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

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

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

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

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:

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

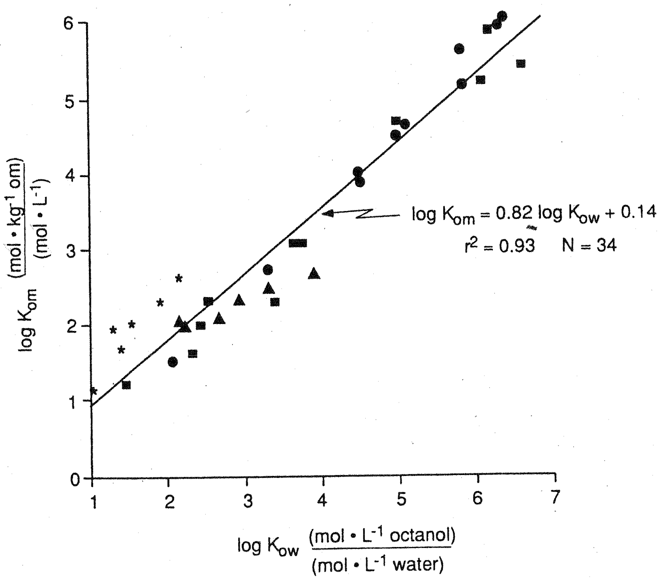

Figure 11.10 Relationship of log K_{om} and log K_{ow} for a series of neutral organic compounds: (●) aromatic hydrocarbons, (■) chlorinated hydrocarbons, (▲) chloro-*S*-triazines, and (∗) phenyl ureas (data compiled by Karickhoff, 1981). See Table 11.2 for correlations of each compound class.

From Schwartzenbach & Gschwend