins, fats,
and pigments)

GEOPOLYMERS:
Humic substances

Treat with
alkali

Insoluble ╱   ╲ Soluble
Humins

Treat with
acid

Precipitated ╱   ╲ Not precipitated

Humic acids   Fulvic acids

Extract with
alcohol

Soluble ╱   ╲ Insoluble

Hymatomelanic acid

Figure 2. Fractionation of humic substances (from Saar and Weber, 1982).

(precipitated in electrolytic solution), and brown humic acid (soluble in electrolytic solution) can be, but is infrequently, performed.

Humic substances originate from the chemical and biological degradation of plant and animal residues. Attempts to identify the general breakdown mechanisms have not been entirely successful, but it is agreed that the more complex, higher-molecular-weight humic substances (> 1,000 amu) are degraded first (oxidized) to lower-molecular-weight materials such as the humic and fulvic acids (Khan, 1980). Consequently, the structure of the three groups is similar, but they differ in ultimate analysis, molecular weight, and functional group content (Rashid and King, 1970). In general, the lower-molecular-weight humic substances are more prevalent in the sediment of rivers, lakes, and seawater, whereas the heavier humic substances predominate in soils (Josephsen, 1982). This difference in distribution reflects the importance of water column degradative processes that are continually active during the transport of the humic materials.

The fulvic acids are described as water-soluble compounds that impart the yellowish to brownish color of certain natural waters. In comparison with the humins and humic acids, the fulvic acids have progressed farther through the chain of chemical and biological degradative processes. Consequently, they have lower molecular weights and more hydrophilic functional groups than do the heavier humic acids and humins (Khan, 1980).

In aqueous solution, the humic acids are less soluble than the fulvic acids and can be precipitated at pHs below neutral. Their molecular weight is intermediate between that of the fulvic acids and humins and changes with variations in pH and ionic strength (Plechanov and others, 1983). As a result of their sensitivity to pH, the molecular structure of the humic acid complex is more aggregated and coiled in acidic conditions and more dispersed and extended in an alkaline environment. The consequences of this reversible change in molecular configuration can potentially affect the ability of the humic acid molecule to interact

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with or sorb other chemical species in water. A detailed study of this effect and its influence on the behavior of humic substances interacting with organic contaminants has yet to be explained fully.

The last and least studied of the humic substance fractions are the humins. In the gradation of bonding strengths found when progressing from the fulvic acids to the humic acids to the humins, the humins possess the most stable configuration. The relative insolubility of the humins, even under a wide range of pH conditions, seems to be due to their association with inorganic constituents of soil and sediment (Schnitzer and Khan, 1972). Their molecular structure and ability to form stable metal and (or) organomineral complexes contribute to their observed resistance to microbial and chemical degradation.

INTERACTIONS BETWEEN SEDIMENT FRACTIONS AND MANMADE ORGANIC COMPOUNDS

The interaction of manmade organic compounds with suspended and surficial sediment fractions is examined in the four parts of this section. The first two parts consider only the humic substance fraction of the sediment. The first focuses on the sorptive interactions between sediment-bound humic substances and nonionic organic compounds and demonstrates that humic substances, as dissolved and colloidal organic matter, are capable of enhancing the apparent solubility of nonionic organic compounds. The second part presents data showing that the sorption of ionic organic compounds by sediment humic materials is more dependent on bulk solution parameters (for example, pH) than is the sorption of nonionic organic compounds. The third part reviews a number of field studies that investigate sediment-contaminant interactions on the basis of sediment-size fractions sampled from rivers, lakes, and estuaries. The last part reviews laboratory studies that attempt to define more accurately the relations observed in the field data. These studies lead to a quantitative description of the sorption of contaminants by sediment fractions, and this forms the basis for the discussion of environmental distribution estimation procedures in the section on Estimation of the Field Distribution of Manmade Organic Compounds.

HUMIC SUBSTANCES AND NONIONIC ORGANIC COMPOUNDS

Humic substances participate in a variety of chemical interactions that play important roles in the fate and transport of organic contaminants. Humic substances may interact with metal ions and hydrous oxides through ion-exchange, complexation, chelation, coagulation, and peptization (Schnitzer and Khan, 1972). The resulting organometal complexes can have a wide solubility range in water and appear as discrete colloids, aggregated masses, or surface coatings of mineral particles. As separate particles or in conjunction with other particulates, humic substances also influence the behavior of organic contaminants primarily through sorption.

The process by which humic and fulvic acids sorb as well as enhance the apparent solubility of nonionic organic compounds can be described in terms of a partitionlike interaction (Chiou and others, 1986). The extent of this interaction is determined by the polarity and size of the organic matter molecules and the magnitude of solute solubility in water. The net effect of this partition interaction on the transport of nonionic organic compounds is twofold. First, the humic and fulvic acids, as dissolved organic matter, can partition nonionic organic compounds to give apparent solubilities greater than usual saturation in water and consequently increase the carrying capacity of the water column for many organic contaminants that are otherwise only slightly soluble. Second, humic substances occurring as components of sediment particles can serve, through partitioning interactions, as vehicles for the movement of anthropogenic organic compounds.

Sorptive interactions are the most common process by which humic substances affect the mobility of organic contaminants. Sorption to settling particulates removes organic compounds from the water column and deposits them in sediment reservoirs that can be overlain by more recent sediment or resuspended by turbulent eddies. Available data indicate that the primary mechanisms for the sorption of cationic species are associations by hydrogen bonding and ion exchange, whereas the sorption of nonionic and anionic organic contaminants is mainly by partitioning into the organic matter associated with surficial sediment or suspended particulates. In addition, even though fulvic and humic acids are more water soluble than the less polar humins, they contain enough nonpolar moieties that uptake relatively water-insoluble organic contaminants by a partitionlike interaction (Chiou and others, 1986).

The distribution and interaction of the nonionic pesticides, especially the chlorinated insecticides, have been investigated in much more detail than their ionic counterparts. The chlorinated hydrocarbons do not dissociate as readily in solution as do the ionic pesticides, and this contributes to their tendency to sorb into

organic matter by partition (Chiou and others, 1979, 1983, 1984). Pierce and others (1974) found that much of the sorptive activity of dichloro-diphenyl-trichloroethane (DDT) could be closely correlated with the organic content of the soil or sediment. Based on the observed correlation of DDT uptake with the organic matter content of the soil and the low heats of DDT sorption (ranging from −4 to +2 kcal/mol (kilocalories per mole)), the results can be effectively rationalized in terms of solute partition into the organic matter. Carter and Suffet (1982) studied the interaction of DDT with dissolved organic matter using a dialysis technique and found that 75 percent of the DDT in water was bound to a 16 mg/L (milligram per liter) solution of dissolved humic acid (that part passing through a 0.22-μm filter), whereas the remainder was free in solution. Their laboratory results showed that the dissolved organic carbon in natural waters at concentrations greater than 16 mg/L can bind a substantial fraction of the total DDT. Thus the DDT that is normally analyzed as dissolved and free may in fact be bound to a significant extent to dissolved humic materials. In isotherm measurements, Carter and Suffet (1982) observed, as did Pierce and others (1974), that the partition coefficients for commercial Aldrich humic acid were commonly an order of magnitude or more higher than comparable values for natural dissolved organic matter.

Landrum and others (1984), in a different experiment using specific resin cartridges instead of dialysis to separate bound and free "dissolved" organics, obtained similar order of magnitude differences between natural dissolved organic matter and humic acid. The work of Landrum and others (1984) showed that the behavior of several chlorinated biphenyls and PAHs was comparable to that of DDT. Landrum and others (1984) attributed the disparity in partition coefficients to differences in the chemical composition and state of aggregation of the various sorbent materials and to the presence of varying amounts of submicron particulate matter. In general, these results are in agreement with the data of R.L. Malcolm (U.S. Geological Survey, personal commun., 1985), who observed distinct differences between the nuclear magnetic resonance spectra of commercial and natural humic and fulvic acids.

Dissolved and colloidal organic matter are categorizations defined on the basis of size but that include many of the compounds also classified as humic substances. Colloidal matter falls approximately within the 1-nm to 1-μm range (Zsolnay, 1979), whereas dissolved matter has been operationally defined in the literature as any compound that can pass through a 0.45-μm filter. Humic substances that change state in reponse to pH and that flocculate form an important intermediary between dissolved and particulate matter. The behavior of organic contaminants, which has been attributed to the presence of natural organic colloids or dissolved organic matter, is also characteristic of reactions involving humic substances. The similarities among natural organic colloids, dissolved organic matter, and humic substances suggest a common compositional linkage among these groups and an integral role in bridging the hierarchy of chemical structure in going from particulate to truly dissolved organic matter.

Dissolved humic substances can stabilize certain hydrophobic organics and cause their apparent solubility to be greater than their actual solubility. Ogner and Schnitzer (1970) and Matsuda and Schnitzer (1971) investigated this phenomenon for dialkyl phthalates (used as plasticizers and lubricants) and tried to quantify the degree of solubilization in the presence of fulvic acid. Both pairs of investigators demonstrated a stoichiometric relation between the amount of fulvic acid and the solubility of several dialkyl phthalates. Boehm and Quinn (1973), also using extracted fulvic acid (3.7 mg/L of carbon), found an increase by a factor of 2–5 in the solubilization of some higher n-alkanes and isoprenoids (representative of petroleum hydrocarbons) but no observable effect on some more water-soluble aromatic hydrocarbons. Infrared spectrophotometry of the solubilized compounds revealed no new functional groups indicative of a chemical reaction between the fulvic acid and the phthalate molecules. This led Matsuda and Schnitzer (1971) to hypothesize that the enhanced solubility resulted from surface adsorption of the substituted phthalates on the fulvic acid, forming water-soluble complexes.

Poirrier and others (1972) investigated the sorption of DDT by color-causing colloids in an acid stream. These colloids were filtered to fall within the 5- to 10-nm range and proved to be iron-organic complexes with an organic composition of 68–78 percent fulvic acid, 3–9 percent humic acid, and 16–28 percent hymatomelanic acid. The colloids were found to concentrate the DDT to levels 15,800 times greater than those found in solution. Poirrier and others (1972) attributed the affinity of DDT for the colloids to their small size, humic composition, and stability in solution.

Wershaw and others (1969) found that the solubility of DDT in 0.5 percent sodium humate solution was at least 200 times the corresponding value in water. Hassett and Anderson (1979) reported that the high-molecular-weight fraction of dissolved organic matter

was responsible for stabilizing and holding cholesterol and a tetrachlorobiphenyl isomer in solution. Both investigators explain the observations as the combined results of the surfactant action of the dissolved organic matter and a sorptive uptake of the organic contaminants. Wershaw and others (1969) demonstrated that sodium humate lowered the surface tension of water as its concentration increased and thereby enhanced solubility. Hassett and Anderson (1979) concluded that the increased affinity of organic contaminants for water resulted from their association with the hydrophobic sites (alkyl chains) on the dissolved organic matter molecules. Simultaneously, the hydrophilic sites on the dissolved organic matter keep the entire complex in solution or colloidal dispersion through their interactions with water.

Boehm and Quinn (1973) speculate that the organic substances in colloids behave as micelles whose hydrophobic core attracts the contaminants while its hydrophilic moieties ionize to keep them in apparent solution. However, direct confirmation is still lacking on the micellar formation of organic substances in colloids. Chiou and others (1985, 1986) consider the high-molecular-weight organic substances in colloids to behave as a microscopic organic phase to which a highly water-insoluble organic solute can readily partition. Such a partition effect does not necessarily require a micelle formation, as the molecular environment of a macromolecular substance would provide an organic medium (although reduced compared to a bulk phase) for solute partitioning. The significance of this interaction is that part of the highly water-insoluble organic contaminants may be held by dissolved organic matter in a manner similar to that sorbed to the high-molecular-weight fraction of natural organic matter (Hassett and Anderson, 1979; Wijayaratne and Means, 1984). Undoubtedly, the ability of the humic substances to solubilize hydrophobic compounds has a significant impact on their transport and fate.

Recently, Chiou and others (1986) studied the solubility enhancement of some nonionic organic contaminants by dissolved humic and fulvic acids. They showed that the extent of solubility enhancement is linear with humic and fulvic acid concentration and is inversely related to solute solubility and proportional to the octanol-water partition coefficient. The results also showed no competitive effect between solutes, supporting the hypothesis that a partitionlike interaction occurs between solutes and dissolved organic matter. This observation is in agreement with other data showing the sorption of nonionic organics by soil/sediment organic matter (Chiou and others, 1979, 1983).

Chiou and others (1986) found that the magnitude of solubility enhancement caused by dissolved organic matter is related to its polarity, size, and molecular configuration. The dissolved organic matter must be sufficiently large and structurally flexible enough so that localized nonpolar regions of the molecules can partition the organic contaminants. This accounts for the greater solubility effect of soil humic acid, which is larger and less polar, than that of soil fulvic acid. In addition, the role of size and polarity support the observation that small organic acids such as phenylacetic acid exhibit little effect on enhancing solute solubility. Moreover, polyacrylic acid—a polar, linear polyelectrolyte similar in composition to fulvic acid—also failed to show an enhancement effect owing to its polarity and unfavorable molecular configuration. The partition hypothesis explains the observation that relatively water-soluble organic solutes (lindane and 1,2,3-trichlorobenzene) show little solubility enhancement at the specified humic and fulvic acid concentration (< 100 mg/L) where highly water-insoluble solutes (DDT and PCBs) exhibit large enhancements of their solubilities. This hypothesis is also in keeping with the findings of disparate solubility enhancement effects found between aliphatic and aromatic organic substances and reported by Boehm and Quinn (1973). It thus appears that the dissolved organic matter or the organic coating of colloids can effectively function as a "microscopic organic environment" for sorbing nonionic organic solutes by partition, thereby giving concentrations far in excess of those expected in pure water.

HUMIC SUBSTANCES AND IONIC ORGANIC COMPOUNDS

The extent and mechanism of sorption of organic pesticides depends on the type of chemical compound and the type of sorbent available for sorption. The ionic pesticides (for example, phenoxy herbicides and triazine herbicides) readily dissociate in solution, and therefore, their speciation is more responsive to solution variables such as pH and ionic strength, which may affect the sorption of the dissociated ions by mechanisms other than partition. The nonionic pesticides do not ionize significantly, and consequently, their sorptive behavior in aqueous systems depends on their ability to partition and on the polarity and composition of the organic matter in the water and sediment columns.

Khan (1974a, b) investigated the adsorption of two cationic bipyridylium herbicides, diquat and paraquat, by different cation saturated humic acids. The

choice of cation-saturated humic acid reflects the belief that free and dissociated humic acids rarely occur in natural waters because of the availability of inorganic ions. For ionic compounds such as paraquat and diquat that have high water solubilities, the sorption mechanism is identified as primarily due to ion exchange with some contribution from charge transfer processes. The extent of the sorption, ranging from 20 to 85 percent of the added herbicide, depends strongly on the strength of retention of the cations by the humic acids and consequently on the stability of the humic acid-inorganic ion complex. The higher valence cations are more firmly retained by the humic acid and thus result in smaller exchange capacities for the herbicides. Within a group of cations of the same valence, differences in adsorption were influenced by the size, shape, and nature of the bipyridylium cation and the steric hindrances generated by the various sizes of cations competing to associate with the humic acid complex.

Basic herbicides tend to undergo significantly greater sorption with humic substances at pHs in the vicinity of their dissociation constants (pK_b values), presumably by an ion-exchange process (Khan and Schnitzer, 1972). At pHs much higher than their pK_b, the high water solubility of the herbicides reduces the partition effect with humic substances. At pHs lower than or around their pK_b, the basic herbicides (for example, organonitrogen triazines) readily become protonated to form positive counterions capable of adsorbing to negative sites of the humic substances through complexation or ion exchange. However, at pH much lower than the pK_b, the resulting high hydrophilicity of the cations, in combination with the increased competition of hydrogen ions for protonation of the functional groups of humic acids, retard the ion-exchange process. This counteracting effect makes the efficiency of cation exchange a maximum at pH around the pK_b of the ionic compound.

Khan (1974a) examined the sorption of the anionic chlorinated phenoxy herbicide, 2,4-D, on a fulvic acid-montmorillonite sorbent. The 2,4-D sorption on the organoclay complex was smaller than that observed in comparable tests using pure fulvic acid but larger than in tests using a pure montmorillonite sorbent. The isotherm data gave low values for heats of sorption in keeping with the partition hypothesis (Chiou and others, 1979, 1983). Miller and Faust (1972), in similar studies with 2,4-D and organoclay complexes, found that 2,4-D uptake increased significantly when the pH was lowered. This agrees with the expectation that the anion of an acidic molecule would not be strongly sorbed because of its high hydrophilicity at high pH (which reduces partition) and because of its inability to ion exchange with acidic humic materials. At low pH, the increased concentration of the neutral form of the acid leads to increased partitioning because of its low solubility in water.

In related studies, Means and Wijayaratne (1982) and Wijayaratne and Means (1984) examined the behavior of atrazine and linuron in the presence of estuarine colloids. They found that sorption of the contaminants by the colloids affected the mobility of the compounds and contributed directly to their degradation by chemical and microbial processes. The composition of the colloids is strongly dependent on pH and salinity (Means and Wijayaratne, 1982) but can be generally characterized as a high-molecular-weight organic substance that is associated with varying quantities of poorly crystallized clay minerals and trace metals (Sigleo and others, 1980, 1982; Sigleo and Helz, 1981).

Humic substances have a demonstrable influence on the rate of chemical transformation of organic contaminants (Perdue, 1983a, b). For the specific case of hydrolysis, transformation rates can increase or decrease depending on the type of organic pesticide (nonionic, cationic, or anionic) and the pH of the aqueous medium. Perdue (1983a, b) observed that for the 1-octyl ester of 2,4-D (acidic herbicide), the rate of alkaline hydrolysis is greatly decreased in humic acid solutions. He states that a portion of the 2,4-D is partitioned into the humic acid, and this form is resistant to further hydrolysis. Li and Felbeck (1972) monitored the acid hydrolysis of atrazine (basic herbicide) and found that the presence of humic acid strongly enhanced the reaction. They hypothesized that the increased reaction rate resulted from a combination of acid catalysis within the aqueous phase and a surface catalysis of atrazine molecules bound to the exterior of the humic acid molecules. Khan (1978) demonstrated a similar effect for atrazine hydrolysis in a fulvic acid solution.

Although these and other studies show that humic substances have a measurable influence on the acid-base hydrolysis of certain organic compounds, the exact mechanism (taking into account aqueous solution parameters) is still only circumstantially defined. What is known is that humic substances, through sorptive processes, can significantly alter the reactivity of an organic contaminant from that of the unbound compound. The effect of these interactions on the reaction kinetics of organic contaminants is significant, and it increases directly with the concentration of humic substances.

FIELD STUDIES

The interactions of nonionic organics with different size sediment fractions affect their transport characteristics to a large extent. If the patterns of association between organic compounds and sediment can be better understood, much of the existing information on sediment transport can be applied to the movement of contaminants. The way that contaminants move provides answers to questions concerning the residence time of compounds in a given surface-water system and the potential they have for affecting other downstream reaches. The preceding part of this section demonstrated how the humic substances affect the water chemistry of anthropogenic organic compounds. This part reviews how the relations between contaminants and different sediment fractions determine their patterns of movement and deposition.

In the literature reviewed, most of the field investigators studying surficial sediment have concentrated their analytical efforts on persistent organic compounds such as the chlorinated insecticides and the PCBs. It is only since the late 1970s that interest in sample analysis has shifted to include the organophosphorus insecticides and other herbicides (Gilliom and others, 1985). This trend reflects the decreasing agricultural use of chlorinated insecticides during the last decade and the increasing application of more efficient and less environmentally persistent insecticides and herbicides. Another feature of the field studies is their emphasis on documenting local concentration levels and then relating (and sometimes extrapolating) those values to the global extent of contamination within a lake basin, riverbed, or estuary. Secondary efforts are directed at explaining the observed spatial pattern of contamination in terms of usage trends and readily measured water-body characteristics.

In a series of comprehensive studies of the Great Lakes, Frank and others (1977, 1979, 1980a, b, 1981) collected more than 1,500 surficial (top 3 cm) sediment samples that revealed an almost ubiquitous distribution of PCBs and chlorinated insecticides. The data demonstrate the retentive ability of the sediment, which typically record concentrations (for PCBs and DDTs) in the 10–300 ppb (parts per billion) range while water-column levels are only in the 1–10 ppt (parts per trillion) range. Other studies of the Great Lakes (Eisenreich and others, 1979, 1980; Simmons and others, 1980) and of different surface-water bodies (Pavlou and Dexter, 1979; Pavlou and others, 1980; Bopp and others, 1981, 1982; Elder and Mattraw, 1984) corroborate these results and show that the concentration

levels measured by Frank and others (1977, 1979, 1980a, b, 1981) are not specific to the Midwest.

In addition to recording the concentration patterns of contaminants, efforts have been made to relate these observations to other possible causative processes such as sediment transport. Through comparison of concentration contours with sediment bathymetry contours, Frank and others (1979, 1980a, b) found that contaminant concentrations were 2–3 times higher in depositional areas (fine-grained sediments ranging from silt to clay) than in nondepositional areas (bedrock, tills, and glaciolacustrine clays). Eisenreich and others (1979, 1980) in studying Lake Superior and Pavlou and Dexter (1979) and Pavlou and others (1980) in studying the Puget Sound found similar trends, implying that contaminants are sorbed and transported by the finer-grained sediment.

Pavlou and others (1980), in examining the PCB concentrations in a dredged spoil deposition area, found that the spatial distribution was fairly heterogeneous but closely approximated the fluid flow patterns and area bathymetry. Eisenreich and others (1979) discovered the highest DDT concentrations in geologic basins where sediment was higher in clay and organic carbon content. Bopp and others (1981, 1982) reported that PCB movements in the Hudson River are seasonal because 80 percent of the sediment is transported during spring runoff and PCBs are associated with this sediment. Frank and others (1979) and Simmons and others (1980) further tested the uptake of contaminants by fine-grained sediment through correlation studies between concentration values, percent organic carbon content, and percent silt-clay fraction. The statistical results demonstrate a significant relation between all combinations of the three variables for two separate data sets with approximately 250 samples per set.

Commonly, sediment cores are taken to complement the surficial sediment samples. Sediment cores encapsulate the history of contaminant accumulation within the vertical section of sediment deposition. Core samples explicitly demonstrate that contaminants such as DDTs and PCBs have persisted for more than 15–25 years since their widespread industrial and agricultural use began (Eisenreich and others, 1979; Frank and others, 1979). Cores also contain independent indicators, such as natural and fission-produced radionuclides, that are used to estimate sedimentation rates. Knowledge of sedimentation rates along with industrial use patterns allows the calculation of basic information concerning the response time of the natural system to a given contaminant input. Bopp and others (1982) have used these techniques to explain the distribution of

PCBs along the vertical and longitudinal axes of the Hudson River. They report that areas of fairly rapid sediment accumulation can be used to reconstruct the contaminant input and distribution history of persistent compounds.

As a result of the observed association of contaminants with fine-grained sediment, several field studies have attempted to determine which water-column or sediment component carries the largest contaminant load. Kuntz and Warry (1983) analyzed suspended sediment and water-column samples for 19 organochlorine compounds on a weekly basis for 3 years. They found that although concentrations in suspended sediment ($>5\ \mu m$) were typically higher than water-column concentrations, the suspended sediment was responsible for only about 40 percent of the total contaminant load. Therefore, sediment concentrations arise from contaminant diffusion out of the water column as well as through deposition of suspended sediment. Miles (1976) compared whole-water samples, suspended sediment, bedload sediment, and bottom sediment. For the five organochlorine compounds compared, he found that the extent of uptake by sediment material increased in a linear but inverse relation to the solubility of the compounds. Additionally, in relating the contaminant concentrations to their transport mechanisms, he found that the concentration values were highest for the suspended sediment and bedload, whereas the bottom material had intermediate values and the water column had the lowest values.

To get a more detailed picture of which sediment components, if any, are primarily responsible for the observed contaminant levels, several field investigators have size-fractionated the sediment prior to analysis. This multiplies the number of samples needed for complete analysis and enlarges the sample sizes of whole sediment necessary so that an analyzable quantity of the smaller size fractions can be obtained by wet sieving, sedimentation, or centrifugation. Choi and Chen (1976) examined the distribution of chlorinated hydrocarbons (DDT, dieldrin, and PCB) and organic carbon (total organic carbon, fulvic acid, and humic acid) in five size fractions encompassing fine silt and clay. Their results show that, for different sediment samples, the distribution of the organic carbon among the five fractions is roughly equivalent, but the sediment samples containing a higher percentage of fine particles also have a higher percentage of organic carbon. In addition, Choi and Chen demonstrate a linear relation within the five size fractions between the concentration of chlorinated hydrocarbons and the organic carbon content. These results indicate that the organic content

of the fine-particle sizes in the sediment is important in contributing to contaminant uptake by partition, especially if the organic carbon content is relatively high (>1 percent).

Goerlitz and Law (1974) examined six sediment samples for total chlorinated hydrocarbons in four size fractions (gravel, sand, silt, and clay). In this study the linear relation between chlorinated hydrocarbon concentration and sediment particle size was not as clearly defined. The trend showing highest concentration in the smallest particle fractions was commonly disrupted in the six sediment samples. The trend of chlorinated hydrocarbon mass with particle-size distribution was even more variable. In most cases, deviations were generally attributable to contamination of the predominantly mineral fractions in each size range by organic sorbents such as clam shells, plant seeds, and other organic detritus. This investigation demonstrates that all particle-size fractions must be considered if a representative bed material sample is to be collected and quantitatively related to stream transport properties.

LABORATORY STUDIES

The fractionation of sediment into components can be done on the basis of the size or type of sorbent. Size fractionation (gravel, sand, silt, and clay) relates more to the hydrodynamic properties associated with particle-size ranges. Fractionation on the basis of sorbent type (organic, mineral, and organomineral) depends on the composition of the particles associated with a particular size class. The classifications provide order and understanding to the vast continuum of particles in the water column and surficial sediment. The classifications are not unique or mutually exclusive because sorbent types that are grouped purely on a compositional basis generally also fall within a corresponding size range (for example, phytoplankton). It is important to recognize that the demarcations between size and type as well as the finer ones within each class are operational and a fair degree of overlap prevails. In addition, some particles are not clearly of any size or type because their dimensions vary (for example, flocculated masses), and they may consist of various biological and mineral fragments cemented together into one mass (for example, detritus). Examples include sorbents like organic aggregates and mineral grains with surface coatings that are under continuous and dynamic modification in response to variations in the aqueous environment.

The laboratory studies seek to better define the discernible patterns between contaminants and

sediment observed in the field. Accordingly, the laboratory studies use model (natural sediment) and sometimes ideal (pure clay) systems to focus on sorption as the dominant sediment-contaminant interaction. Although column flow-through experiments have been thought of as being more representative of the vertical movement of contaminants in soils, the majority of sediment-related experiments use batch equilibrations. Stirred tank reactor experiments are more representative of particle-contaminant mixing and interaction in the water column and surficial sediment (Pionke and Chesters, 1973; Presley and Trefry, 1980). Sorption and desorption isotherms are derived from batch experiments by interpolation between values measured at a number of contaminant-sediment and contaminant-water concentrations. These uptake and release isotherms are taken as a quantitative representation of actual contaminant-sediment interactions in a wide range of surface-water environments.

In addition to the determination of partition coefficients, batch experiments seek to isolate those sediment components and contaminant properties that control sorptive behavior. To this end, tests on different sediment-size fractions (gravel, sand, silt, and clay) and different sediment sorbent types (mineral, organic, organomineral, and detrital) seek to ascertain the relative contribution of each component compared to tests on the bulk sediment. The objective in examining the behavior of contaminants with sediment components is to identify the major factors affecting sorption from the large set of available contaminant-sediment variables. Ideally, the partition coefficient would be estimated from a two-factor set: one factor descriptive of the sediment and the other of the sorptive tendencies of the contaminant.

The isotherm studies based on sorbent type use field-identifiable classes of sorbents and subject them to various concentrations of contaminants in batch-equilibration experiments. The classes of sorbents include bacteria, phytoplankton, zooplankton, suspended sediment, natural surficial sediment, natural clay, and sand. Commonly, this list is supplemented with other "ideal" sorbents such as kaolinite, illite, and montmorillonite or natural sorbents that have been treated to remove various components such as organic carbon, lipid fractions, or humic fractions. Ideal or treated sorbents are compared to natural sorbents for two reasons. First, they demonstrate the effect of removal of a particular component on the overall sorption capacity. Second, they make it possible to interpret the observed sorptive behavior in terms of more fundamental characteristics of the sorbent as it relates to the sorption mechanism.

The studies reviewed employ a number of site-specific sorbent types as well as a large variety of organic chemicals. On the basis of these investigations, a few generalizations can be made. They should be interpreted with the understanding that sorbent groups are general classifications that might have significant compositional variations from one study site to another.

The effect of organic matter content on the sorption of pesticides by soil has been well documented (Hamaker and Thompson, 1972; Hamaker, 1975). A similar dependence would be expected for particles in the water column and sediment because of their variable organic matter content. Table 9 demonstrates for PCBs that the magnitude of the partition coefficient increases with the organic carbon content of the various sorbent types (Nau-Ritter and others, 1982; Nau-Ritter and Wurster, 1983). This relation also appears to characterize other organochlorine compounds, although it has not been documented as extensively as in the case of PCB (Hiraizumi and others, 1979; Weber and others, 1983). Additional sorbent characteristics found to correlate with sorbent uptake concentrations include surface area, particle size, mineral content, and cation-exchange capacity, but none of these properties appears as consistently significant as organic carbon content.

The most common technique for investigating how bulk sediment components interact with contaminants is to divide the sediment into fractions on the basis of size. Nine such studies were identified from the literature, and they encompass laboratory experiments conducted with more than a dozen chemical compounds and many different size ranges of the sediment fractions. In general, the results indicate that organic compounds sorb preferentially to the fine-sediment (silt and clay) fraction because of its typically high organic carbon content (Morris and Calvert, 1975; Karickhoff and Brown, 1978; Karickhoff and others, 1979). This observation, which corroborates the field results, is consistent with the partitioning of nonionic organic solutes from water into the organic matter of the soil/sediment components (Chiou and others, 1979, 1983) and is in general agreement with the trend of increasing organic carbon content with decreasing particle size (Wildish and others, 1980; Nkedi-Kizza and others, 1983).

For those studies that fractionated the fine sediment into size classes, measured partition coefficients were essentially homogeneous across groups except for the distinct difference of the sand-sized particles

Table 9.—*Partition coefficient ranges of polychlorinated biphenyls and various sorbent types*

Substrate type	Log partition coefficient	References
Live and dead bacteria	5 – 6	1,5,8
Live and dead algae	3 – 6	1,2,8
Zooplankton	4 – 5	2
Suspended sediment	3 – 6	1,2,3,8
Surficial sediment	2 – 5	1,2,3,4,6,8,9
Organic purged sediment	3 – 5	1,4,8
Natural clay	3 – 4	1,8
Soil	2 – 4	2,7
Montmorillonite, kaolinite, illite	2 – 4	1,3,4,6,7,8,9
Sand	< 1 – 2	2

Sources: (1) Voice and others (1983)
(2) Hiraizumi and others (1979)
(3) Horzempa and Di Toro (1983a, b)
(4) Weber and others (1983)
(5) Steen and Karickhoff (1981)
(6) Di Toro and Horzempa (1982)
(7) O'Connor and Connolly (1980)
(8) Voice and Weber (1983)
(9) Di Toro and others (1982)

(Karickhoff and Brown, 1978). This distinction in behavior between sand and other particle groups was still apparent even after the partition coefficients were normalized to account for differences in organic carbon content (Nkedi-Kizza and others, 1983; Isaacson and Frink, 1984). Choi and Chen (1976) found only small differences in the magnitude of partition coefficients when they looked at different subdivisions of the clay-sized particles in a number of sediment samples. This sorptive uniformity in all but the sand-sized fraction led Frank and others (1979, 1980a, b, 1981) to correct all their Great Lakes data for the difference in sand content of the different surficial sediment samples. The rationale used in this approach is that sand has a small retentive capacity for contaminants and therefore dilutes the other smaller sediment fractions.

In contrast to the aforementioned studies, Goerlitz and Law (1974), in assessing sorption, concluded that all particle-size fractions are necessary to obtain a representative sample. They found that the general trend of higher concentration with smaller grain size was not always applicable. They concluded that the sorptive capabilities of the larger fractions are not negligible because of the presence of organic sorbents that are sand sized and have significant sorptive capacities. In addition, although not specifically mentioned by Goerlitz and Law, sand-sized particles are commonly enveloped with metal oxides and (or) organic coatings that can alter the sorptive behavior of pure quartz grains. Schwarzenbach and Westall (1981) have shown that repeated washing of sediment particles (as is typical in wet sieving procedures) removes particle sheaths and, for more representative isotherm results, excessive washing and pretreatment should be avoided.

The studies on sediment fractions also showed that, in many samples, the peaks of contaminant mass and concentration commonly fell within different size groups (Richardson and Epstein, 1971; Goerlitz and Law, 1974; Karickhoff and Brown, 1978). The peak of the contaminant-mass distribution depends on the particle-size distribution, whereas the peak of concentration reflects the distribution of organic carbon content. Studies comparing samples from different stream-beds (Karickhoff and Brown, 1978; Hassett and Anderson, 1979; Hassett, 1980), showed that, even though the actual concentration in a given size fraction varied widely across different sediments, the distribution of contaminant concentration was similar among the size fractions of most sediment samples.

Several investigations have supplemented their batch equilibrations with similar tests using organic-carbon-purged sediment. These studies indicate that, although organic carbon dominates sorption, it is not the sole factor. Schwarzenbach and Westall (1981) found that in the absence of organic carbon the type of mineral surface has a significant effect on the degree of sorption. Richardson and Epstein (1971) and Choi and Chen (1976) found that for silt and sand the organic carbon controls sorption, whereas for clay, mineral composition is also important. Moreover, the greater the solubility of the organic contaminant, the smaller the influence of organic carbon and consequently the more uniform the sorbed concentrations across sediment fractions. In this case, the sorbed concentrations would probably be low.

Isaacson and Frink (1984) found for different substituted phenols that sorption is initially affected largely by the aqueous solubilities of the contaminants. However, as the contaminants move into the bulk of the sediment organic matter, the environment becomes progressively less aqueous and more strongly affected by the nature of the organic matter associated with that sediment fraction. From isotherm studies on purged sediment fractions, they found that the fine fractions had a higher content of labile organic matter—that is, a higher percentage of removal by peroxide treatment compared to the refractory organic compounds associated with the coarse fractions. Consequently, the observed differences in sorption between fractions may be attributable to the kind as well as the amount of organic matter (Morris and Calvert, 1975).

Laboratory studies have also been used to examine the release of sorbed contaminants. For many

organic contaminants, uptake and release by the sediment is considered an equilibrium and reversible process. However, some laboratory experiments suggest that the release of slightly soluble organic compounds from the sediment (desorption) is not complete. These studies show that the sorption and desorption isotherms generated from the contaminant uptake and release data do not always coincide (Di Toro and Horzempa, 1982; Di Toro and others, 1982). The deviation between the uptake and release data is attributed to different factors by different investigators. Some researchers believe that the difference is a laboratory artifact which results from the presence of sediment colloids that are not readily separable from the dissolved phase (Horzempa and Di Toro, 1983b; Voice and others, 1983). These sediment colloids have an organic matter content that is capable of partitioning contaminants and thereby preventing a true separation of the dissolved and sorbed states of the contaminant in the isotherm measurement (Gschwend and Wu, 1985). Other investigators argue that a "true" equilibrium is not attained and attribute the desorption behavior to a kinetic effect (Karickhoff, 1980, 1984; Jaffe, 1986). They believe that the desorption kinetics are better described by the combination of an initial rapid release of contaminant followed by a slower, time-dependent removal. This process by which contaminants desorb from sediment is only partially understood and is an area of current research. A more detailed understanding of desorption from sediment will help provide better estimates of the residence time of contaminants in surface-water systems and, consequently, of their availability for interacting by other transformation processes.

TRANSPORT OF SORBED MANMADE ORGANIC COMPOUNDS

The previous section demonstrated that various sediment particles, because of their organic matter content, can sorb nonionic organic compounds through partitioning processes. This sorptive capability makes sediment particles into potential carriers for the hydrodynamic transport of organic contaminants. To understand better how contaminants exchange with the surficial sediment layer during their downstream movement, this section reviews some of the different physical forces controlling sediment particle transport. In addition, a discussion of flocculation is included as a physicochemical process important in the estuarine movement of colloids.

The distribution of sorbed contaminants depends on the physical processes controlling sediment-particle transport. Sediment originates from the soil, but transport processes segregate the soil fractions continuously throughout their travel history. Consequently, sediment may resemble soil in mineral composition, while varying dramatically in particle-size distribution (Colby, 1963). Contaminants associate with sediment particles, and thus the physical processes segregating the soil into sediment fractions also determine the organic contaminant deposition patterns. A summary of the different mineral and organic matter particle sizes and the dynamic forces controlling their transport helps explain some of the particle-contaminant associations found in surface-water surficial sediment.

Many physical processes act in conjunction with the downstream flow of water to move different sizes of particles found in the water column and in the surficial sediment. O'Melia (1980) and Hunt (1982) have identified and investigated three major physical processes affecting particle transport and removal in the water column. First, gravity causes the sedimentation of particles on the basis of their size, shape, and density. The influence of gravity relative to other physical processes is greater in controlling the transport of silt and larger-sized particles. Second, and in conjunction with gravity, the fluid shearing forces generated by velocity differences between adjacent layers of moving water cause transport of silt- and clay-sized particles. Although these silt- and clay-sized particles settle vertically by gravity, they also are transported laterally and longitudinally by fluid-shearing forces that arise from the mixing of water currents of different densities and velocities. The third physical process identified by O'Melia (1980) and Hunt (1982) is molecular diffusion (also called Brownian diffusion) and is only of importance for particles of submicron dimensions. Diffusion is the apparently random motion of molecules caused by minute thermal gradients in the fluid medium. Transport by diffusion is independent of both the fluid motion and gravitational forces. Its influence is only noticeable for very small colloids where gravity and fluid-shearing forces exert a smaller relative effect on particle transport. The size of particles and the ranges over which gravity, fluid-shearing forces, and diffusion exert the most influence on particle transport are depicted graphically in figure 1.

In contrast to O'Melia's (1980) and Hunt's (1982) studies, the description of sediment transport has historically been approached by differentiating between the movement of coarse and fine particles. The

movement of coarse mineral particles results from the combination of sedimentation, resuspension, and suspended and bedload transport. The description of the vertical settling of gravel, sand, and silt is approximated by Stokes' relation for ideal spherical bodies falling under quiescent conditions (table 10). The settling velocity depends on the balance between the upward buoyant forces and the downward gravitational forces for a particular particle geometry, particle density, and water density (Guy, 1969, 1970). For larger particles (sand and gravel) and for less spherical particle shapes, the velocities deviate progressively more from those predicted on the basis of an ideal Stokes' settling behavior. These deviations increase in magnitude as the inertial effects become more significant as a result of surface and form drag forces.

As the coarse particles settle, they are distributed longitudinally and laterally as suspended particulates caught in the advection of flow. Once settled, the particles may resuspend when currents are sufficiently strong to cause turbulent eddies capable of scouring the surficial sediment layer. Transport of settled particles occurs chiefly by rolling or sliding within the bedload layer—the uppermost layer of the sediment, commonly only a few grain diameters in thickness. Overall, the transport of coarse sediment depends primarily on the flow characteristics, the particle properties and dimensions, and the streambed geometry.

Because the supply of coarse particles commonly exceeds the carrying capacity of a stream (Guy, 1969, 1970), the concentration of coarse sediment in suspension is a function of the flow and sediment characteristics. For fine sediment (clay- and colloid-sized particles) the suspended concentration depends less on flow characteristics and more on the available supply of particles from erosion and biological processes. For fine sediment, unlike coarse sediment, the carrying capacity of the stream is typically much greater than the supply of particles from upstream and adjacent hill slopes (Colby, 1963).

The transport of small particles (micron and submicron sized) of fine sediment is less dependent on the influence of gravity than are larger particles of silt and sand dimensions. Clay- and colloid-sized particles are more buoyant and more responsive than are larger-sized particles to fluid shear and Brownian diffusive forces within the water column. Mineral colloids settle orders of magnitude more slowly than sand grains, and organic colloids are even slower as their densities approach that of water. These properties give fine particles longer residence times in the water column and make them more susceptible to the shearing forces

Table 10.—*Theoretical settling velocities of particle-size classes*

Particle groups	Size in mm	Size in μm	Settling velocity in s/cm
Boulders	>256		
Cobbles	256 – 64		
Very coarse gravel	64 – 32		
Coarse gravel	32 – 16		
Medium gravel	16 – 8		
Fine gravel	8 – 4		
Very fine gravel	4 – 2		
Very coarse sand	2 – 1	2,000 – 1,000	
Coarse sand		1,000 – 500	
Medium sand		500 – 250	
Fine sand		250 – 125	
Very fine sand		125 – 64	<1 – 3
Coarse silt		64 – 32	3 – 13
Medium silt		32 – 16	13 – 48
Fine silt		16 – 8	48 – 180
Very fine silt		8 – 4	180 – 700
Coarse clay		4 – 2	700 – 2,800
Medium clay		2 – 1	2,800 – 11,000
Fine clay		1 – 0.5	
Very fine clay		0.5 – 0.25	

Source: Guy (1969, 1970)
Note: Settling by Stokes law assumes spherical geometry for particles, specific gravity of 2.65, and a temperature of 20°.

at the benthic boundary layer that resuspend sediment components. The combined effect of their transport characteristics and their natural abundance makes colloid-sized particles significant in terms of their potential impact on contaminant transport (Bilby and Likens, 1979).

Of all the particles found in the water column and sediment, the transport of organic particles, both dead and alive, and of organomineral assemblages has been the least accurately described in terms of particle dynamics. Discrete particles such as dead organisms vary in size, shape, and density, depending on their degree of fragmentation, decay, and dissolution (Lorenzen and others, 1983). The sizes range from that of the parent organisms to those below the 0.45-μm division between particulate and dissolved matter. Below this demarcation, the motion of particles is considered indistinguishable from the motion of water molecules (Sheldon and others, 1972; Lal, 1977).

The movement of living particles is further complicated by the various degrees of motility with which different species respond to environmental variables. Phytoplankton respond to changes in season, nutrient concentration, population age, time of day, and relative brightness of the sun. Burns and Rosa (1980) investigated

the settling velocities of 10 different species of phytoplankton (size range of 10–64 μm) and found that values were as high as 0.8 m/day for flagellates and as high as 0.2–0.5 m/day for nonflagellates. These velocities are for ascending and descending movement in the water column because light-dependent organisms such as phytoplankton follow diurnal cycles of respiration and photosynthesis. This type of behavior is important within the euphotic zone of the water column because it is the primary source of natural particles. These particles also are the main food source for higher trophic organisms and form the basis of detrital matter.

In an analysis of the settling behavior of organomineral aggregates in the 5- to 500-μm range, Chase (1979) found that measured sedimentation velocities were different from values predicted by Stokes' law. For aggregates from lake and marine waters, the settling velocities were as much as an order of magnitude faster than the Stokes' law predictions. Edzwald and others (1974) found similar order of magnitude departures for the difference between discrete and flocculated minerals. The deviations from ideal behavior are attributable in part to approximating the actual shapes of aggregates by spheroids, but Chase (1979) has shown that three other factors are important. He found that natural surface coatings, the presence of solution electrolytes, and dissolved organic substances combine to increase the settling velocity of aggregates by reducing the skin friction of their outer layer. Although a more exact description of the transport of aggregates is hampered by their amorphous structure and composition, more evidence is accumulating on their integral role in the cycling of organic and mineral compounds, natural and anthropogenic, in the water column and sediment.

Because the hydrodynamic behavior of colloid-sized particles depends largely on the electrochemical balance within the aqueous solution (Stumm, 1977), surface coatings can be expected to affect the physical and chemical properties of colloid particles (for example, their sorptive capacities). By masking differences among mineral colloids, surface coatings affect the flocculation behavior of particles and may help to explain the lack of field evidence verifying laboratory studies that suggest differences in the flocculation behavior of different minerals (Gibbs, 1977). From a hydrodynamic standpoint, surface coatings reduce the frictional drag on settling particles and increase their downward velocities (Chase, 1979). All of these results indicate the effects surface coatings can have on particle properties and also raise questions on the accuracy of laboratory studies that purposefully wash or purge particle coatings from suspended and surficial sediment (Schwarzenbach and Westall, 1981; Davis, 1982).

FLOCCULATION

Flocculation has been identified as an important removal mechanism for organic and inorganic compounds in at least 10 estuaries on 16 separate occasions (Boyle and others, 1977; Fox, 1983a, b). Its primary effect is the aggregation of discrete particles (clay minerals, metals, and humic substances) into larger and denser masses, called flocs, that settle 1–2 orders of magnitude faster than their component discrete particles (Edzwald and others, 1974). This process removes colloidal particles and reduces the residence time of other larger particles in the water column. In addition, as the flocculated masses settle, they remove organic contaminants through surface sorption reactions or by enmeshment within their aggregation matrices.

Estuaries serve as natural coagulation tanks because of their salinity variations and the effects of tidal motion on mixing processes (Stumm, 1977). Tidal excursions provide downstream saline water with abundant electrolytes to interact with and destabilize colloids. Natural colloids (organic and inorganic) have a net negative surface charge and once in solution become surrounded by double layers of ions. The electrochemical balance is such that individual particles repel each other and remain stable in suspension until additional electrolytes neutralize the surface charges. After the repulsive energy barrier is removed, the tidal motion of the estuary increases the number and efficiency of collisions between discrete particles. Interparticle contact increases as a result of the Brownian motion of colloids (perikinetic coagulation), the effects of velocity gradients within the water column (orthokinetic coagulation), and the different settling velocities caused by the various shapes and densities of particles (Edzwald and others, 1974). The tidally forced mixing provides the necessary electrolytes and enhances flocculation so that particles can rapidly coalesce into masses that settle.

Flocculation is a complex process also involving electrostatic and chemical interactions (Eckert and Sholkovitz, 1976; Preston and Riley, 1982). Although the exact mechanism is not yet fully understood, salinity has been ascertained to be the primary controlling factor, and pH is only of secondary importance (Sholkovitz, 1976; Boyle and others, 1977). The effect of pH is exerted more on the precipitation behavior of humic substances and the role they play in controlling the

concentration of inorganic trace elements (Sholkovitz, 1976; Saar and Weber, 1982). Sholkovitz and others (1978) have experimentally added various amounts of seawater to freshwater samples and demonstrated that the reaction kinetics of flocculation are rapid and are on the order of tens of minutes. Seemingly, no minimum activation salinity is required to initiate flocculation, and the process is considered to be continuous throughout the entire salinity range. However, maximum removals occur when salinities reach the 15–20 ppth (parts per thousand) levels (Sholkovitz and others, 1978). Dyer (1972) reported that, with adequate particle concentrations, illite and kaolinite are completely flocculated at salinities exceeding 4 ppth, whereas montmorillonite continues to flocculate until marine salinities are reached (35–37 ppth). The stability of the flocculated mineral colloids depends on the type of clay mineral, the ionic strength, and the composition (valence of counterions) of the aqueous solution.

As a removal process, the extent of flocculation varies for the clay minerals, metal ions, and humic materials. As was previously indicated, the three major types of clay colloids are rapidly flocculated if salinities are sufficient (Dyer, 1972). In estuaries, metal ions such as iron, manganese, and aluminum are almost completely removed and are commonly referred to as nonconservative substances (Sholkovitz, 1979). On the other hand, because only a small proportion (about 3–11 percent) of dissolved organic matter, including humic substances, is removed, dissolved organic matter is considered a conservative substance (Moore and others, 1979). Closer examination shows a preferential removal of the higher-molecular-weight dissolved organic matter constituents such as the humic acids (60–80 percent removals), whereas lower-molecular-weight dissolved organic matter constituents are removed in much smaller percentages (Sholkovitz, 1976; Fox, 1983b).

Overall, flocculation has a demonstrable effect on varying the number of particles in suspension. In addition, studies show that particles of colloidal size are capable of partitioning organic contaminants to large concentrations. Consequently, it seems probable that flocculation also exerts a significant effect on the movement of organic compounds associated with colloidal particles (O'Melia, 1980; Hunt, 1982).

ESTIMATION OF THE FIELD DISTRIBUTION OF MANMADE ORGANIC COMPOUNDS

An understanding of the large number of isotherm studies utilizing many chemical compounds and many types of sorbents requires a synthesis of the collected data within a general, yet simple, physico-chemical framework. The first step is reduction of the complex contaminant-sorbent interactions of sorption to a set of controlling variables that can be related to measurable physical properties. Because sorption is a solute-sorbent interaction, the initial efforts involved identification of a two variable set, with one variable characteristic of the sorbent and the other characteristic of the organic contaminant.

Isotherm studies conducted on soil-pesticide systems and more recently on sediment indicate that several sorbent properties affect the sorption capacity and mechanism. The soil and sediment investigations both point to the organic carbon content as the dominant controlling factor for nonionic and anionic organic pesticides. However, cation-exchange capacity, clay mineral composition, and particle-size distribution also contribute significantly to the sorption of basic pesticides. Studies correlating the organic carbon content and partition coefficients of sorbents, such as aquifer constituents, soil, sediment, and activated sludge, show a linear relation (Khan, 1972, 1978). This correlation holds for natural sorbents with an organic carbon content in excess of 0.1 percent and suggests that the organic matter composition and partitioning properties of the various sorbents are similar (Schwarzenbach and Westall, 1981). For sorbents with an organic carbon content of less than 0.1 percent, the nature of the mineral surface has a greater effect on the degree of sorption.

The strong correlation between organic carbon content and partition coefficient can be used to reduce the description of sorption by a multicomponent sorbent to that of a single hypothetical reference sorbent that is 100 percent organic carbon (Karickhoff, 1984). Mathematically, the normalization procedure results in a single variable—the organic carbon (matter) partition coefficient—that represents the field partition coefficient divided by the organic carbon content of either the bulk sediment or any one of its component fractions. Strong correlation between the organic carbon content and the partition coefficient has been found in several soil/sediment studies (Hamaker and Thompson, 1972; Chiou and others, 1979, 1983; Means and others, 1980, 1982), and the normalization approach has been applied in sorption quantitation (Karickhoff and Brown, 1978).

Expressing the sorptive behavior of a specific organic compound on the basis of the organic carbon content in soil/sediment also reduces the variability in partition coefficients across sediment types and within sediment fractions. Based on a set of 14 soil/sediment

samples from a large multistate area, Hassett (1980) was able to reduce the twentyfold to thirtyfold variation in partition coefficient to a factor of 2 by normalizing the sorption on the basis of organic carbon content. Karickhoff and others (1979) and Nkedi-Kizza and others (1983) found a similar reduction in partition coefficient variability when looking at sediment fractions separated on the basis of size. After normalizing the partition coefficients, they were able to discern differences between the sorptive capacity of the sand and that of the other fractions. It should be noted that these results are specific to the sorptive behavior of neutral organic compounds in water, where the mineral components are not significantly active in the sorption process and where dissociation, precipitation, and other chemical interactions are minimal. The relative inertness of the mineral fraction to neutral organic compounds in aqueous systems is attributed to the strong dipole interaction between water and the minerals (Chiou and others, 1983). In these types of partitioning processes, the role of organic matter is similar to that of a water-immiscible organic solvent capable of solubilizing organic compounds (Chiou and others, 1979, 1983).

Characterizing the sorptive differences between organic contaminants has centered on estimating the organic-carbon-normalized partition coefficient from either the water solubility of the compound or its octanol-water partition coefficient. The choice of these two chemical properties is based on the assumption that partitioning of an organic chemical between an organic phase and water is mechanistically similar to partitioning an organic chemical between itself and water (Chiou and others, 1977). Because organic solutes have better compatibilities with an organic phase than with water, the magnitudes of solute partition coefficients in a solvent-water system should be inversely related to solute-water solubilities. Statistical correlation studies have verified that organic-carbon-normalized partition coefficients vary linearly with octanol-water partition coefficients and inversely with solubility (Chiou and others, 1977, 1981a, b; Mackay and others, 1980). These studies also show that, in general, the octanol-water partition coefficient is a more convenient basis for estimating the organic carbon partition coefficient than is water solubility. This occurs because for solid compounds the octanol-water partition coefficient is not sensitive to the melting-point effects associated with the solid solubility in water (Karickhoff and others, 1979; Chiou and others, 1983). However, the melting-point effect on solid solubility can be readily corrected if data

on heat of fusion and melting points are available (Mackay and others, 1980; Chiou and others, 1981a, b).

Many correlations seeking relations between physical properties of chemicals and their organic carbon partition coefficients are based on water solubility or the octanol-water partition coefficient as the correlating variable. Significant correlations have been found between octanol-water partition coefficients and aqueous solubilities for more than 50 organic compounds with solubilities spanning 8 orders of magnitude (1,000 ppm (parts per million) to 1 ppb) and octanol-water partition coefficients spanning 6 orders of magnitude (1 to 1 million) (Chiou and others, 1977, 1979, 1981a, b, 1983; Campbell and others, 1983; Yalkowsky and others, 1983). More compounds and additional accuracy for the correlations are possible with a melting-point correction factor for solid organic compounds and by restricting the correlations to chemical families rather than to all organic compounds (Banerjee and others, 1980). For highly water-soluble organic compounds, deviations from the linear relation between partition coefficient and water solubility may be expected because these compounds violate the dilute solution approximation assumed for both partition coefficient and water solubility (Chiou and others, 1981a, b). In general, the correlations and the regression equations describing the functional relations are applicable for low water solubility, nonionic organics that are not susceptible to speciation changes, or other types of complex formation (Brown and Flagg, 1981). Other attempts have centered on calculating the octanol-water partition coefficient by applying the molecular-fragment concept (Leo and others, 1971) and by using activity coefficients of the solute in water (Arbuckle, 1983).

The correlation studies using solute and sorbent properties measured in laboratory studies serve as the basis for estimating field partition behavior. With knowledge of the sediment organic carbon content and the contaminant octanol-water partition coefficients (or water solubility), derived regression equations have been tested in many studies of sediment contamination. Verification of the regression estimates has been possible to some extent through laboratory experiments and some field measurements. The groups and chemical families investigated include pesticides (Chiou and others, 1979), methylated and halogenated benzenes (Schwarzenbach and Westall, 1981; Chiou and others, 1983), triazine and dinitroaniline herbicides (Brown and Flagg, 1981), PAHs and substituted PAHs (Karickhoff and others, 1979; Karickhoff, 1980, 1981; Hassett, 1980; Hassett and others, 1983), and some PCBs (Chiou and others, 1983). The accuracy of the

estimates for the range of nonionic organic compounds and sorbents (>0.1 percent organic carbon) tested gives results within a factor of 2–3 of the measured values (Schwarzenbach and Westall, 1981). If more detailed information is available on the individual sediment fractions (organic carbon content and particle-size distribution), the bulk partition coefficient can be estimated from a weighted sum of the component coefficients (Karickhoff and others, 1979). Table 11 presents a number of representative regression equations used in estimating field partition coefficients and bioconcentration factors from solubility and octanol-water partition coefficients.

Recent investigations suggest that a third variable—the sorbent concentration—is required to estimate accurately the field partition coefficient of an organic contaminant from laboratory measurements (Horzempa and Di Toro, 1983b; Weber and others, 1983). In addition to the sorbent organic carbon content, the concentration of the sorbent has been observed to influence the field partition coefficient. These observations indicate that the partition coefficient decreases as the concentration of solids increases (O'Connor and Connolly, 1980; Connolly and others, 1983). This phenomenon has been called the "solids effect." On a log-log scale spanning 4 orders of magnitude in solids concentration and partition coefficient, the inverse relation is linear for certain organic compounds and heavy metals sorbed on either soil or sediment (O'Connor and Connolly, 1980; Voice and others, 1983). The solids effect appears most pronounced for organic compounds with large partition coefficients or very low water solubilities.

Observations from a diverse number of solutes and solid to water ratios indicate that the solids effect is not caused by specific chemical interaction but rather involves a nonspecific physical process (Voice and others, 1983). Horzempa and Di Toro (1983a) state that direct interactions between solid phase particles at different concentrations change the availability of binding sites and potentially the binding energies necessary for sorption. Independently, Voice and others (1983) and Gschwend and Wu (1985) have demonstrated the presence of nonsettling particles with submicron dimensions, whose concentration in the water column increases as the solids concentration of the bulk phase increases. These particles (which do not settle even under centrifugation) are capable of sorbing significant quantities of organic compounds and thereby enhancing the apparent solubilities of the organic solutes (Chiou and others, 1984; Gschwend and Wu, 1985). The extent of such effects increases directly with solids

concentration, leading to the apparent variation of the partition coefficient. Incorporation of the solids concentration as a third variable in the regression equation to estimate the field partition coefficient has been proposed as a method to account for the solids effect (O'Connor and Connolly, 1980; Voice and others, 1983). It should be noted, however, that the solids effect is significant only for highly water-insoluble organic solutes at sufficiently high concentrations of suspended solids or particulate-bound organic matter. A more thorough account of this effect in terms of dissolved organic matter has recently been given by Chiou and others (1986).

The ability of sediment organic matter to partition nonionic organic compounds from the water column is paralleled by a similar capability in aquatic organisms. The aquatic biota contain lipid pools with solvent properties analogous to but more effective than the organic matter found in sediment. The effect of lipids in bioconcentration and the variables affecting the lipid-water partition coefficient have recently been accounted for by Chiou (1985). He found that on a unit weight basis, the lipid is far more effective in concentrating nonionic organic solutes than soil/sediment organic matter. Consequently, biological organisms represent another "dynamic reservoir" capable of accumulating, concentrating, and releasing organic contaminants.

Neely and others (1974) and Chiou and others (1977) first demonstrated a significant correlation between the physicochemical property of a variety of chemicals (octanol-water partition coefficient) and their ability to bioconcentrate in fish. Kenaga (1975b, 1980), Oliver and Nimi (1983), and Mackay (1982) also presented BCF values for a wide range of organic compounds and developed regression equations relating BCFs to water solubility and octanol-water partition coefficient (see table 11). Recently, Chiou (1985) specifically dealt with the effect of lipids in bioconcentration and found the lipid-based BCFs to be essentially the same as the triolene-water partition coefficients of a large number of environmentally significant organic compounds. In Chiou's study, triolene (glyceryl trioleate) was used as a model lipid compound because of its abundance and structural similarity to other triglycerides commonly found in aquatic organisms. Estimation of BCFs on the basis of lipid content appears to help converge and normalize the BCFs among fish species. Based on this analysis, the amount of a compound accumulated by a fish can be readily estimated with available data on the solute concentration in water and

Regression equation	Number of compounds	R^{2}*	Units for solubility	Compound groups	References
1. $\log K_{ow} = -0.747 \log S + 0.730$	156	0.874	Moles per liter	Low-molecular weight-organics	Hansch and others (1968)
$\log K_{ow} = -0.670 \log S + 5.00$	33	0.970	Micromoles per liter	Pesticides and PCBs	Chiou and others (1977)
2. $\log K_{om} = -0.557 \log S + 4.040$	15	0.988	Micromoles per liter	Pesticides and hydrocarbons	Chiou and others (1979)
$\log K_{oc} = -0.54 \log S + 0.44$	10	0.940	Mole fraction	Chlorinated hydrocarbons	Karickhoff and others (1979)
$\log K_{oc} = -0.686 \log S + 4.273$	22	0.933	Micrograms per liter	PAHs	Means and others (1980)
$\log K_{oc} = -0.594 \log S - 0.197$	5	0.945	Mole fraction	PAHs	Karickhoff (1981)
$\log K_{oc} = -0.83 \log S - 0.93 - 0.01(\text{MP-25})$**	47	0.93	Mole fraction	Chlorinated hydrocarbons	Karickhoff (1984)
3. $\log K_{oc} = 1.00 \log K_{ow} - 0.21$	10	1.00	NA	Chlorinated hydrocarbons	Karickhoff and others (1979)
$\log K_{oc} = 1.00 \log K_{ow} - 0.317$	22	0.98	NA	PAHs	Means and others (1980)
$\log K_{oc} = 0.72 \log K_{ow} + 0.49$	13	0.95	NA	Substituted benzenes	Schwarzenbach and Westall (1981)
$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	9	0.95	NA	Herbicides	Brown and Flagg (1981)
$\log K_{oc} = 0.989 \log K_{ow} - 0.346$	5	0.997	NA	PAHs	Karickhoff (1981)
$\log K_{oc} = 1.029 \log K_{ow} - 0.18$	13	0.91	NA	Pesticides	Karickhoff (1984)
4. $\log BCF = -0.802 \log S - 0.479$	7	0.95	Moles per liter	Rainbow trout chlorinated HCs	Neely and others (1974)***
$\log BCF = -0.508 \log S + 3.41$	6	0.93	Micromoles per liter	Rainbow trout insecticides	Chiou (1977)
$\log BCF = -0.873 \log S + 0.803$	6	0.93	Moles per liter	Guppies chloro-benzenes	Chiou (1981)
5. $\log BCF = 0.542 \log K_{ow} + 0.124$	8	0.90	NA	Rainbow trout chlorinated HCs	Neely and others (1974)
$\log BCF = 0.980 \log K_{ow} - 0.063$	5	0.98	NA	Guppies chloro-benzenes	Chiou (1981)
$\log BCF = 0.893 \log K_{ow} + 0.607$	18	0.904	NA	Rainbow trout chlorobenzenes	Chiou (1985)

Note: NA = not applicable
HC = hydrocarbons
S = water solubility of the organic solute.
K_{ow} = the octanol-water partition coefficient. Unitless.
K_{oc} = measured partition coefficient/organic carbon content of soil or sediment sample. Unitless. Organic matter, depending on composition, contains about 58 percent organic carbon (Hamaker and Thompson, 1972) and consequently $K_{oc} = 1.72 K_{om}$.
K_{om} = measured partition coefficient/organic matter content of soil or sediment sample. Unitless.
BCF = bioconcentration factor. Unitless.
* The linear regression coefficient of determination.
** The last term in this equation compensates for melting-point effects which occur in the phase transition of organic compounds that are initially solids.
*** Original data are from the source cited but the regression equation is found in Chiou (1981).

the fish lipid content along with the triolene-water (or octanol-water) partition coefficient of the compound.

SUMMARY AND CONCLUSIONS

The primary determinant of the behavior and fate of a contaminant in a surface-water system is its physicochemical properties. For the persistent organic contaminants, low water solubility and high octanol-water partition coefficients are the two most common characteristics found among the different chemical classes. Therefore the primary transformation process contributing to the environmental persistence of nonionic organic contaminants is sorption. Nonionic organic compounds tend to partition from water into the organic matter associated with soil/sediment particles and into the lipid deposits of aquatic organisms (bioconcentration). A partition model is consistent with experimental observations of linear sorption isotherms by different sorbents up to solute concentrations approaching solubility, the absence of competitive effects in binary solute systems, and low exothermic heats of sorption. The environmental behavior of ionic organic compounds is more complex because sorption depends on system variables such as pH and ionic strength. Sorption of anionic organic compounds is likely to be influenced by a partitioning process (although usually quite weak), whereas the sorption of cationic compounds is characterized by a surface adsorption model that can involve covalent bonding, electrostatic attraction, and ion-exchange processes.

Several sediment fraction properties influence the transport and transformation of persistent manmade organic compounds. Biological organisms, by virtue of their lipid contents, bioconcentrate nonionic organic compounds. In addition, because of their presence in the water column and surficial sediment layer, aquatic organisms contribute to the movement and exchange of contaminants between these two surface-water compartments. Inorganic particles such as sand, silt, and clay possess small sorptive capacities for nonionic organic compounds relative to other organic sorbents. These inorganic particles are commonly coated with organic matter, which significantly enhances their ability to sorb and transport contaminants. Humic substances, in the form of dissolved and colloidal organic matter, partition organic contaminants into a micro-organic environment and effectively increase the apparent solubility of highly water-insoluble compounds. The solubility enhancement is more pronounced as the water solubility of the contaminant decreases. This phenomenon depends on organic sorbent properties such as polarity, molecular size, molecular configuration, and composition. The importance of the humic substances lies in their partitioning capability, alone or in conjunction with other sediment particles, for nonionic organic contaminants. This makes it possible for them to increase the carrying capacity of the water column beyond the solubility limits of the nonionic organic compound.

The field and laboratory studies reviewed indicate that the organic carbon content of diverse sediment samples and fractions controls the sorption of nonionic organic compounds. Increased sediment organic carbon content correlates significantly with increased sorption. Similarly, a higher capacity for sorption is present in the finer-sized particles of a given sediment sample because they tend to have higher organic matter contents. The mineral component of a sediment provides only a relatively small contribution to sorption except, perhaps, in the case of certain ionic organics because water (through dipole interactions) is preferentially adsorbed over the nonionic organic compounds by the mineral adsorption sites. Normalizing field partition coefficients to a hypothetical reference sorbent that is 100 percent organic matter shows that the variation in partition coefficients among different organic contaminants results primarily from differences in the water solubility of the contaminants and secondarily from differences in the organic matter composition of the soil and sediment samples.

The transport of manmade organic compounds is considered in conjunction with the transport of sediment. In view of the sorptive interactions between sediment particles and contaminants, the hydrodynamic description of the movement of contaminants needs to be considered in terms of the transport of a dissolved species in addition to the transport of sediment particles having a certain contaminant capacity (based on their organic matter contents). In this respect, emphasis needs to be placed on the finer-grained particles (cohesive sediment) because of their typically higher organic matter content. In river-estuary systems, additional attention is needed on flocculation processes to understand the dynamics of contaminant transport because the tidal motion and the salinity changes in estuaries combine to destabilize and aggregate colloidal particles into settleable masses that are more rapidly removed from the water column.

One of the valuable results of the basic research investigating sediment-contaminant interactions is the development of methodologies to estimate the probable field behavior of newly synthesized organic compounds.

Regression equations have been derived that allow the estimation of field partition coefficients from laboratory-measurable contaminant and sorbent properties. For example, sediment partition coefficients can be estimated from information on the organic compound, such as water solubility or octanol-water partition coefficient, and the organic matter content of the bulk sediment. More detailed estimates are possible that take into account the particle-size distribution and the organic matter content of each fraction. Similar regression equations are available for estimating the BCFs of nonionic organic compounds in aquatic organisms. These estimates are based on the triolene-water (or octanol-water) partition coefficient of the compound and the body content of lipid in the species of interest. For newly synthesized organic compounds, these regression approaches provide a relatively easy way of obtaining an initial glimpse of the environmental behavior of compounds that have yet to be monitored under field conditions.

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