PART I,

3.5.1 CHEMICAL SORPTION BY ORGANIC CARBON

A large number of organic chemical pollutants are *hydrophobic,* literally "afraid of water." These chemicals have limited solubility in water but do tend to dissolve easily into oils, fats, nonpolar organic solvents, and organic carbon in the soil. To a first approximation, the partition coefficient for many hydrophobic chemicals in soil is not especially sensitive to the exact source or nature of the organic carbon. Accordingly, K_{oc}, the organic carbon–water partition coefficient, can be used to estimate the extent of sorption. K_{oc} can be expressed as

$$K_{oc} = \frac{\text{chemical concentration sorbed to organic carbon (mg/g)}}{\text{chemical concentration in water (mg/ml)}}. \qquad [3\text{-}25]$$

Because the fraction of organic material in porous media is rarely 100% and is typically less than 1% (notable exceptions exist in wetland sediments and peatlands), the partitioning of a hydrophobic organic compound between water and bulk soil can be estimated by the equation

$$K_d = f_{oc} \cdot K_{oc}, \qquad [3\text{-}26]$$

where f_{oc} is the fraction of soil that is organic carbon [M/M].

TABLE 3-5 **Relationships to Calculate K_{oc} from K_{ow}[a]**

Equation[b]	No.[c]	r^2 [d]	Chemical classes represented
$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	45	0.74	Wide variety, mostly pesticides
$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	19	0.95	Aromatics, polynuclear aromatics, triazines, and dinitroaniline herbicides
$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	10	1.00	Mostly aromatic or polynuclear aromatics; two chlorinated
$\log K_{oc} = 0.94 \log K_{ow} + 0.02$	9	NA	*s*-Triazines and dinitroaniline herbicides
$\log K_{oc} = 1.029 \log K_{ow} - 0.18$	13	0.91	Variety of insecticides, herbicides, and fungicides
$\log K_{oc} = 0.524 \log K_{ow} + 0.855$	30	0.84	Substituted phenylureas and alkyl-*N*-phenylcarbamates

[a] Lyman *et al.* (1990). NA, not available.
[b] K_{oc}, organic carbon-water partition coefficient; K_{ow}, octanol–water partition coefficient.
[c] Number of chemicals used to obtain regression equation.
[d] Correlation coefficient for regression equation.

The preceding expression is useful for soils in which f_{oc} is greater than approximately 0.001; in these soils, sorption to organic carbon dominates. For lower values of f_{oc} (values of 10^{-4} may occur in some aquifer materials), direct sorption onto mineral phases of the soil can become important, and K_{oc} is no longer a good predictor of sorption.

K_{oc} can be estimated from K_{ow}, the octanol–water partition coefficient (defined in Section 1.8.3). Table 3-5 shows some correlations between K_{oc} and K_{ow} for different classes of hydrophobic organic compounds. For further descriptions of the hydrophobic behavior of chemicals, the reader is referred to Schwarzenbach *et al.* (1993).

EXAMPLE 3-7

For an aquifer solid with a bulk density of 2 g/cm³ containing 0.5% organic carbon, estimate the retardation factor for the common polycyclic aromatic hydrocarbon (PAH) naphthalene ($C_{10}H_8$; see Fig. 1-11), used in mothballs. If the porosity of the aquifer is 0.24, the hydraulic conductivity is 10^{-3} cm/sec, and the hydraulic gradient is 0.001, how fast will a plume of naphthalene travel?

From Table 1-3, $\log K_{ow} = 3.36$. By using Table 3-5, an estimate of K_{oc} for PAHs is

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006.$$

Therefore,

$$\log K_{oc} = (0.937) \cdot (3.36) - 0.006$$

$$K_{oc} \approx 1400 \text{ ml water/g organic carbon.}$$

Use Eq. [3-26] to estimate K_d:

$$K_d = (0.005 \text{ g carbon/g soil}) \cdot (1400 \text{ ml water/g carbon}) = 7 \text{ ml water/g soil.}$$

Use Eq. [3-24b] to estimate the retardation factor:

$$R = 1 + (7 \text{ ml/g}) \cdot (2 \text{ g/cm}^3)/0.24 = 59.$$

Use Eq. [3-2] to estimate specific discharge:

$$q = 10^{-3} \text{ cm/sec} \cdot 0.001 = \frac{10^{-6} \text{ cm}}{\text{sec}}.$$

Use Eq. [3-5] to estimate seepage velocity:

$$v = \frac{10^{-6}\ \text{cm}}{\text{sec}}/0.24 = 4.2 \times 10^{-6}\ \text{cm/sec}.$$

Then divide by the retardation factor to estimate how fast a plume of naphthalene will travel:

$$\frac{v}{R} = \frac{4.2 \times 10^{-6}\ \text{cm/sec}}{59} = 7.1 \times 10^{-8}\ \text{cm/sec}.$$

6

PART II

Organic Compounds in Natural Waters

NATURAL ORGANIC MATTER

All natural waters contain dissolved organic compounds. In the past, geochemists have tended to ignore organic solutes because of the complexity of the mixture and the analytical difficulties. Recently, however, there have been numerous studies of dissolved organic compounds, both natural and anthropogenic, and the role they play in geochemical processes. It is now recognized that organic solutes play a major role in weathering processes, in diagenesis, in light attenuation and photochemical reactions, and in the transport of trace metals.

The simplest measure of the total concentration of organic solutes is the concentration of *dissolved organic carbon* (DOC), which is measured by converting all the organic material in solution to CO_2 and then measuring the CO_2 produced. Organic matter is considered dissolved if it passes through a 0.45-μm filter, and it is particulate if it is retained by the filter. This definition, although easy to apply, is arbitrary, as organic materials occur in a range of molecular sizes, and 0.45 μm does not represent a fundamental break, except that a 0.45 μm filter excludes almost all bacteria. The term *TOC (total organic carbon)* is the organic carbon content of an unfiltered sample.

Rainwater has DOC concentrations of about 0.5 to 1.5 mg/ℓ (Hoffman et al., 1980), much of it in the form of formate, acetate, and oxalate, derived largely from photochemical reactions involving larger organic molecules (Keene and Galloway, 1984; Sedlak and Hoigné, 1993). These compounds tend to biodegrade rapidly, so the rain must be analyzed or preserved quickly if these simple organic solutes are to be observed. DOC concentrations in groundwaters and the ocean are typically about 0.5 mg/ℓ, in rivers and lakes they are typically 2 to 10 mg/ℓ with values up to 60 mg/ℓ in rivers draining swamps and wetlands (Thurman, 1985); values in soil water can be as high as 260 mg/ℓ (Antweiler and Drever, 1983). Some typical values for DOC in natural waters are shown in Fig. 6-1.

River waters with DOC concentrations above about 10 mg/ℓ are distinctly colored. High-DOC waters, most common in tropical lowlands, are called *black waters*.

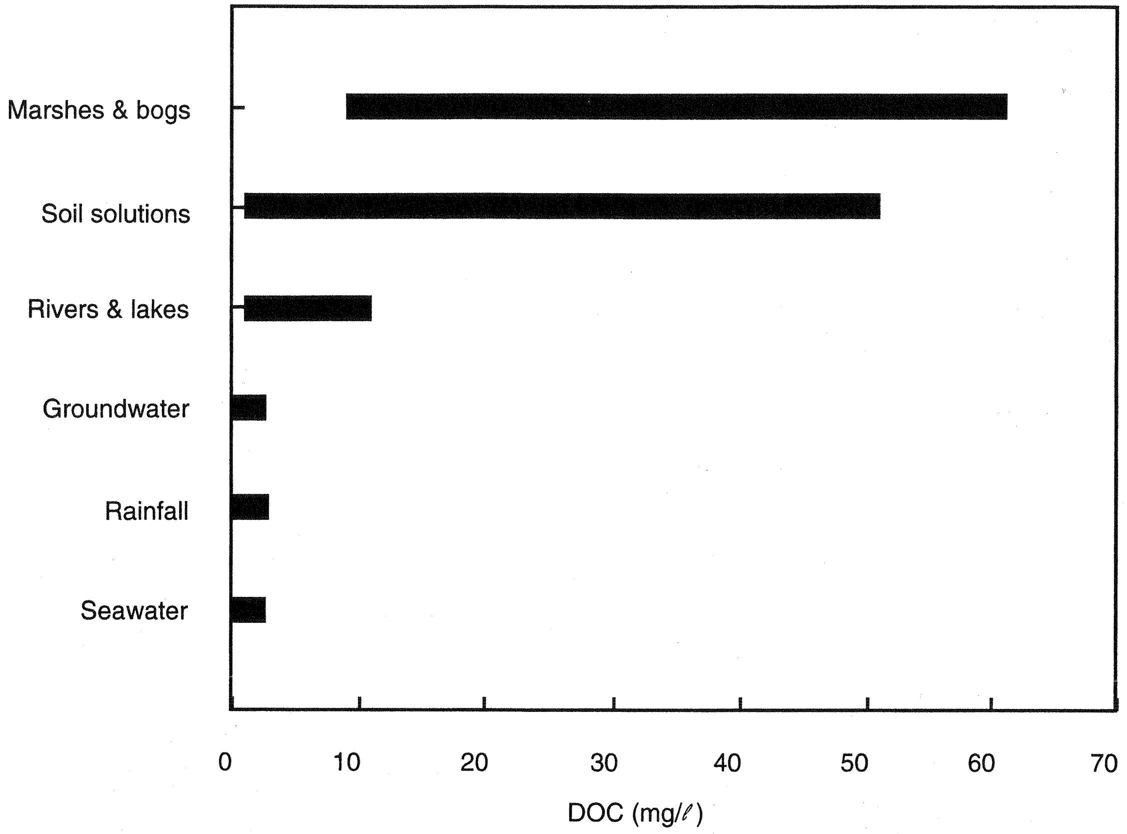
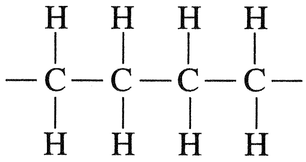


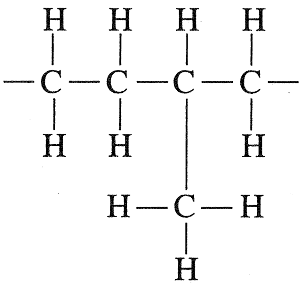
FIGURE 6-1 Typical values for natural DOC in natural waters (data from Thurman, 1985, and other sources).

Structure of Natural Organic Solutes

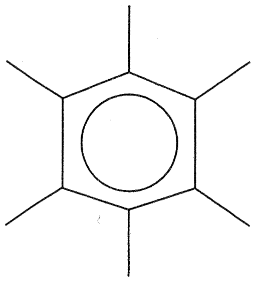
In the simplest view, organic compounds can be regarded as a carbon skeleton to which various functional groups are attached. The main components of the carbon skeleton are straight-chained or branched carbon units (aliphatic units):



$$\begin{array}{ccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

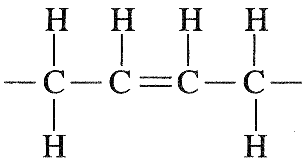


and aromatic units based primarily on the benzene ring:



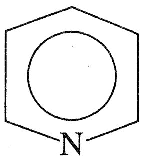
The color in black waters is due to conjugated aromatic units.

The carbon skeleton may also contain olefinic (double-bonded) groups:

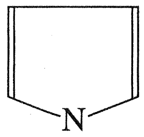


$$-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-$$

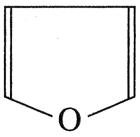
and heterocyclic units (rings containing one or more atom that is not carbon):



pyridine



pyrrole



furan

Functional Groups

Functional groups are small groups of atoms attached to the carbon skeleton. They normally contain atoms other than carbon (typically oxygen, nitrogen, or sulfur) and have specific chemical properties that affect the properties of the molecule as a whole. Functional groups containing oxygen and nitrogen are typically *polar*, that is to say they either have an electrical charge (ionized groups such as —COO^- or $\equiv\text{NH}^+$) or an electric dipole—a separation of charge in the group such that one "end" has a partial negative charge and the other a partial positive charge. Polarity is important because water is a highly polar solvent: polar functional groups tend to increase solubility in water, whereas organic molecules without polar functional groups tend to be relatively insoluble.

Carboxylic Acids. The most important group in natural DOC is the carboxylic acid group:

$$\text{—COOH}$$

The carboxylic group is important because it is the most abundant functional group in natural DOC. In fact, it is the largely the presence of this functional group that makes natural organic matter soluble in water (see discussion below). It is the dominant contributor to the acid-base behavior of natural DOC and a major contributor to complexation of metals. Carboxylic acids are produced by microbial oxidation of other (particularly plant-derived) organic matter. The diversity of carboxylic acids in nature reflects the diversity of precursor plant material and the diversity of microbial oxidation pathways.

As the name implies, this group behaves as an acid. If R is used to represent the remainder of the molecule, dissociation of the acid is described by

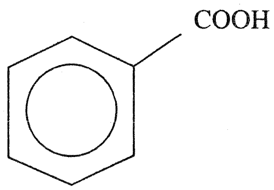
$$\text{RCOOH} = \text{RCOO}^- + \text{H}^+$$

$$K_a = \frac{a_{\text{H}^+} a_{\text{RCOO}^-}}{a_{\text{RCOOH}}} \tag{6–1}$$

The "strength" of an acid is measured by its dissociation constant, K_a, which is commonly reported (by analogy with pH) as pK_a, where $pK_a = -\log_{10}K_a$. As can be seen from Eq. (6–1), the pK_a is numerically equal to the pH at which half of the acid is dissociated and half is undissociated. The smaller the pK_a, the lower the pH at which dissociation occurs and hence the stronger the acid. The pK_a value of a particular carboxylic acid group depends on the nature and position (see, e.g., Schwarzenbach et al., 1993) of other functional groups close to it in the same molecule (Table 6-1). Note that oxygen-containing functional groups adjacent to the carboxylic acid group generally cause an increase in acid strength (compare, for example benzoic and salicylic acids in Table 6-1). Most carboxylic acid groups have pK_a, values around 3.5 to 5 (Fig. 6-2); thus most are completely dissociated in most natural waters. In high-DOC waters with low concentrations of inorganic ions, organic acids typically buffer the pH at about 4.5 (McKnight et al., 1985).

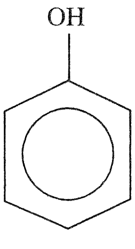
A second important property of carboxylic acids (or, more importantly, the corresponding anions) is the ability to complex metals, especially transition metals and aluminum. Complexation is particularly strong when two adjacent functional groups on a single molecule can coordinate with a cation and form a chelate (see Chapter 2).

A third important property of the carboxylic acid group is its effect on solubility and related properties. An ionized carboxylic acid greatly increases the solubility in water of the compound to which it is attached. Thus, for example, undissociated benzoic acid

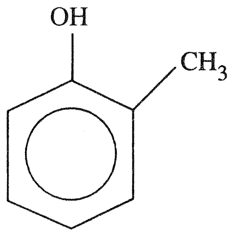


is relatively insoluble in water (3 g/ℓ), but sodium benzoate is highly soluble (660 g/ℓ). Even undissociated carboxylic acid groups contribute to solubility; benzoic acid is more soluble in water than is benzene. Somewhat related to solubility is the *hydrophobic* (water-hating) or *hydrophilic* (water-loving) property of an organic compound. Hydrophobic compounds are more soluble in organic solvents (e.g., octanol or dichloromethane) than in water, and hydrophilic compounds are more soluble in water than in organic solvents. This is important in fractionation schemes for dividing natural organic compounds into classes and in determining the adsorption properties of the compound. Compounds with a high ratio of polar functional groups (such as carboxylic acid groups) to framework carbon atoms tend to be hydrophilic, whereas those with a lower ratio tend to be hydrophobic.

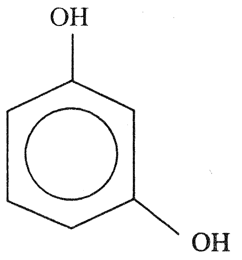
Phenols. A phenolic group is an —OH group attached to an aromatic ring, for example:



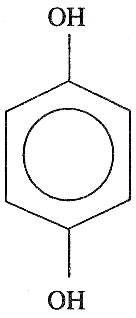
phenol



o-cresol

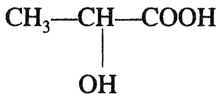
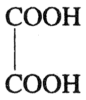
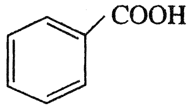
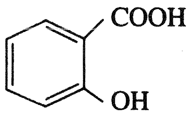
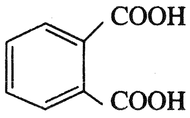


resorcinol

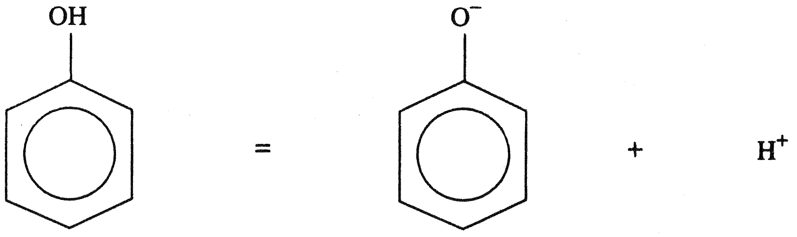


hydroquinone

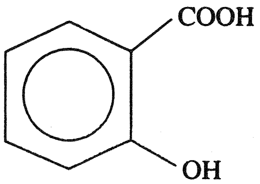
TABLE 6-1 Dissociation Constants for Some Organic Acids

		pK_a
Acetic	CH_3COOH	4.9
Lactic	 $CH_3-\underset{\mid \atop OH}{CH}-COOH$	3.1
Oxalic	 $\begin{matrix} COOH \\ \mid \\ COOH \end{matrix}$	1.2, 4.2
Benzoic		4.2
Salicylic		2.9
o-Phthalic		2.9, 5.5

The properties of phenols resemble those of carboxylic acids in several ways. They can dissociate into H^+ and the corresponding anion:



Although they are generally much weaker acids than carboxylic acids (Fig. 6-3), the pK_a value likewise depends on the nature of other functional groups nearby in the molecule. Phenolic groups form strong complexes with metal cations, and a phenolic group adjacent to a carboxylic acid group as in salicylic acid,



is a very effective chelator. Phenolic groups also contribute to the hydrophilic properties of a compound.

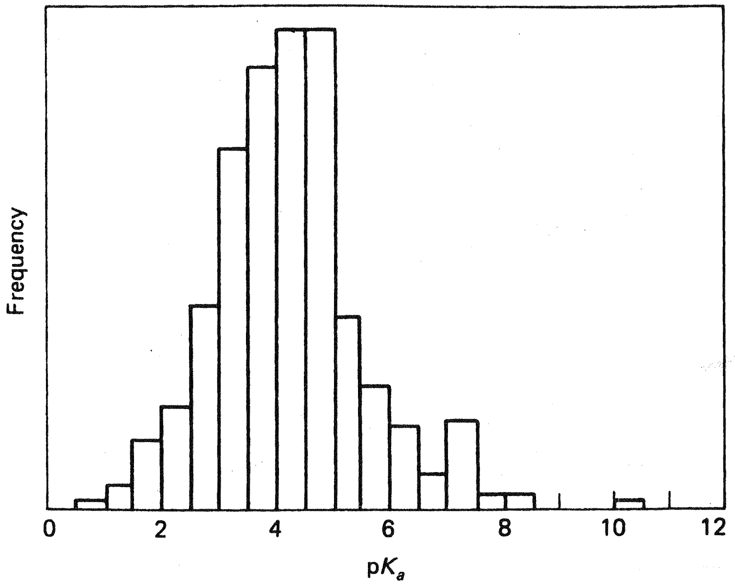
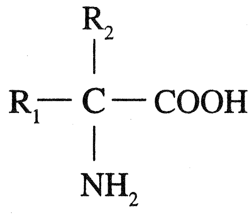


FIGURE 6-2 Distribution of pK_a values for simple carboxylic acids (after Perdue, 1985).

Amines and Amino Acids. The amino group (—NH_2) behaves like ammonia in that it can accept a proton and become —NH_3^+. The nitrogen atom can coordinate with metal cations and contributes to the hydrophilic character of the molecule.

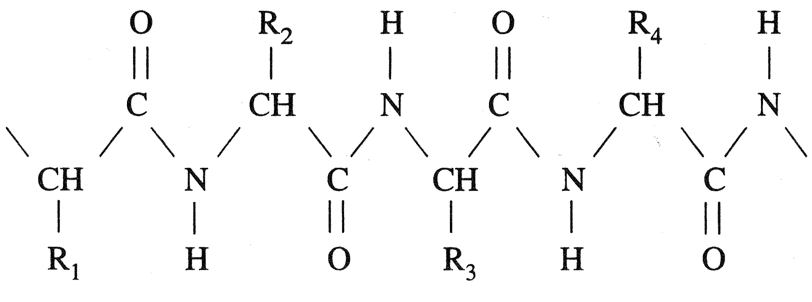
Natural amino acids contain an amino group adjacent to a carboxylic acid group:



$$\mathrm{R_1-\underset{\substack{|\\ NH_2}}{\overset{\substack{R_2\\ |}}{C}}-COOH}$$

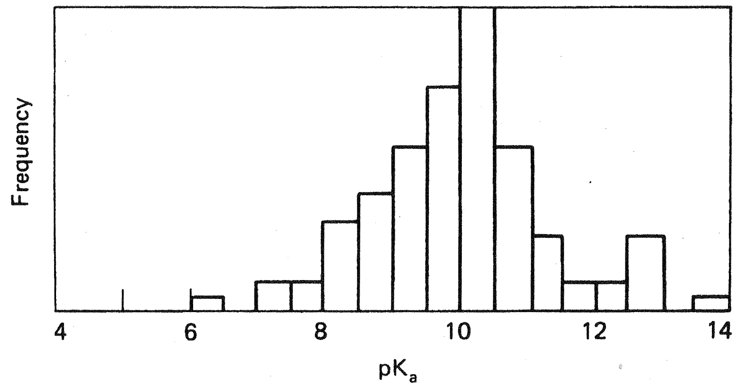
The remainder of the molecule (represented by R_1 and R_2) may be quite complex and commonly contains other functional groups. The group can behave as both an acid (from the —COOH) group and as a base (from the —NH_2 group).

Amino acids are the building blocks of proteins and are essential components of all living organisms. They may be present in natural waters as free amino acids, as peptides (chains of amino acids linked through their amino and carboxylic acid groups),



or as components of humic substances (see below). As a group, amino acids make up about 1 percent to 3 percent of the DOC in natural waters (Thurman, 1985).

FIGURE 6-3 Distribution of pK_a values for phenolic groups (after Perdue, 1985).



Sulfur-Containing Functional Groups. Relatively little is known about sulfur-containing functional groups in natural DOC. Microbial processes produce dimethyl sulfide:

$$\mathrm{CH_3{-}S{-}CH_3}$$

and various other reduced sulfur compounds. Leenheer et al. (1994) speculate that sulfur in fulvic acids (see below) is present as an ester sulfate:

$$\mathrm{R{-}O{-}SO_3^-}$$

Synthetic detergents commonly contain sulfonate groups:

$$\mathrm{R{-}SO_3^-}$$

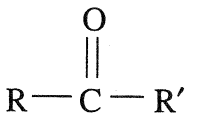
Neutral Functional Groups. Natural organic matter contains several oxygen-containing functional groups,

$$\mathrm{R{-}OH}$$

alcohol

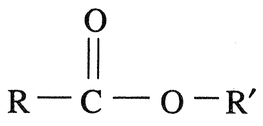
$$\mathrm{R{-}O{-}R'}$$

ether



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'}$$

carbonyl



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R'}$$

ester, lactone

that do not contribute directly to the acid-base properties of the molecule, but, because they are polar, they increase (to varying degrees) the solubility in water and the hydrophilic properties of molecules in which they are present.

Humic Substances

Humic substances have been defined as "A general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight, and refractory" (Aiken et al., 1985). In general terms, they are the products of the decomposition of primarily plant material by microbes. They are refractory in the sense that they are not easily decomposed further by microbes. Humic substances are subdivided into: *humin*, the fraction of humic substances that is insoluble in water at all pH values; *humic acid*, the fraction that is insoluble in water at pH 2 but becomes soluble at higher pH; and *fulvic acid*, the fraction that is soluble under all pH conditions. Most of the dissolved organic carbon in natural waters is in the form of humic and fulvic acid, with fulvic acid predominating in surface waters and humic acid tending to predominate in soil solutions. Humic and fulvic acids are general terms that cover a wide range of individual compounds. The exact structures of the individual compounds have not been elucidated. Since *humic* and *fulvic acid* are general terms for mixtures of compounds, the detailed properties of humic or fulvic acid from one location may be different from those of humic or fulvic acid from another location. The differences are presumably related to different original source material and different degradation pathways.

Attempts to characterize soluble humic substances by identifying the individual compounds present have generally been unsuccessful (Hayes et al., 1989), and the common approach has been to measure the properties of either the bulk mixture or of fractions separated from the mixture. The simplest fractionation is the division into humic and fulvic acid on the basis of solubility at low pH. Fractionation can also be based on molecular size, electrical charge characteristics, and adsorption. The main purpose of fractionation is to provide more uniform material for characterization by other techniques.

Some of the more important characterization methods are:

Elemental Analysis. The composition of the humic material (C, H, O, N, S, and sometimes other elements) is measured by standard chemical techniques (Huffman and Stuber, 1985). Bulk analysis constrains the amount of individual functional groups that can be present and constrains the relative amounts of aliphatic versus aromatic carbon. The chemical compositions of fulvic and humic acids are shown in Table 6-2.

Molecular Size and Weight Determinations. *Colligative properties*: A colligative property is a property of a solution that depends only on the number of solute molecules present and not on their properties. Thus, if the number of molecules associated with a given concentration of fulvic acid is determined, a number-averaged molecular weight can be calculated. Colligative properties include vapor-pressure lowering, changes in freezing point and boiling point, and changes in osmotic pressure (Aiken and Gillam, 1989). Because solutions of humic substances are generally dilute in terms of the number of molecules present in solution, measuring these properties with sufficient precision is technically difficult. The most commonly used technique is vapor-pressure osmometry (e.g., Aiken et al., 1994). They report number-averaged molecular weights for aquatic fulvic acid of about 600 to 900 daltons. (The dalton is the standard unit of molecular weight; the weight of the isotope ^{12}C is defined as

TABLE 6-2 Average Values for Elemental Composition of Soil Humic Substances (from Steelink, 1985)

	Humic Acids	*Fulvic Acids*
Carbon	53.8–58.7%	40.7–50.6%
Hydrogen	3.2–6.2	3.8–7.0
Oxygen	32.8–38.3	39.7–49.8
Nitrogen	0.8–4.3	0.9–3.3
Sulfur	0.1–1.5	0.1–3.6

12.0000 daltons.) One disadvantage of colligative-property measurements is that they provide only a mean molecular weight and provide no information on the spread or distribution of molecular weights.

Gel permeation chromatography: The most commonly used method for molecular size determination is gel permeation chromatography. A solution of the humic substance is passed through a column of Sephadex gel, and the extent to which fractions are retarded is a measure of their molecular size. Conceptually, the gel can be regarded as a framework with holes of a certain size in it. Molecules that are too large to fit the holes pass straight through the column and are not retarded. Smaller molecules diffuse through the holes into the gel, and hence take longer to pass through the column. If gels with different-sized "holes" (characterized by retention of known compounds) are used, the molecular size distribution of the humic substance can be measured. Molecular "size" is usually reported as molecular weight, although the conversion is only approximate.

Other methods for molecular size determination include ultrafiltration, and scattering of light or X-rays (Wershaw and Aiken, 1985). The general molecular-weight range of fulvic acids is 500 to 2,000 daltons and that of humic acids is 2,000 to 10^6 or more daltons.

Acid-base Titration. Acidic functional groups can be determined by titration with a strong base, such as barium hydroxide (see the discussion of alkalinity titrations in Chapter 3). In the past, such titration curves were "fitted" by assuming the existence of two types of functional groups: carboxylic acid with a pK_a of about 4 and phenol with a pK_a of about 10 (cf. Figs. 6-2 and 6-3). With this assumption, the number of carboxylic and phenolic groups per gram of humic substance could be readily measured. Unfortunately, the functional groups of "real" humic substances show a large spread in pK_a values, and there are several theoretical complications to the titration of a polyelectrolyte such as humic or fulvic acid (Ephraim et al., 1986; Marinsky and Ephraim, 1986; Perdue, 1985.)

Nuclear Magnetic Resonance (NMR) Spectroscopy. NMR spectroscopy measures transitions involving the nuclear spin of a suitable nucleus (^{13}C or ^{1}H) in an externally imposed magnetic field. The resonant frequency of the nucleus depends on the strength of the magnetic field to which it is exposed. The electrons surrounding the nucleus shield it partially from the external magnetic field, and so the resonant frequency varies as a function of the distribution of electrons around the nucleus. Thus NMR gives information on the electron configuration surrounding the ^{1}H or ^{13}C atom; the electron configuration is itself determined by the functional group in which the nucleus occurs. Proton NMR is capable of distinguishing between and estimating the relative amounts of protons on aromatic rings, aliphatic chains (several subclasses), carboxylic acids, hydroxyl groups, methoxyl groups, and lactone groups (Wershaw, 1985). ^{13}C NMR can distinguish between aromatic carbon, aliphatic (alkyl) carbon, carboxyl carbon, carbon in aldehydes and ketones, and carbon in alcohols, esters, ethers, and so on. NMR (especially ^{13}C NMR) is thus capable of estimating the amounts of various functional groups present and also the amounts of different types of carbon atom in the carbon skeleton.

Suwannee River Humic Substances. The Suwannee River drains the Okefenokee Swamp in the southeast portion of the state of Georgia. It is a "black" river, with low concentrations of inorganic ions, and a DOC concentration of 35-50 mgC/ℓ. Interestingly, the DOC appears to be derived from decomposition of contemporary vegetation and not from the peat that underlies the swamp (Malcolm et al., 1994) Large quantities of fulvic acid have been extracted from the Suwannee by workers at the U.S. Geological Survey. This fulvic acid has been extensively analyzed and characterized (Averett et al., 1994). It is thought to be typical of fulvic acid in rivers. Some properties of Suwannee River fulvic acid are listed in Table 6-3. Three proposed structural models consistent with the information are shown in Fig. 6-4. Note that the structures contain only two aromatic rings and have a large number of oxygen-containing functional groups. It must be emphasized, however, that fulvic acid is not a single compound: these models would thus be typical of the types of molecule that might make up a major fraction of the mixture.

Humic acids would be expected to be similar in structure to fulvic acids with the exception that the average molecular weight is higher and the proportion of oxygen-containing functional groups lower.

TABLE 6-3 Average Properties of Suwannee River Fulvic Acid (from Leenheer et al., 1994)

Number-average molecular weight	800 daltons
Elemental composition (corrected for ash & moisture)	
Carbon	53.8%
Hydrogen	4.3%
Oxygen	40.9%
Nitrogen	0.7%
Sulfur	0.6%
Phosphorus	<0.1%
Average molecular formula	$C_{33}H_{32}O_{19}$
Carbon distribution by type of carbon by ^{13}C NMR (normalized to 33 total carbon atoms)	
Aliphatic	7
H–C–O (alcohol, ether, acetal, ketal)	5
O–C–O (acetal, ketal, inc. aromatic)	2
Aromatic	8
Phenols, phenolic esters, aromatic ethers	3
Carboxyl plus ester	6
Ketone	2
Hydrogen distribution (normalized to 32 total)	
Carboxyl	4
Phenol	2
Alcohol	1
Bound to carbon	25
Oxygen distribution (normalized to 19 total)	
Carboxyl	8
Ester	4
Ketone	2
Phenol	2
Alcohol	1
Acetal and ketal	1
Ether	1

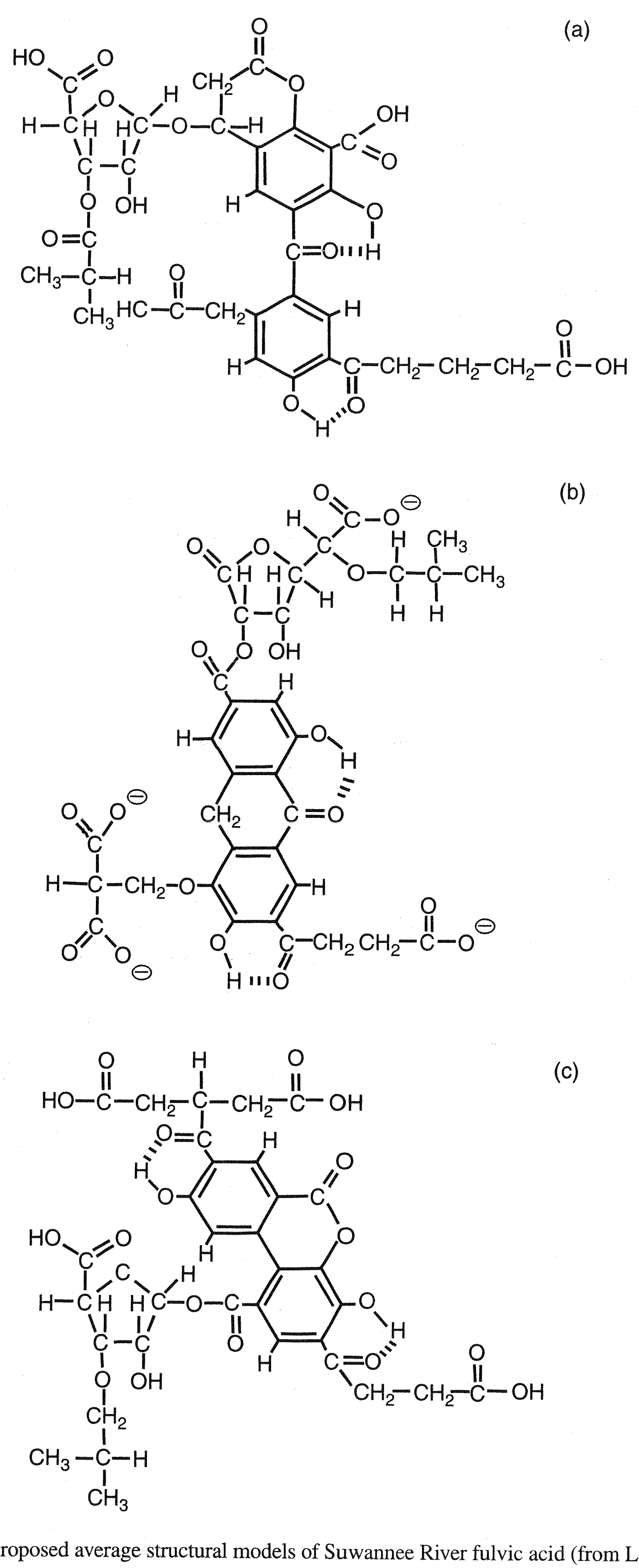


FIGURE 6-4 Three proposed average structural models of Suwannee River fulvic acid (from Leenheer et al., 1994).

Dissolved Organic Carbon (DOC) in Natural Environments

Soil Solutions. The organic layer in soils is a major source of soluble organic compounds. Cronan and Aiken (1985) report concentrations of 21 to 32 mg C/ℓ in solutions from the O/A horizon of soils from the Adirondack Mountains of New York State; concentrations there decreased to 5 to 7 mg C/ℓ in the B horizon (50 cm depth). Yavitt and Fahey (1985) showed a similar decrease in DOC with depth in soils from the Rocky Mountains of Wyoming. Yavitt and Fahey also observed a strong seasonal effect: solutions from the organic layer at the time of first snowmelt contained high (greater than 70 mg C/ℓ) concentrations of DOC, and the concentrations decreased to less than 20 mg C/ℓ as the season advanced. The early-season solutions contained relatively high concentrations of low-molecular-weight, readily metabolizable compounds such as amino acids and short-chain aliphatic acids, whereas the late-season solutions were dominated by refractory humic substances. The seasonal changes are a result of seasonal changes in microbial activity. The decrease in DOC with depth is caused by some combination of microbial decomposition, adsorption, and precipitation as a solid (Stevenson, 1994).

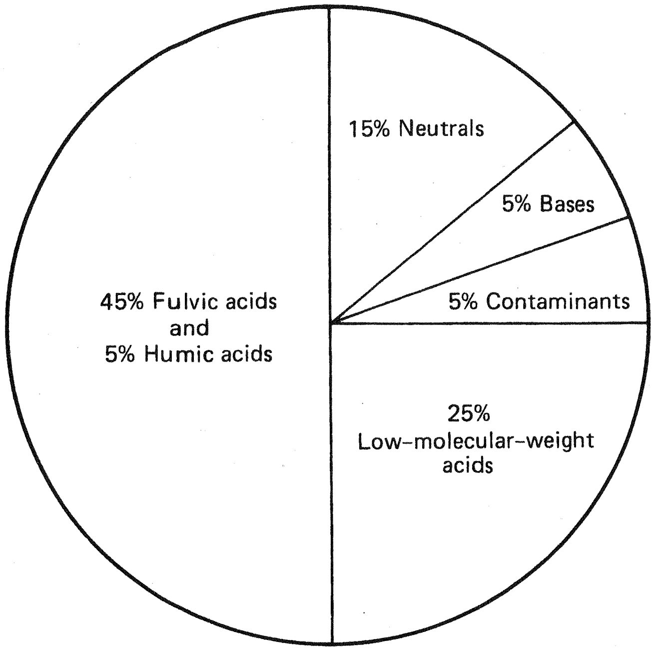
The presence of organic acids has a strong influence on weathering and soil formation (e.g., Antweiler and Drever, 1983; Fahey et al., 1985; Graustein et al., 1977). They control the pH of soil solutions and hence, in part at least, the rate of mineral weathering. Aluminum and iron are complexed by organic solutes, which results in leaching of these elements from upper horizons and deposition in deeper horizons (as the DOC is removed from solution), forming the characteristic profiles of podsols or spodosols (although there is some debate about the relative importance of transport of Al in solution and transport by physical movement of particles in soil profile development).

Groundwater. Most groundwaters that are not affected by pollution have DOC concentrations below 2 mg C/ℓ, with a median value of about 0.7 mg C/ℓ (Leenheer et al., 1974). As mentioned previously, water percolating through soil loses its DOC by several processes. By the time the water reaches the water table, most of the DOC has been removed. Locally, groundwaters associated with swamps or with coal or oil shale may have much higher DOC concentrations. Oilfield brines may contain very high (more than 1,000 mg C/ℓ) concentrations of short-chain aliphatic acids produced by thermal degradation of kerogen (Lundegard and Kharaka, 1994).

Rivers and Lakes. DOC concentrations in rivers vary with the size of the river, climate, and the nature of vegetation in the river basin (Thurman, 1985). Excluding waters draining swamps and wetlands, the normal range is about 2 to 15 mg C/ℓ with a mean of about 4 to 6 mg C/ℓ (Degens, 1982). About half of the DOC is fulvic/humic acids (Fig. 6-5). Waters draining swamps and wetlands range from about 5 to 60 mg C/ℓ with a mean of 25 mg C/ℓ (Thurman, 1985). Again, the major component is fulvic acids. Organic species are often the dominant anions in such waters, and aluminum and iron, complexed by dissolved organic matter, may be major cations (Beck et al., 1974). DOC concentrations in rivers commonly vary with discharge. At low flow, when most of the water is derived from groundwater, DOC concentrations tend to be low. At high flow, when water is entering the river directly from the soil, DOC concentrations tend to be higher.

The DOC concentration in lakes varies with the biological productivity of the lake. Lakes with low productivity typically have 1 to 3 mg C/ℓ, whereas eutrophic (see Chapter 8) lakes

FIGURE 6-5 Distribution of different classes of organic compounds in surface water DOC in rivers of the United States (after Malcolm, 1985).



typically have 2 to 5 mg C/ℓ (Thurman, 1985). Lakes associated with swamps or peat bogs may have much higher values. The DOC in lakes is a mixture of substances from river input (with a higher proportion of humic substances) and substances produced by the biota, primarily algae, in the lake (a wide range of compounds with a smaller portion of humic substances) (Wetzel, 1983). The relative importance of the two sources depends on the size of the lake; very roughly, the larger the lake, the smaller the relative contribution from river input.

DOC in surface waters is strongly involved in photochemical reactions (e.g., Sulzberger and Hug, 1994). Humic substances absorb ultraviolet and visible light, which both breaks down the humic molecules and provides free radicals that may influence the redox chemistry of iron, manganese, and other metals. Such photochemical reactions may be important in providing iron in a bioavailable form to phytoplankton, and in converting humic substances to smaller molecules that can be metabolized by microorganisms.

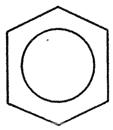
The Oceans. The mean DOC concentration in the surface layers (0 to 300 m) of the oceans is 1 mg C/ℓ, with a range of 0.3 to 2.0 mg C/ℓ (Williams, 1971). The mean DOC concentration of deeper water is 0.5 mg C/ℓ. The DOC is derived both from marine biota and from continental runoff. Marine DOC contains a wide range of compounds, of which fulvic/humic acids are a relatively small proportion. Marine humic substances are quite different in chemical character from terrestrial humic substances, reflecting derivation, in part at least, from planktonic organisms rather than terrestrial plant material (Harvey and Boran, 1985).

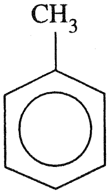
ORGANIC POLLUTANTS

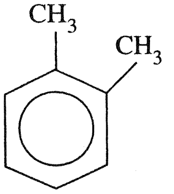
Human activities have introduced a vast number of synthetic organic compounds into the environment, and many are causing significant pollution of ground and surface waters. Although many different compounds cause problems locally, the most important overall are aromatic hydrocarbons (mostly from gasoline, diesel, and other fuels), chlorinated hydrocarbons (used in various industrial processes, mostly as solvents), and pesticides (Table 6-4). Aromatic hydrocarbons and chlorinated hydrocarbons have a number of properties in common: they are relatively nonpolar, they are somewhat soluble in water, they are volatile, and some members of each group are relatively resistant to biodegradation. Although aliphatic hydrocarbons are also a major component of fuels, they are generally less of a problem as pollutants in groundwater

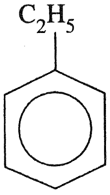
TABLE 6-4 Examples of Some Common Organic Pollutants

Aromatic Hydrocarbons

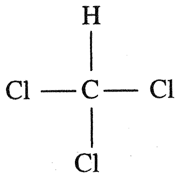

benzene

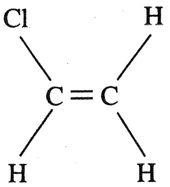

toluene
(methylbenzene)

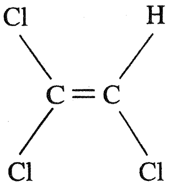

o-xylene
(1, 2-dimethylbenzene)

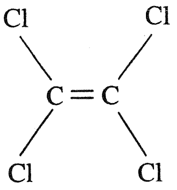

ethylbenzene

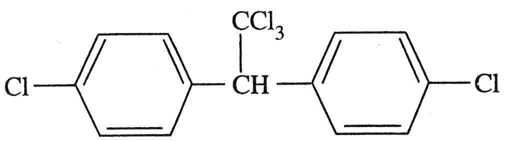
Chlorinated Hydrocarbons

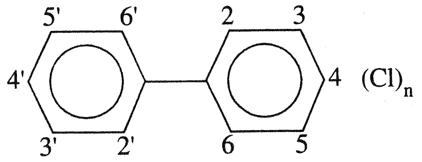

chloroform
(trichloromethane)


vinyl chloride
(chloroethene)


trichlorethylene, TCE
(trichloroethene)

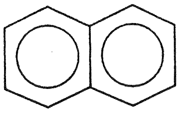

perchlorethylene, PCE
(tetrachlorethene)

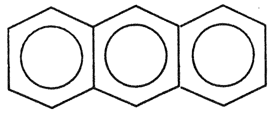

DDT

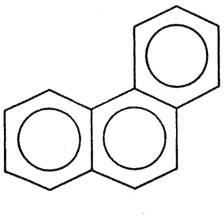


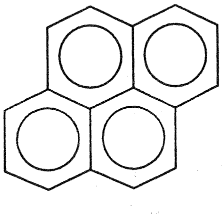
polychlorinated biphenyls (PCB)
(Chlorine atoms attached at various points around both benzene rings)

Polynuclear Aromatic Hydrocarbons


naphthalene


anthracene


phenanthrene


pyrene

because they are much less soluble in water and are generally biodegradable. Another class of compound associated with petroleum is *polynuclear aromatic hydrocarbons* (PAH) (Table 6-4). These are relatively insoluble in water but are of environmental concern because many members of the group are carcinogens. The properties of pesticides are highly variable, so one cannot assign general properties to the group. Some (e.g., DDT) are chlorinated hydrocarbons (nonpolar, insoluble), whereas others are highly polar and soluble in water.

Solubility and Related Properties

Much of the behavior of organic pollutants is determined by their hydrophobicity, that is the extent to which they tend to partition into an organic phase such as octanol rather than into water. The most general measure of hydrophobicity is the *octanol-water partition coefficient*. If a compound is allowed to distribute itself between octanol and water in contact with each other, the octanol-water partition coefficient (K_{OW}) is simply the ratio of its concentration in the octanol phase to its concentration in the aqueous phase. There is nothing "special" about octanol; other organic solvents would give a similar pattern. The octanol–water partition coefficient is a good predictor of adsorption behavior and of bioaccumulation. Compounds with very high K_{OW} values (for example the pesticide DDT) tend to accumulate in fat and not be excreted, and as a result their concentration increases up the food chain. The solubilities of nonpolar organic compounds also correlate fairly well with their octanol-water partition coefficients (Table 6-5). Note that the solubilities of many aromatic hydrocarbons and chlorinated hydrocarbons are quite high, as high as several hundred mg/ℓ. Note also that low solubility in water corresponds to a high octanol-water partition coefficient, reflecting the "incompatibility" of that compound with water.

Because of their limited solubilities in water, nonpolar organic liquids commonly form a separate phase in the subsurface; such liquids are referred to as NAPLs (Non-Aqueous Phase Liquids). NAPLs are subdivided into LNAPLs (Light NAPLs), whose density is less than that of water, and DNAPLs (Dense NAPLs), whose density is greater than that of water. The most common LNAPLs are gasoline and other fuels; the most common DNAPLs are chlorinated hydrocarbons (particularly chlorinated ethylenes) used as solvents. If an LNAPL is spilled on the ground (Fig. 6-6), it tends to flow down through the unsaturated zone and form a pool at the water table. A DNAPL, by contrast (Fig. 6-7), will flow downward through the groundwater until it encounters an impermeable layer. It then tends to spread laterally, following the topography of the surface of the impermeable layer.

The theory of multiphase flow in a porous medium is complex, and will not be discussed here (for an introduction, see Fetter, 1993). As a liquid percolates downward through the unsaturated zone, it does not drain completely; some of the liquid remains in the pores, held by capillary forces. The amount of liquid remaining is referred to as the *residual saturation*. Similarly, if an NAPL is displaced by moving groundwater, the NAPL is not completely displaced by the water; a fraction, the *irreducible saturation*, remains behind. These phenomena contribute greatly to the difficulty of cleaning up aquifers contaminated by NAPLs. Even if all the "free" NAPL is pumped from the ground, a significant fraction remains behind in the pores of the vadose zone and the aquifer. The common pollutants are sufficiently soluble (Table 6-5) that the residual amounts can severely contaminate any groundwater moving through an affected volume, yet they are sufficiently insoluble that cleanup by pumping water through the affected volume to dissolve the residual amounts ("pump and treat") is rarely an effective treatment by

TABLE 6-5 Solubilities and Octanol-Water Partition Coefficients for Some Common Organic Pollutants (from Mackay et al., 1992; Sangster, 1991; and other sources)*

Compound	*Specific gravity*	*Solubility in water at 25°C (mg/ℓ)*	*log K_{OW}*
Aliphatic hydrocarbons			
n-heptane	0.68	3	4.50
n-octane	0.70	0.7	5.15
Aromatic hydrocarbons			
Benzene	0.88	1800	2.13
Toluene	0.87	500	2.73
o-Xylene (1,2-dimethylbenzene)	0.88	180	3.12
Ethylbenzene	0.87	170	3.15
Chlorinated hydrocarbons			
Chloroform (trichloromethane)	1.48	8000	1.97
Carbon tetrachloride (tetrachloromethane)	1.59	800	2.83
1, 2 Dichloroethane	1.25	8500	1.48
1,1,2 Trichloroethane	1.44	4500	2.1
1,1,2,2 Tetrachloroethane	1.59	3000	2.4
Vinyl chloride	gas		1
Trichloroethylene (trichloroethene)	1.46	1200	2.4
Perchlorethylene (tetrachloroethene)	1.62	200	3
Chlorobenzene	1.11	450	2.84
1,3 Dichlorobenzene	1.29	120	3.5
p,p′–DDT		0.003	6.19
2,4,2′,4′–Tetrachlorobiphenyl (PCB-47)	1.20	0.1	6.0
Polynuclear aromatic hydrocarbons (PAH)			
Naphthalene	1.15	32	3.35
Anthracene	1.3	0.07	4.50
Phenanthrene	1.2	1.2	4.52
Pyrene	1.3	0.13	5.00

*There is considerable uncertainty associated with some of the solubility and log K_{OW} numbers.

itself. "Pump and treat" may, however, be an effective way of containing the contaminant and preventing its spread. It is also used in combination with other strategies such as bioremediation (see below). For volatile NAPLs, circulating air through the vadose zone (vapor extraction) can be an effective cleanup strategy. These topics are well reviewed in the National Research Council (1994) publication "Alternatives for Ground Water Cleanup."

Adsorption

Nonpolar Compounds. Dissolved organic compounds are often strongly adsorbed by solid phases in the subsurface, which greatly affects their mobility in groundwater. For nonpolar compounds such as hydrocarbons and chlorinated hydrocarbons, the important substrate is solid organic matter in the aquifer. "Solid organic matter" does not generally consist of large particles such as coal or wood fragments, but organic coatings on minerals. Natural minerals are very commonly coated by organic matter and, as a result, a

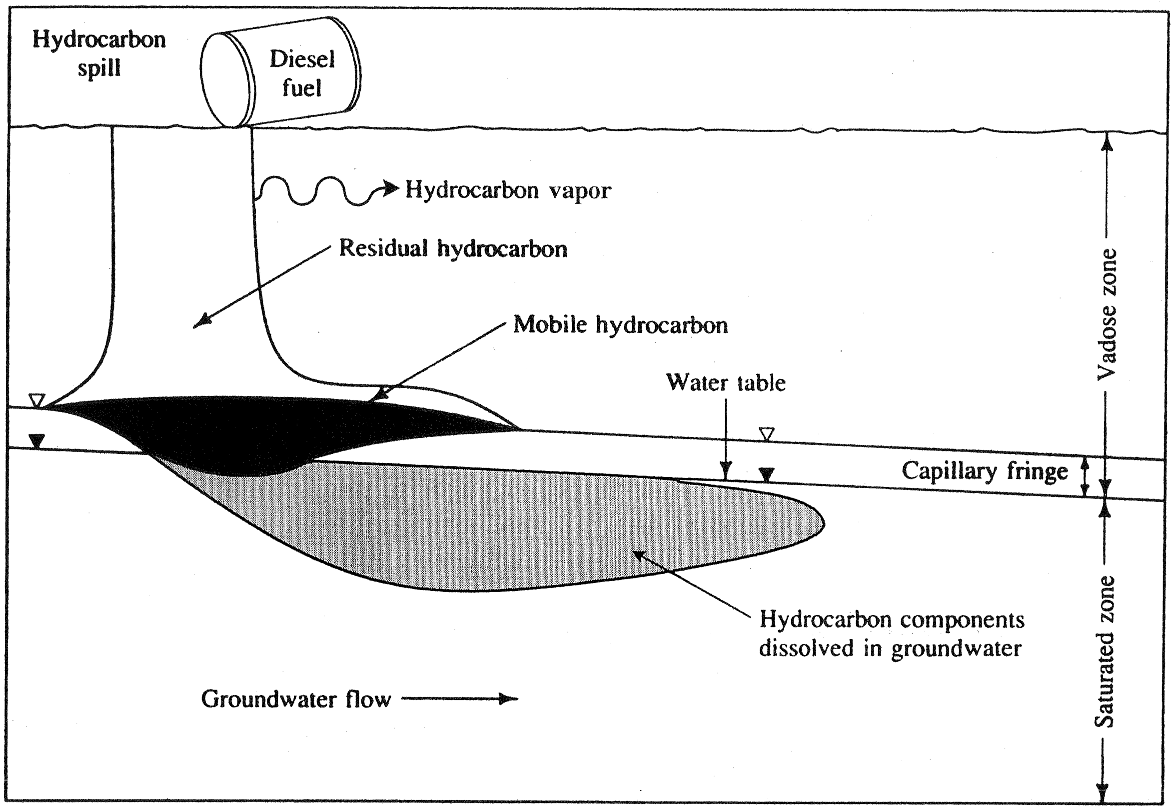


FIGURE 6-6 General distribution of an LNAPL in the subsurface following a spill. CONTAMINANT HYDROGEOLOGY by Fetter, C. W., ©1993. Reprinted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

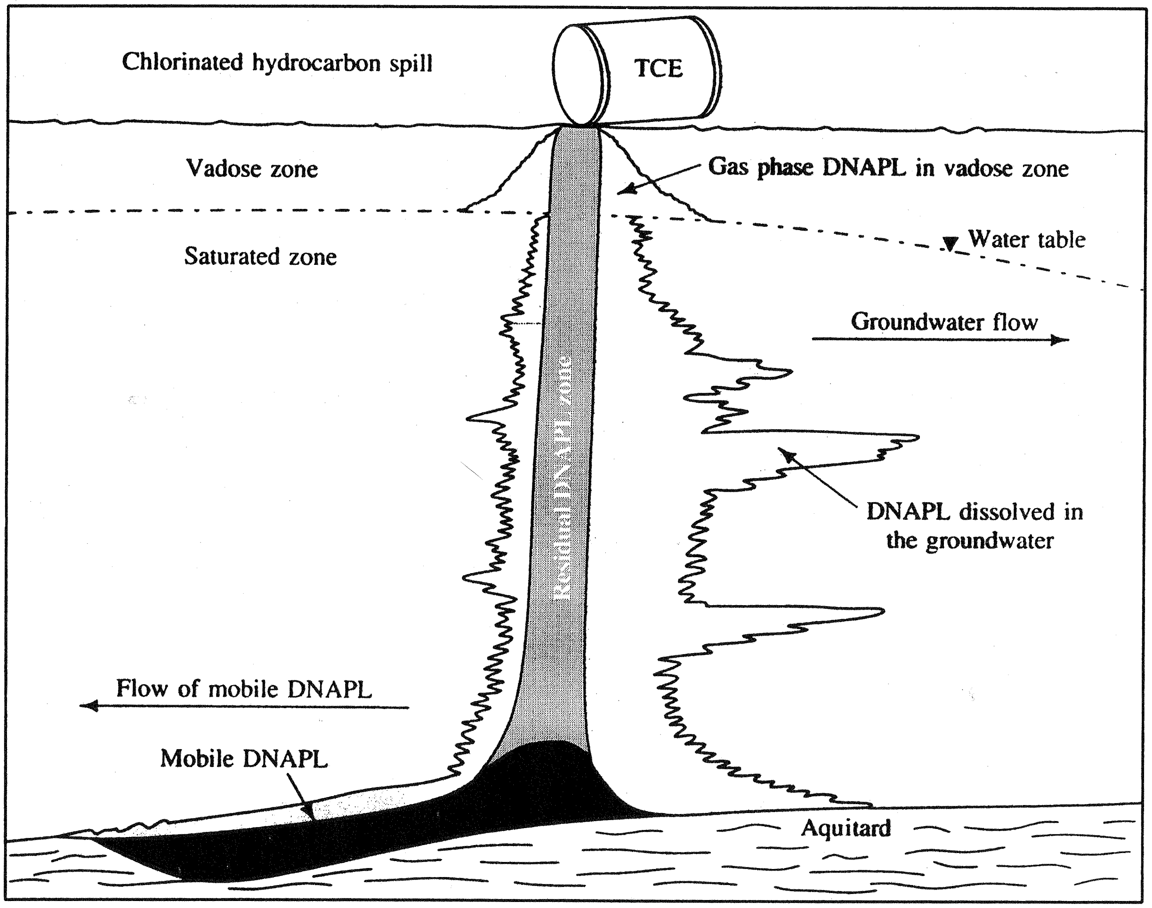


FIGURE 6-7 General distribution of a DNAPL in the subsurface following a spill. CONTAMINANT HYDROGEOLOGY by Fetter, C. W., ©1993. Reprinted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

relatively small weight percent organic matter can correspond to a relatively large surface area available for adsorption. The principal adsorption mechanism is *hydrophobic partitioning*. Hydrophobic compounds are, by definition, incompatible with water and so tend to partition out of water onto any available organic substrate. Since the main driving energy is the incompatibility with water, the extent of adsorption is relatively insensitive to the exact nature of the solid organic matter. On the other hand, adsorption of nonpolar organic compounds by silicate minerals is generally unimportant. In aquifers containing more than about 0.1 to 1 percent organic carbon, adsorption of nonpolar compounds follows a simple distribution law:

$$C_{\mathrm{ads}} = K_d C_{\mathrm{soln}}$$

where C_{ads} is the concentration of the adsorbed solute (commonly moles or g per kg solid), C_{soln} is the concentration of the solute in aqueous solution (commonly moles or g per ℓ) and K_d is a distribution coefficient (Chapter 5) which commonly has units ℓ/kg. Because adsorption is determined by the amount of organic matter present, the distribution coefficient, K_d, is proportional to the fraction of the aquifer solids that is organic matter

$$K_d = K_{\mathrm{OM}} f_{\mathrm{OM}} \tag{6–2}$$

where f_{OM} is the fraction of the aquifer solids that is organic matter and K_{OM} is the extrapolated value that K_d would have if the aquifer solids were 100 percent organic matter.

K_{OM} reflects basically the hydrophobicity of the organic solute, and it can thus be predicted from the octanol-water partition coefficient, K_{OW}. For adsorption onto natural organic matter, many nonpolar organic compounds follow the equation (Schwarzenbach et al., 1993)

$$\log K_{\mathrm{OM}} = 0.82 \log K_{\mathrm{OW}} + 0.14$$

Combining these equations gives

$$\log K_d = 0.82 \log K_{\mathrm{OW}} + \log f_{\mathrm{OM}} + 0.14 \tag{6–3}$$

Slightly different coefficients for this equation have been reported by different authors (for reviews, see Karickhoff, 1984, and Schwarzenbach et al., 1993).

Organic matter is usually measured and reported as organic carbon, in which case Eq. (6–2) becomes

$$K_d = K_{\mathrm{OC}} f_{\mathrm{OC}}$$

where f_{OC} is the fraction of the aquifer that is organic carbon (the weight percentage organic carbon divided by 100), and K_{OC} is the (extrapolated) value that K_d would have if the aquifer were 100 percent organic carbon. Natural organic matter is approximately 50 percent C (Schwarzenbach et al., 1993), so $f_{\mathrm{OM}} = 2f_{\mathrm{OC}}$ and, written in terms of organic carbon, Eq. (6–3) becomes

$$\log K_d = 0.82 \log K_{\mathrm{OW}} + \log f_{\mathrm{OC}} + 0.44$$

Polar Compounds. Adsorption of polar organic compounds, including many pesticides, is a complex subject (for reviews, see Schwarzenbach et al., 1993, and Stevenson, 1994). If the compound contains a cationic functional group (typically an amino group or pyridine), it will be adsorbed electrostatically by negatively charged surfaces such as clay minerals. Oxygen-containing functional groups may be adsorbed by ligand exchange with surface OH groups, by hydrogen bonding, or by dipole–dipole interaction. Many polar organic compounds are strongly adsorbed by clay minerals and oxides. The mechanisms are not well understood.

Surfactants (Detergents). Surfactants are molecules containing a hydrophilic "head" and a hydrophobic "tail." The hydrophilic part may be a cationic group such as a quaternary ammonium group:

$$R—N^+(CH_3)_3$$

It may be an anionic group such as a carboxyate or a sulfonate:

$$R—SO_3^-$$

or it may be a neutral group such as a polyether:

$$R—O-CH_2-CH_2(-O-CH_2-CH_2)_n-O-CH_2-CH_2-OH$$

where n is typically about 8. The hydrophobic part of the molecule (R— in the examples above) is generally a straight-chain aliphatic hydrocarbon with 10–20 carbon atoms; it may also contain a benzene ring.

Cationic surfactants adsorb strongly on negatively charged surfaces such as clay minerals, including the interlayer spaces in smectites. Neutral surfactants generally adsorb less strongly onto minerals; anionic surfactants are much less adsorbed. Once a layer of surfactant has been adsorbed, the hydrophobic "tails," which project into the solution away from the surface, form a hydrophobic organic layer that can adsorb nonpolar organic solutes. In general, the behavior of nonpolar solutes can be manipulated through addition of surfactants. The surfactants affect surface tension and "wetting," miscibility/solubility, and adsorption/desorption. They are used extensively in enhanced oil recovery; their use in cleanup of NAPLs is the subject of considerable research. One problem is that surfactants themselves are not necessarily environmentally benign, so any surfactant that is injected into an aquifer must itself be cleaned up.

Biodegradation and Bioremediation

The concept of bioremediation is relatively simple: microbes are capable of breaking down many organic compounds, ultimately to environmentally benign compounds such as CO_2, water, and inorganic forms of Cl, N, and S. They do this basically to obtain energy from the carbon in the contaminant molecule. Although the concept is simple, the implementation is complex and there are many limitations to the applicability of the method. The enzyme systems of microorganisms have evolved to deal with the compounds commonly encountered by the microorganisms in their natural environments. Such enzyme systems are not adapted to dealing with many synthetic organic compounds (or *xenobiotics,* as they are sometimes called), which limits the ability of such organisms to degrade organic pollutants. However, microorganisms have a remarkable ability to adapt, by a variety of mechanisms, and to develop enzymatic pathways that result in a breakdown of xenobiotic compounds (Schwarzenbach et al., 1993). It may require some considerable time for a natural community of organisms to acquire the ability to degrade an introduced contaminant and, of course, some organic compounds are not biodegraded to any significant extent.

Bioremediation (or, more strictly, *in-situ bioremediation*) may simply involve allowing naturally occurring microbes to act on the contaminant without further intervention, it may involve addition of oxygen and/or nutrients*, it may involve extracting indigenous microbes, adapting them to the specific contaminant and reinjecting, or it may involve injecting specific organisms cultured in the laboratory. Although the concept of injecting a specific organism has received a great deal of publicity, the approach has not been particularly successful in practice. This is in part, at least, because biodegradation is usually not the result of a single organism, but of a *consortium* of microorganisms that interact with each other in complex ways. A further complication of bioremediation is that microorganisms may not degrade the target compound all the way to CO_2 and water, but to some intermediate compound that may itself be hazardous. As an example, vinyl chloride is commonly produced as an intermediate in the biodegradation of various chlorinated hydrocarbon solvents. Vinyl chloride is a carcinogen and considerably more hazardous than the original solvents.

Microorganisms use various metabolic pathways to oxidize organic carbon to CO_2 (see Chapter 8). The different pathways are characterized by the *terminal electron acceptor*, that is to say the "oxidizing agent." For aerobic microorganisms, the terminal electron acceptor is molecular oxygen. For anaerobic organisms, it may be nitrate, ferric iron, sulfate, or bicarbonate (and some other less important species). Although biodegradation of contaminants does occur under anaerobic conditions, particularly when nitrate is available as an electron acceptor, many more compounds are degraded under aerobic conditions, and the rate of degradation is generally much faster; however, some chlorinated hydrocarbons degrade more rapidly (by reductive dehalogenation) under anaerobic conditions (Mohn and Tiedje, 1992). Thus, in general, one requirement for successful bioremediation is the availability of oxygen. The solubility of oxygen in water is quite small. Water in equilibrium with the atmosphere contains about 10 mg/ℓ (0.3 mM) of dissolved oxygen (the exact amount depends on temperature; see Table 8-1). This is a rather small amount. If much organic matter is present to be metabolized, oxygen in the groundwater will be rapidly depleted, and the bioremediation process is likely to be limited by the rate at which oxygen is transported to the site of reaction, either by advection (flow) of groundwater or by diffusion. Because of this limitation, bioremediation is currently most useful as a "polishing" step once the bulk of a contaminant has been removed. A great deal of research is currently being conducted on bioremediation under both aerobic and anaerobic conditions. The subject is reviewed in National Research Council (1993).

REVIEW QUESTIONS

1. Suppose a river water contains 10 mg/ℓ DOC, and that the DOC represents ionized fulvic acid with the composition described in Table 6-3:
   a. Now many milliequivalents per liter of organic anions would be present?

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*Nutrients may be inorganic species such as nitrogen and phosphorus compounds, or may include a readily metabolized substrate such as acetate to stimulate microbial growth and degradation of the target compound by a process called *cometabolism*.

b. If the organic anions were balanced by Ca^{2+}, how many ppm calcium would this represent?

c. If it requires two functional groups (either two carboxyl acid groups or a phenol group plus a carboxylic acid group) to complex an aluminum ion, how many ppm aluminum could be present in the water as complexes with fulvic acid?

2. What should be the distribution coefficient for toluene in an aquifer containing 0.5 percent organic carbon? What would be a reasonable estimate for the retardation coefficient (Chapter 16) of toluene in the aquifer?

3. A groundwater contains a dissolved oxygen concentration of 5 mg/ℓ. How many liters of groundwater would it take to oxidize 1 g of toluene to CO_2?

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