Water-Quality Principles
QW1022–TEL

Lesson 8—Environmental Organic Chemistry

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

Octanol/Water Partition Coefficient

In the study of the environmental fate of organic compounds, the **octanol/water partition coefficient (K_{ow})** has become a key parameter. It has been shown to correlate with water solubility, soil/sediment **sorption coefficient**, and bioconcentration. Of these three properties that can be estimated from the K_{ow}, water solubility is the most important because it affects both the fate and transport of chemicals. Highly soluble compounds are quickly distributed by the hydrologic cycle, have low sorption coefficients for soils and sediments, and tend to be more easily degraded by microorganisms. In addition, chemical reactions, such as hydrolysis and photolysis, tend to occur more readily if a compound is soluble.

The solvent 1-octanol is an amphiphilic solvent and has both hydrophobic and hydrophilic natures. Figure 14.4 shows that the amphiphilic nature of octanol gives it a solvating capability that is similar to that of humic acid or other naturally occurring colloids that have the ability to associate with both polar and nonpolar compounds. The K_{ow} provides a convenient experimental test that will predict whether an organic compound will dissolve in water or be absorbed by organic material contacting the natural water.

As organic molecules increase in size, they decrease in polarity and water solubility; they are becoming more hydrophobic, which can be measured by the octanol/water partition coefficient. K_{ow} is defined as the ratio of the molar concentrations of a chemical in n-octanol and water, in dilute solution.

$$K_{ow} = C_{octanol}/C_{water}$$

The K_{ow} is determined by measuring the concentration of a particular compound in the water and the octanol phases after a period of mixing. The K_{ow} is constant for a given compound at a certain temperature. Because the K_{ow} is a ratio of two molar concentrations, it has no units. K_{ow} values can be in the millions for important environmental contaminants (PCBs, chlorinated pesticides, dioxins, and furans); they are usually reported as the base 10 logarithm, log K_{ow}. The K_{ow} expresses a tendency of an organic contaminant to move from the water phase to the immiscible 1-octanol phase. Octanol, a long-chain alcohol, mimics fat (lipids), and the K_{ow} is an indication of the tendency of an organic contaminate to bioaccumulate.

The K_{ow} has two characteristics that make it especially useful in environmental assessments. First, it varies in predictable ways within classes of organic compounds. For example, Figures 14.5 and 14.6 show that if K_{ow} is known for one member of a class of compounds, it can be used to estimate a value for other members of the same family. In these figures, the K_{ow} can be correlated to the number of chlorine atoms in a compound or the number of aromatic rings in polynuclear aromatic compounds (polyaromatic hydrocarbons [PAHs]). The log K_{ow} of some nonpolar organic molecules is listed in Table 14.3.

The second characteristic is that the K_{ow} can be correlated with the sorption of organic compounds on soil. By using the K_{ow}, it is possible to estimate the potential sorption of organic contaminants based on the structure of the compounds and the organic carbon content of the soil.

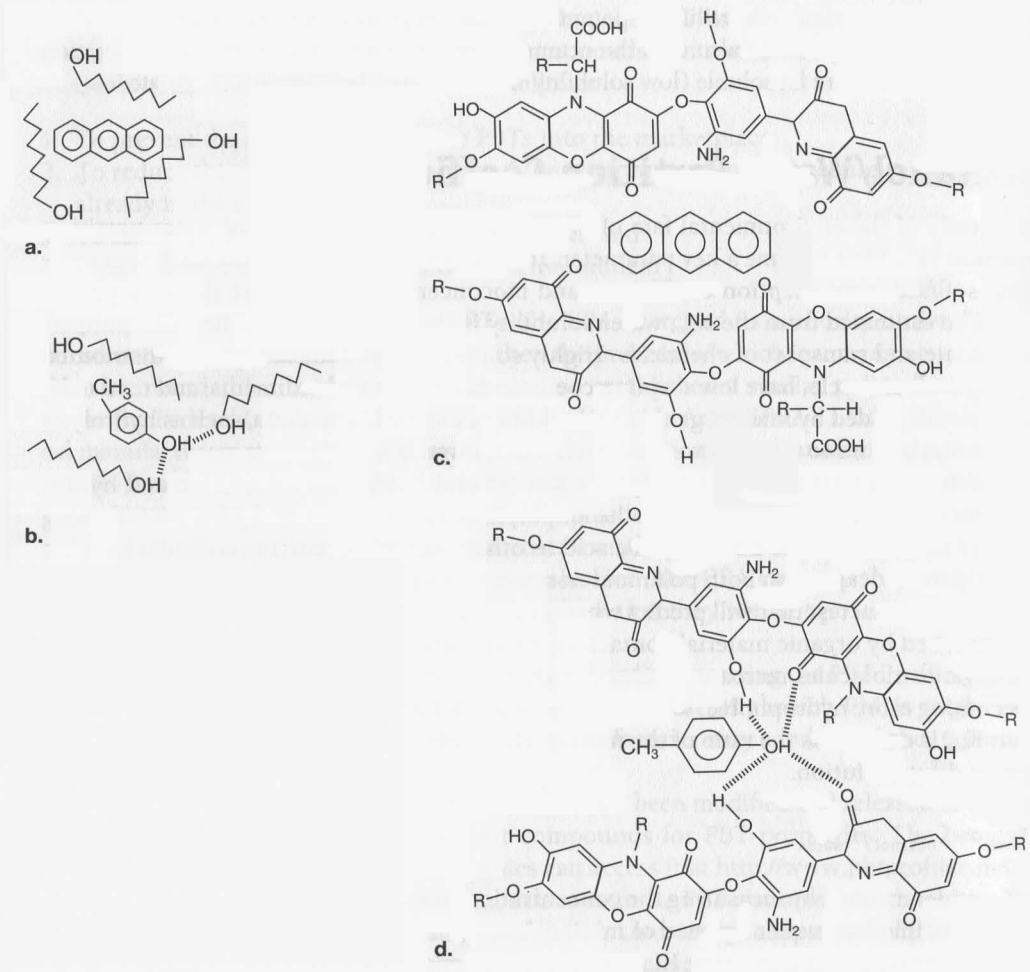

Figure 14.4 The solvent *n*-octanol is used to mimic the behavior of humic substances. Octanol solubilizes nonpolar (a) (naphthalene) and polar (b) (phenol) solutes in different ways. Humic materials (c and d) interact with the same solutes. Hydrophobic portions of the octanol and humic material associate with hydrophobic organic solutes (naphthalene). Hydrogen bonding dominates their interaction with polar groups of the hydrophilic solutes (phenol).

Sorption on Soils

Generally speaking, nonpolar organic molecules are sorbed by soils as a function of their **hydrophobicity** (K_{ow}) and the organic content of the soil. The sorption coefficient (K_p) is defined as follows:

$$K_p = \frac{\text{concentration solid phase}}{\text{concentration solution}} = \frac{\text{mg/kg}}{\text{mg/L}} = \frac{\text{L}}{\text{kg}}$$

Experimental studies using flow-through techniques produce K_p values that are sensitive to the flow rate and suggest that increased sorption occurs with longer exposure times. The sorption is also dependent on the amount of organic carbon in the soil aquifer.

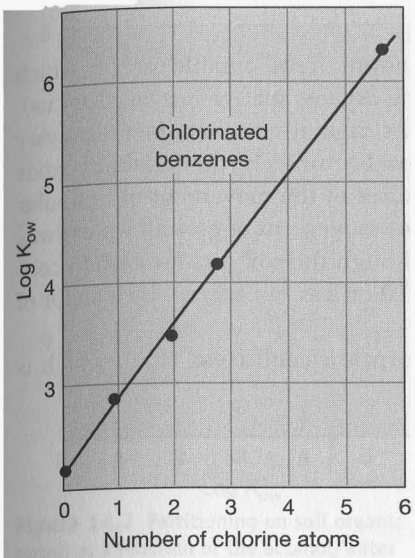

Figure 14.5 Relationship of number of chlorine atoms in a compound and log K_{ow}.

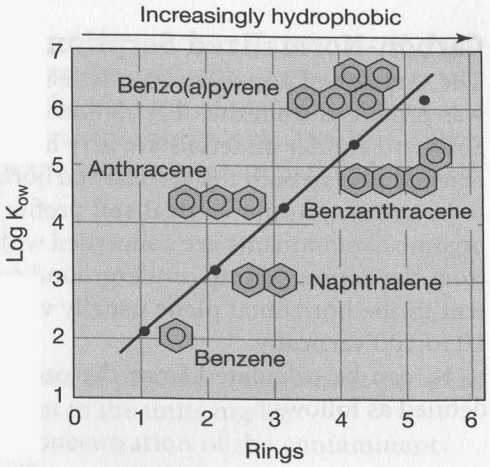

Figure 14.6 Relationship of number of aromatic rings in a compound and log K_{ow}. Adapted from M. D. Piwoni and J. W. Keeley, *Basic Concepts of Contaminant Sorption at Hazardous Waste Sites*. EPA Ground Water Issue 6, EPA/540/4-90/053, October 1990.

Table 14.3

Log K_{ow} of Some Nonpolar Organic Molecules

Compound	Log K_{ow}
aldrin	6.5
DDT	6.2
hexachlorobenzene	5.6
chlordane	5.5
heptachlor	5.3
toxaphene	4.8
fluoranthene	4.7
Endrin	4.6
phenanthrene	4.5
Dieldrin	4.3
1,2,4-trichlorobenzene	4.2
dibutyl phthalate	4.1
dibenzyl	4.0
1,4-dichlorobenzene	3.6
ortho-dichlorobenzene	3.7
chlorobenzene	2.8
toluene	2.7
benzene	2.1
phenol	1.5

Carbon-Normalized Sorption Coefficient

The sorption of nonpolar organics also depends on the amount of soil organic carbon, which was produced from the degradation of naturally occurring organic matter (leaves, detritus). Soils and aquifer materials are very heterogeneous, and the organic carbon content can vary considerably in both the vertical and horizontal dimensions. Fortunately, the variability tends to be greatest in the vertical soil profile. Most of the studies of the movement of nonpolar organic contaminants are concerned with the contaminant movement in ground water away from the source (dump, underground storage tank). Although the soil organic carbon content in the horizontal plane usually varies by a factor of 10 or less, it can vary by a factor of 10 to 100 vertically.

K_p can be calculated from the **carbon-normalized sorption coefficient** (K_{oc}), which is defined as follows:

$$K_{oc} = \frac{\text{sorption coefficient, } K_p}{\text{fraction organic carbon, } f_{oc}}$$

To determine the soil organic carbon content at a site, samples are taken back to the laboratory, where they are first acidified to dissolve and remove the inorganic carbon (carbonates). Weighed samples of the soil are then burned in an oxygen atmosphere, and the CO_2 that is produced is quantitatively measured by infrared spectroscopy. If, for instance, the soil organic content is 0.2% for a specific sample, then the f_{oc} is 0.002.

The octanol/water partition and soil/water partition experiments are very similar, with soil replacing octanol in the test. As a result, there have been several empirical relationships developed for estimating sorption using K_{ow} and the organic carbon content of the soil. One of these is commonly used for estimating the sorption of common environmental contaminants in an aquifer with low carbon content.

$$\log K_{oc} = 0.69 \log K_{ow} + 0.22$$

Usually empirical relationships such as this require the selection of reference organic compounds in which structure is similar to those of interest. Figure 14.7 shows that there is a linear relationship between log K_{ow} and log K_{oc} for a series of chlorinated benzenes. Even when a structurally dissimilar compound, such as anthracene, which contains no chlorines and is a PAH, is compared with the chlorinated benzenes, its K_{oc} can be estimated with reasonable accuracy.

Experimentally Measuring Absorption

To obtain the best information on which to base an estimate of sorption, tests should be made with the contaminates of concern using soil and aquifer material from the site of interest. The goal is to experimentally measure the partition coefficient (K_p) for use in the prediction of contaminant movement.

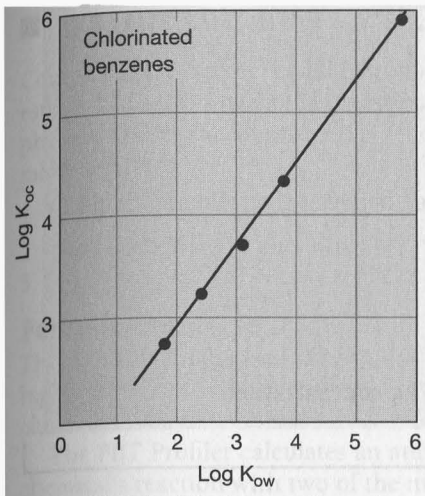

Figure 14.7 Partitioning on soil organic carbon as a function of the octanol/water coefficient.

The standard approach to determine K_p is to generate a sorption isotherm, a graphical representation of the amount of material sorbed at a variety of solute concentrations. The Freundlich isotherm is the most common relationship used:

$$S = K_p C$$

Where

S is the mass of organic contaminant per mass of sorbent in the units mg/kg.
C is the concentration of the contaminant in mg/L.

EXAMPLE 14.1

An industrial landfill is contaminated with 1,4-dichlorobenzene. Preliminary tests indicate that most of the contamination is below the water table. The contaminant concentration in ground water averages 1 mg/L. The measured soil organic carbon is 0.2%, and pore water occupies 50% of the aquifer volume. Estimate the K_{oc} and the K_p and S.

Solution

From Table 14.3, we find that the K_{ow} for 1,4-dichlorobenzene is 3.6.

Using this equation

$$\log K_{oc} = 0.69 \log K_{ow} + 0.22$$

Therefore:

$$\log K_{oc} = 0.69(3.6) + 0.22$$

$$\log K_{oc} = 2.70$$

$$K_{oc} = 506$$

Since

$$K_p = K_{oc}(f_{oc})$$

$$K_p = 506(0.002) = 1.01$$

Thus, the 1,4-dichlorobenzene is equally distributed between the solid and liquid phases.

$$S = K_pC$$

$$S = 1.01(1.0) = 1.01\ \text{mg/kg}$$

Thus, we would expect the solid to have a 1.0-mg/kg concentration.

Henry's Law

If the contaminant is a gas, one of the physical properties that the PBT Profiler uses is its solubility in water. The solubility of a gas in water is described by Henry's law, which states that at constant temperature the solubility of a gas in a liquid is proportional to the partial pressure of the gas that is in contact with the liquid. The **Henry's law constant (K_H)** is really the air/water partition coefficient. The EPA expresses K_H in two ways; the first is a nondimensional value that relates the chemical concentration in the atmosphere (gas phase) to its concentration in the water phase. The K_H also can be determined by dividing the vapor pressure of a chemical (in atmospheres) by its solubility in water (in mol/m^3) to give K_H in atm-m^3/mol.

The PBT Profiler uses K_H to predict the fate of a chemical once it is released into surface water. A large K_H (of more than 10^{-3}) indicates that the chemical is likely to evaporate from the water and partition into air. A low K_H (10^{-5} to 10^{-7}) indicates that the chemical is not likely to volatize and will remain in surface water. Table 14.4 lists the K_Hs for several chemical contaminants of interest. K_H provides an indication of the partition between air and water at equilibrium and is also used to calculate the rate of evaporation from water.

Table 14.4

Henry Law Constants (K_H)

CAS Number	Chemical	K_H (atm-m^3/mole)
75092	Dichloromethane	3.0×10^{-3}
50000	Formaldehyde	6.1×10^{-5}
67641	Acetone	4.0×10^{-5}
67561	Methanol	4.4×10^{-6}
60571	Dieldrin	5.4×10^{-7}