Water-Quality Principles
QW1022–TEL

Lesson 8—Environmental Organic Chemistry

Source: Drever, J. I., 1997, Geochemistry of natural waters: surface and ground water environments (3d ed.): Upper Saddle River, N.J., Pearson Higher Education, p. 119–126. Electronically reproduced with permission of the author.

U.S. Department of the Interior
U.S. Geological Survey

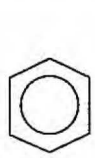
ORGANIC POLLUTANTS

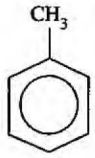
Human activities have introduced a vast number of synthetic organic compounds into the environment, and many are causing significant pollution of ground and surface waters. Although many different compounds cause problems locally, the most important overall are aromatic

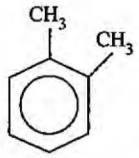
hydrocarbons (mostly from gasoline, diesel, and other fuels), chlorinated hydrocarbons (used in various industrial processes, mostly as solvents), and pesticides (Table 6-4). Aromatic hydrocarbons and chlorinated hydrocarbons have a number of properties in common: they are relatively nonpolar, they are 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

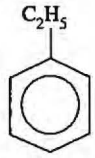
TABLE 6–4 Examples of Some Common Organic Pollutants

Aromatic Hydrocarbons

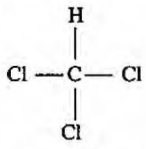

benzene

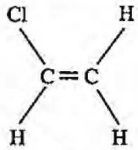

toluene (methylbenzene)

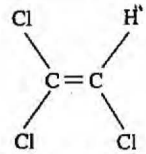

o-xylene (1, 2-dimethylbenzene)

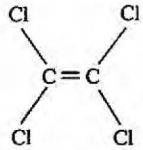

ethylbenzene

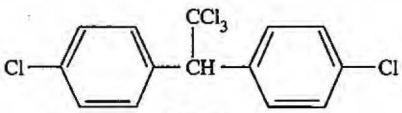
Chlorinated Hydrocarbons

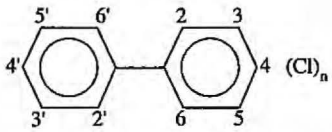

chloroform (trichloromethane)


vinyl chloride (chloroethene)

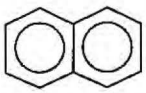

trichlorethylene, TCE (trichloroethene)

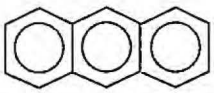

perchlorethylene, PCE (tetrachlorethene)

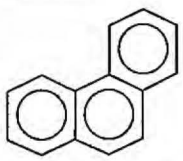

DDT


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

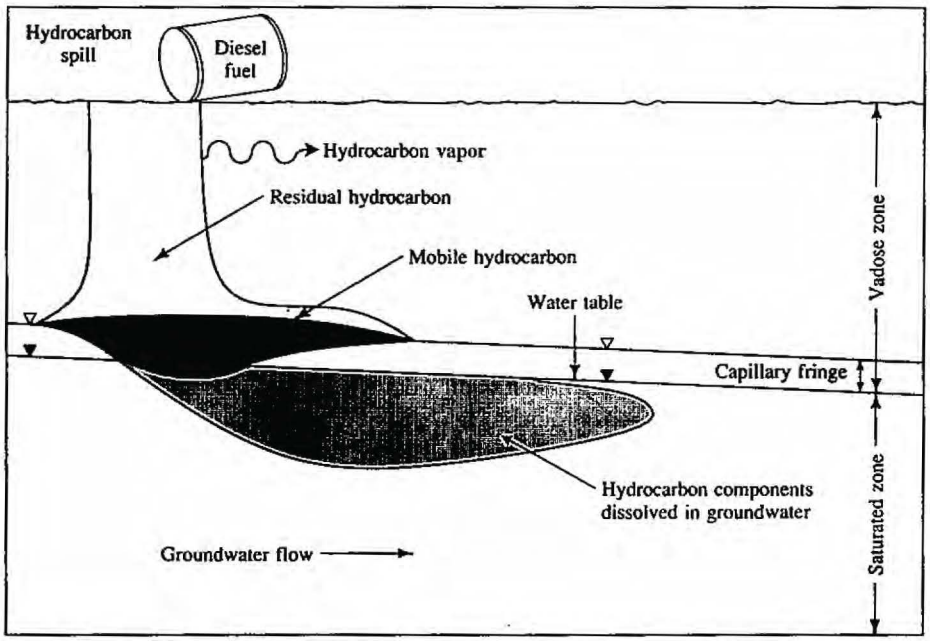


FIGURE 6-6 General distribution of an LNAPL in the subsurface following a spill. CONTAMINANT HYDROGEOLOGY by Fetter, C. W., ©1993. Reprinted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

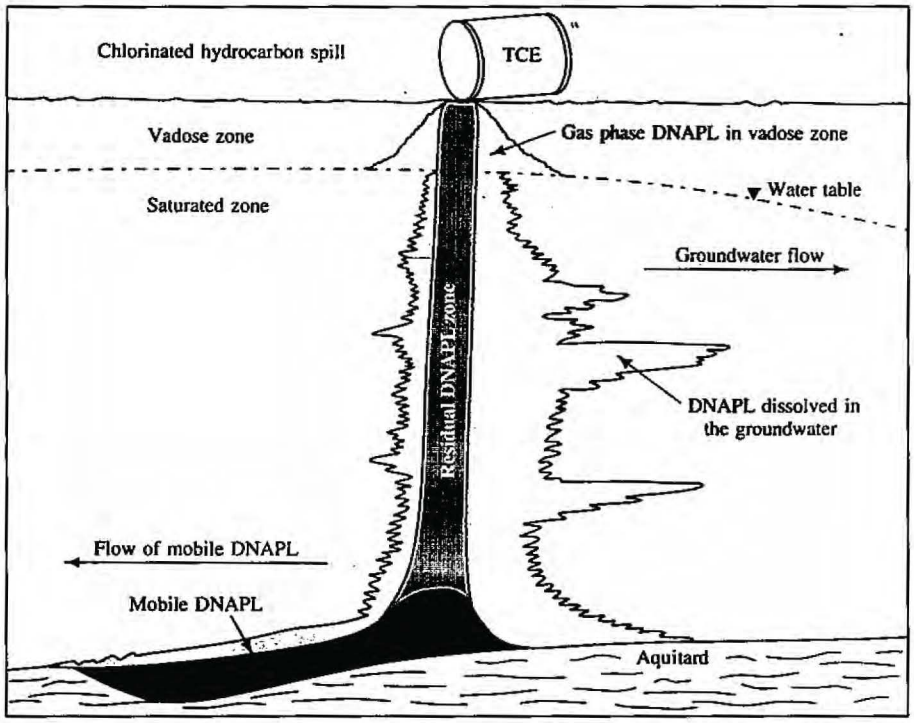


FIGURE 6-7 General distribution of a DNAPL in the subsurface following a spill. CONTAMINANT HYDROGEOLOGY by Fetter, C. W., ©1993. Reprinted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

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:

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

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

$$K_d = K_{OM} f_{OM} \tag{6–2}$$

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)

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

Combining these equations gives

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

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

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

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 $f_{OM} = 2f_{OC}$ and, written in terms of organic carbon, Eq. (6–3) becomes

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

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 min-

erals. 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).

*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*.