

SORPTION & DISTRIBUTION

In the environment, organic contaminants accumulate in other organic phases such as natural organic matter (plant residues, lipids, chars, etc.) in soils and sediments. The accumulation may be linear (i.e., independent on concentration) or concentration-dependent (usually decreases relatively with increasing concentration). The former indicates a partitioning process (or absorption), and the latter indicates a limited number of sorption sites (adsorption). The scope of this chapter is to describe the partitioning processes and the distribution of solutes over different phases (e.g., water, soil, air). Nonlinear sorption and models describing these processes are discussed in the next chapter.

1. SORPTION PHENOMENA

1.1 PARTITIONING VS. DISTRIBUTION

In nature, two sorption phenomena are common: **adsorption** and **absorption**. **Adsorption** describes a process in which the solute accumulates at a surface or interface (e.g., solid/liquid; solid/gas; liquid/gas). In contrast, **absorption** describes a process in which the solute penetrates the sorbent - similar to dissolution in a solvent. Due to the heterogeneous nature of soils and sediments, both processes may take place simultaneously. Since they cannot be separated from each other experimentally, the term sorption here encompasses both adsorptive and absorptive processes. Besides, uptake in micropores or capillary condensation is also a type of sorption. The sorbent refers to the soil or sediment solids. Whereas the term sorbate refers to the solute sorbed onto the solids, respectively (in German, a third term "Sorptive" refers to the free - not yet sorbed - solute in solution).

Sorption of organic chemicals in soils and sediments may result from various attractive forces between sorbate and sorbent or solute and solvent. In general, chemical, physical and electrostatic interactions may contribute to the sorption of organic pollutants in soils and sediments. "Chemical" interactions, for example, include covalent and hydrogen bonds. Electrostatic forces are involved in ion-ion and ion-dipole interactions (e.g., ion exchange). Sorption of nonionic organic contaminants mainly involves relatively weak physical forces. These physical attractions ("Van der Waals-London forces") between sorbate and sorbent include dipole-dipole, dipole-induced dipole, and instantaneous dipole-induced dipole interactions (due to quantum fluctuations, even neutral molecules can attract each other).

The relatively weak bonding forces associated with physical sorption are also involved in the so-called "hydrophobic effect" which essentially contributes to the sorption of nonionic organic molecules from an aqueous solution. Hydrophobic sorption is mostly considered an entropy-driven interaction. If an organic molecule dissolves in water, it is surrounded by a clathrate cage of water molecules. This results in an increase in the structuring of the water molecules ("iceberg effect": Frank and Evans, 1945) and a decrease of the system entropy. Sorption of solute becomes thermodynamically more favorable because it results in an increase of entropy (less structured water). Therefore, sorption in aqueous systems depends strongly on the water solubility of an organic compound.

The process of adsorption/desorption at a sorption site is reasonably fast, as Pignatello (1989) concluded from the interactive energies involved in the sorption/desorption process of organic compounds in soils. He stated that "with few exceptions, the microscale sorption and desorption steps of organic contaminants in soils and sediments should be instantaneous on a practical time scale". Very slow sorption/desorption dynamics are observed if the transport to and from the sorption site is limited by slow aqueous diffusion over a certain distance (e.g., diffusion into an aggregate or porous particle).

The sorptive uptake of a solute by soils or sediment solids from aqueous solution or vapor phase is commonly described by sorption isotherms, which relate the aqueous to the sorbed concentration at a constant temperature. In the most simple case, the sorbed concentration in the solid (C_s) (e.g., in mg kg^{-1}) is directly proportional to the equilibrium solute concentration in aqueous (C_w) (e.g., in mg l^{-1}) or vapor phase (C_g). Here C_{eq} is used to represent both C_w and C_g :

$$C_{s,eq} = K_d C_{eq} \quad (1.1)$$

The distribution coefficient K_d (e.g., L kg^{-1}) is the ratio between the solute concentrations in water and solids. K_d represents the slope of a sorption isotherm at a given concentration, and if sorption is linear, like in partitioning, K_d is often called partition coefficient (K_p). If sorption isotherms are nonlinear, K_d is also used, but K_d values may depend on the solute concentration (C_s and C_{eq}) (Chiou and Kile, 1998; Grathwohl, 1990; Kleineidam et al., 2002).

1.2 THE K_{oc} -CONCEPT: PARTITIONING INTO NATURAL ORGANIC MATTER

Sorption of hydrophobic organic compounds in soils and sediments can be attributed to the soil organic matter content (Lambert et al., 1965; Briggs, 1981; Brown and Flagg, 1981; Karickhoff et al., 1979; Karickhoff, 1984; Grathwohl, 1990; Allen-King et al., 2002) in many cases. According to Chiou et al. (1979; 1983), uptake of these compounds by natural organic matter (om) may be interpreted as the partitioning of the solute between the organic and the aqueous phases, comparable to the dissolution of the compound in a suitable solvent (e.g., octanol). Sorption may then be quantified by a simple partition coefficient K_{om} , which is denoted by the ratio between the concentration of a compound in organic matter and water ($K_{om} = C_{om}/C_w$ [l kg^{-1}])

The concept of partitioning in natural organic matter predicts a linear relationship between the solute concentration in the organic phase and that in the aqueous phase over a wide range of solute concentrations relative to the water solubility of the solute. Hydrophobic sorption is analogous to solute uptake in organic solvents, which is described by "linear free energy relationships (LFER)" (Hansch et al., 1968; Leo et al., 1971) (e.g., empirical relationships between uptake in organic matter and octanol). In practice, K_{om} is seldomly used. Instead, organic carbon normalized coefficients (K_{oc}) are preferred, since the amount of organic carbon (oc) can be easily measured, commonly by high temperature ($> 900^\circ\text{C}$) combustion of a sample under pure oxygen and subsequent quantification of the generated CO_2 by infrared spectroscopy (the classical conversion factor is $\text{oc} = 0.58 \text{ om}$). K_{oc} then is:

$$K_{oc} = \frac{C_s}{f_{oc} C_w} = \frac{K_d}{f_{oc}} \approx \frac{K_d}{f_{om} 0.58} \approx \frac{K_{om}}{0.58} \quad (1.2)$$

f_{oc} denotes the fraction of organic carbon [M M⁻¹] (e.g., in g g⁻¹), and K_{oc} (like K_d) comes in units of [L³ M⁻¹, e.g., L kg⁻¹, ml g⁻¹, etc...]. Organic carbon normalized partition coefficients (K_{oc}) can be simply derived based on Raoult's law:

$$K_{oc} [\text{l kg}^{-1}] = \frac{C_{oc}}{C_w} \approx \frac{C_{oc}}{\chi_{om} \gamma_{om} S} = \frac{1}{\frac{M_{om}}{M_i} \gamma_{om} S [\text{kg l}^{-1}]} \quad (1.3)$$

Activity coefficients and molecular weights of organic matter are mostly unknown and typically empirical relationships are used to estimate K_{oc} ; typically they have the form:

$$K_{oc} = \frac{b}{S^a} \quad (1.4)$$

a and b are empirical exponents [-]. b accounts for molar volume ratios and activity coefficients while a ideally is one or less and then accounts for the dependency of the activity coefficient on compound properties. Since K_{oc} and S of organic compounds cover orders of magnitude, log-log relationships are commonly used:

$$\log K_{oc} = -a \log S + \log b \quad (1.5)$$

Fig 1.1. shows a comparison of various empirical relationships from the literature which are listed in Tab. 1.1. Although they are all different, a reasonable overlap is observed in Fig. 1.1 where K_{oc} is plotted vs. S in mol l⁻¹. Since K_{ow} is also inversely related to S , K_{oc} also increases with K_{ow} and many empirical relationships are based on the latter (Fig. 1.1). As listed in Table 1.1, a is usually close to 1 but often smaller indicating higher activity coefficients for compounds with lower solubility (or high K_{ow}). Fig. 1.2 shows a slightly better relationship by plotting K_{oc} vs. S in kg l⁻¹. From eq. 1.3, it is expected that K_{oc} increases with an increasing molar mass of the compound (M_i) which apparently compensates increasing activity coefficients to some extent and leads to more linear relationships in Fig. 1.2. If K_{oc} is linearly inverse to S , the product of both (K_{oc}^*) is a constant and this is also observed to some extent in Fig. 1.2. In the most ideal case (everything in the denominator in eq. 1.3 is 1 but S), the product of partition coefficient and water solubility is one (i.e. K is the inverse of S). In Fig. 1.2, however, much lower values than 1 are obtained (approx. 0.06 kg kg⁻¹). This indicates that soil organic matter is, by far, not an "ideal" partitioning phase. K_{oc} in natural organic matter is typically also lower than partitioning into organic liquids (such as octanol) (see Fig. 1.1, Schwarzenbach et al., 1993, p. 275).

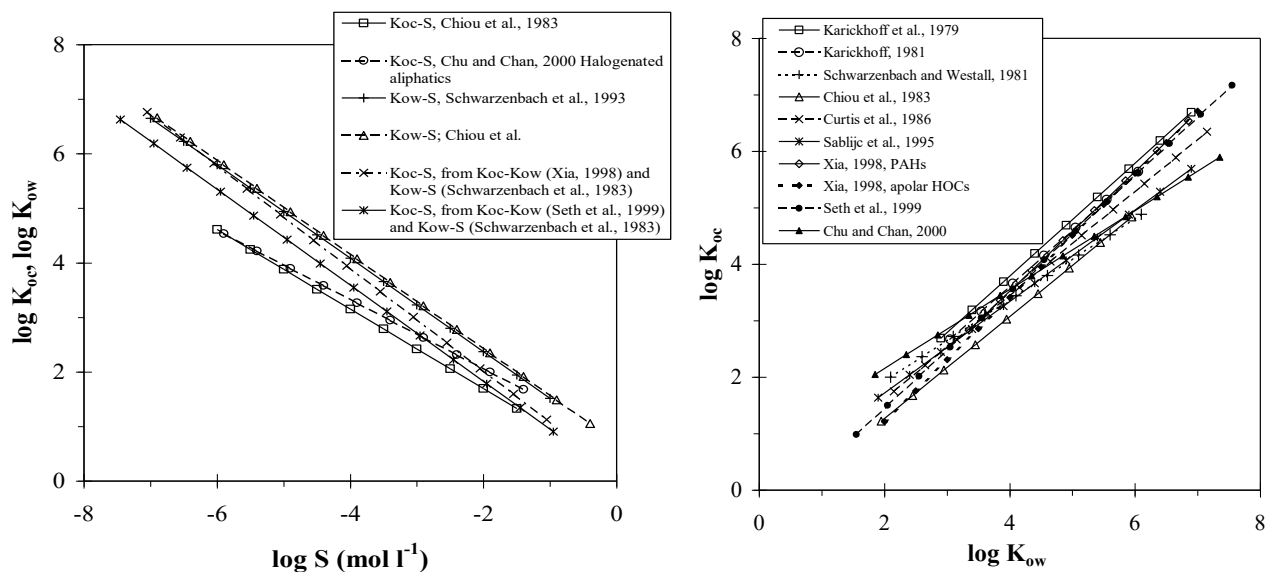


Fig. 1.1: $\log K_{oc}$ (and $\log K_{ow}$) of various organic compounds vs. their water solubility (S); since K_{ow} is inverse related to S , K_{oc} increases with increasing K_{ow} (right). From Allen-King et al., 2002 (for refs. see the original paper).

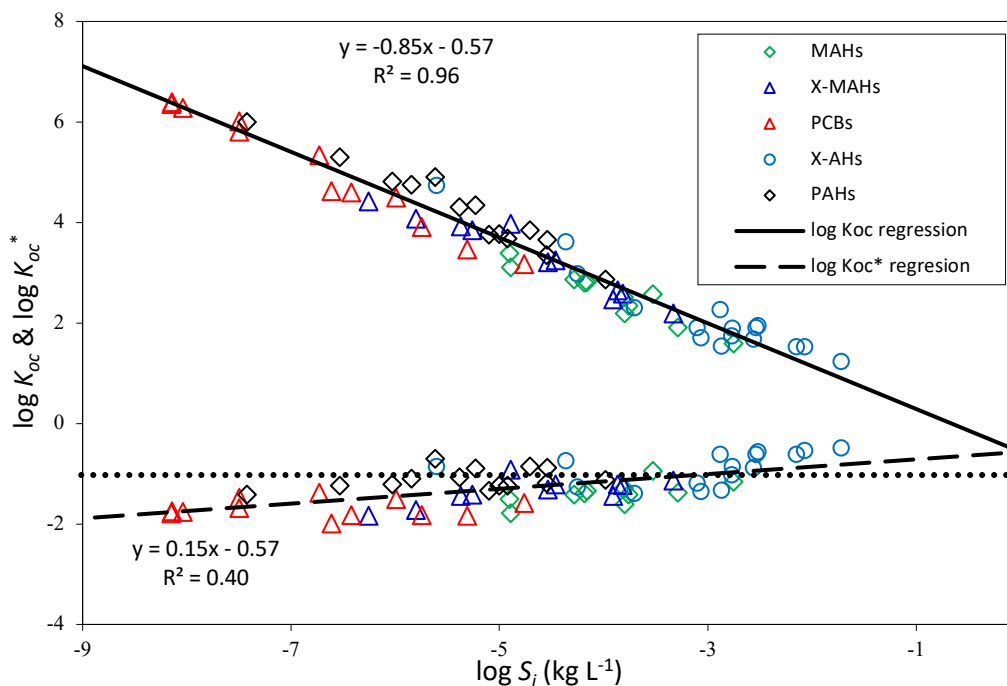


Fig. 1.2: $\log K_{oc}$ and $\log K_{oc}^*$ ($= K_{oc} S$) of various organic compounds vs. their water solubilities (S) in kg l^{-1} ; linear regression: $\log K_{oc} = -0.85 \log S_i - 0.57$ ($n = 64$, $R^2 = 0.95$, $\Delta|_{\text{avg}} = 0.25$), from Razzaque and Grathwohl (2008). The average K_{oc}^* here is 60 g kg^{-1} (dotted horizontal line), 57 g kg^{-1} for phenanthrene and 73 g kg^{-1} for TCE.

Table 1.1: Parameters a and b for correlations shown in Figure 2 (from Allen-King et al., 2002).

a	b	r^2	n	Compound Class	Solids description	Reference
$\log K_{oc} = a \log K_{ow} - b (K_{oc} [l \text{ kg}^{-1}]; K_{ow} [l \text{ l}^{-1}])$						
1.00	0.21	1	10	B, 7 PAHs, 1 PCB, methoxychlor	aquatic sediments	*Karickhoff <i>et al.</i> , 1979
0.97	0.12	0.934	106	B, PAHs	aquatic sediments	† Xia, 1998
0.97	0.50	0.918	67	B, SBs, CBs, PCBs	aquatic sediments	† Xia, 1998
1.06	0.72	0.962	37	PAHs	high f_{oc} soils	† Xia, 1998
0.904	0.543	0.989	12	B, SBs, CBs, PCBs	one soil; $f_{oc} = 0.019$	Chiou <i>et al.</i> , 1983
0.85	0.22	0.820	105	B, SBs, CBs, PCBs	high f_{oc} soils	† Xia, 1998
0.989	0.346	0.997	85	PAHs)	sediments and soils	Karickhoff, 1981
0.72	- 0.49	0.95	72	SBs, CBs	sediments and soils	Schwarzenbach and Westall, 1981
0.92	0.23	0.940	40	PAHs, SBs, CBs	sediments and soils	Curtis <i>et al.</i> , 1986
0.81	- 0.10	0.887	81	apolar HOCs	sediments and soils	Sabljić <i>et al.</i> , 1995
0.699	- 0.755	0.692	148	various HOCs	sediments and soils	Chu and Chan, 2000
1.03	0.61	0.98	117	apolar HOCs	sediments and soils	Seth <i>et al.</i> , 1999
1.10	0.99	0.948	418	apolar HOCs	sediments, high f_{oc} soils	† Xia, 1998
$\log K_{oc} = - a \log S + b (K_{oc} [l \text{ kg}^{-1}]; S [\text{mol l}^{-1}])$						
0.634	0.794	0.865	30	Halogenated aliphatics	sediments and soils	Chu and Chan, 2000
0.639	0.669	0.856	19	PAHs	sediments and soils	□ Chu and Chan, 2000
0.532	1.056	0.692	148	various HOCs	sediments and soils	□ Chu and Chan, 2000
0.557	0.698	0.988	15	PCBs, halogenated alkanes, DDT, Lindane	sediments and soils	*□ Chiou <i>et al.</i> , 1979
0.729	0.001	0.996	12	B, SBs, CBs, PCBs	soils only	* Chiou <i>et al.</i> , 1983
0.88	0.07		117	apolar HOCs	sediments and soils	§ Seth <i>et al.</i> , 1999, Schwarzenbach <i>et al.</i> , 1993
0.94	0.14		418	apolar HOCs	sediments, high f_{oc} soils	§† Xia, 1998, Schwarzenbach <i>et al.</i> , 1993
$\log K_{ow} = - a \log S + b (K_{ow} [l \text{ l}^{-1}]; S [\text{mol l}^{-1}])$						
0.856	0.66	0.96	124	various HOCs		Schwarzenbach <i>et al.</i> , 1993
0.862	0.710	0.994	36	BTEX, CBs, PCB, PAH		Chiou <i>et al.</i> , 1982

* Note, that for these studies, the values for a and b were determined for K_{om} . Conversion to C-normalized values is achieved here using $K_{oc} = 1.72 K_{om}$.

† Xia (1998) provided separate regressions based on critical review of literature data with different chemical classes for both (a) aquatic sediments and (b) “non-clay subsurface solids“ with $f_{oc} > 0.0025$.

□ These regressions include some solid, rather than sub-cooled liquid, aqueous solubilities and so are not included

§ These regressions are linear combinations of the cited $\log K_{oc}$ - $\log K_{ow}$ and $\log K_{ow}$ - $\log S$ regressions. These are based upon the sources which provide $\log K_{oc}$ - $\log K_{ow}$ determined from critically-reviewed literature data sets encompassing data for a variety of HOCs and including both sediments and soils.

Compound or compound class abbreviations are: B, benzene; TEX, other monoaromatic hydrocarbons (toluene, ethyl benzene, xylenes); CB(s), mono or poly-chlorobenzene(s); PAHs, polynuclear aromatic hydrocarbons; PCBs, polychlorinated biphenyls; SBs substituted benzenes.

1.3 RATIOS OF PARTITIONING COEFFICIENTS

In the environment, hydrophobic pollutants commonly get distributed between different "phases", which besides water and air include soil and sediment organic matter, plant residues, lipids of organisms. Since there is always a mixture of organic materials in contaminated soils, hydrophobic pollutants will redistribute among the various phases. In ecotoxicology, the ratios of pollutant concentration in lipid and soil organic matter are of concern; based on Raoult's law this may be expressed as:

$$\frac{K_{lipid/w}}{K_{om}} = \frac{\gamma_{i,om} V_{m,om} S_i}{\gamma_{i,lipid} V_{m,lipid} S_i} = \frac{\gamma_{i,om} M_{om} \rho_{lipid}}{\gamma_{i,lipid} M_{lipid} \rho_{om}} \quad (1.6)$$

If we assume that activity coefficients in organic matter and lipids are similar, same for the densities, then eq. 1.6 reduces and can be approximated as the ratio of the molecular weights. Since M_{om} is likely bigger than M_{lipid} , K_{lipid} is larger than K_{om} as often observed. This pattern is also apparent from K_{ow} , which is typically larger than K_{oc} .

2. DISTRIBUTION IN MULTIPHASE SYSTEMS

Once introduced into the environment, organic chemicals will distribute among different compartments (or phases), e.g. water (in soils and sediments the pore water), solids (soils, sediments, atmospheric particles) and gas (atmospheric air, soil gas) and many others such as organic matter or nonaqueous phase liquids if present. Here, we look into the frequent case of distribution of a compound in the unsaturated soil zone (water, gas and solids), which is a 3-phase system (Fig. 2.1).

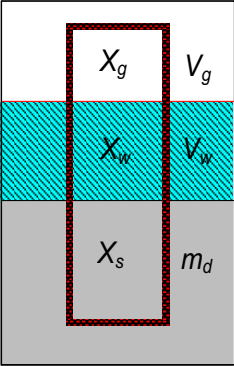
	Mass in compartment	Capacity of each compartment	%
	$C_g (n - \theta)$	$(n - \theta)$	$100 (n - \theta) / \alpha$
	$C_w (w \rho_b) = (\theta) C_g / H$	θ / H	$100 (\theta / H) / \alpha$
	$C_s \rho_b = (K_d \rho_b) C_g / H$	$(K_d \rho_b) / H$	$100 (K_d \rho_b / H) / \alpha$
	Sum: $C_g [(n - \theta) + \theta / H + K_d \rho_b / H]$	Capacity factor, α : $[(n - \theta) + \theta / H + K_d \rho_b / H]$	Total conc. per unit volume of soil: $C_g \alpha$ [e.g. mg m ⁻³]

Fig. 2.1: Distribution of a compound (red rectangle) in the 3-phase system: gas – water – solids. n , θ , and ρ_b denote porosity [-], volumetric water content [-] and bulk density of the porous media [g ml⁻¹, kg l⁻¹], respectively. Note, the volumetric water content θ at water saturation equals n (θ is calculated from the gravimetric water content w (mass of water/mass of dry solids) times ρ_b/ρ_w (density of water $\cong 1$)); the bulk density is $(1 - n)$ times the density of the solids (for quartz = 2.65 g cm⁻³; calcite = 2.71 g cm⁻³). Distribution of a compound between different phases is crucial in all transient transport

processes. The “capacity factor” as shown in Fig. 2.1 represents a storage term which appears in diffusive and advective transport equations. For example, for contaminant spreading by diffusion second Fick’s law applies:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2.1)$$

D is the diffusion coefficient, C , x and t denote concentration, distance and time. For gas diffusion in a porous media the pore diffusion coefficient (D_p) has to be applied and we need to account for the storage terms in water, solids and air:

$$(n - \theta) \frac{\partial C_g}{\partial t} + \theta \frac{\partial C_w}{\partial t} + \rho_b \frac{\partial C_s}{\partial t} = D_p (n - \theta) \frac{\partial^2 C_g}{\partial x^2} \quad (2.2)$$

$n - \theta$ represents the gas-filled pore space (pore volume minus the water volume), θ is the volumetric water content and ρ_b the dry solid mass per unit volume (= bulk density). Applying the distribution coefficients ($C_w = C_g / H$ and $C_s = K_d C_w = K_d C_g / H$) leads to:

$$\begin{aligned} \frac{\partial C_g}{\partial t} \left[(n - \theta) + \frac{\theta}{H} + \frac{\rho_b K_d}{H} \right] &= D_p (n - \theta) \frac{\partial^2 C_g}{\partial x^2} \\ \frac{\partial C_g}{\partial t} &= D_p \frac{(n - \theta)}{[(n - \theta) + \theta/H + \rho_b K_d/H]} \frac{\partial^2 C_g}{\partial x^2} = \frac{D_p}{R} \frac{\partial^2 C_g}{\partial x^2} \end{aligned} \quad (2.3)$$

R is the retardation factor [-], which is just the ratio between the capacity factor [here: $(n - \theta) + \theta/H + \rho_b K_d/H$] and the solute fraction in the mobile phase ($n - \theta$):

$$R = \frac{(n - \theta) + \theta/H + \rho_b K_d/H}{n - \theta} \quad (2.4)$$

This is a universal concept which also applies to advective transport in many other scenarios. Thus, understanding of the distribution of a compound between different phases is absolutely crucial for any transport calculations. In groundwater (only two phases: solids and water) this reduces to:

$$R = \frac{n + K_d \rho_b}{n} = 1 + K_d \frac{\rho_b}{n} \quad (2.5)$$

The retardation factor is also important for remedial actions as it denotes the number of pore volume of the mobile phase (e.g., groundwater or soil air) which has to be displaced in order to remove the contaminant from the system.

3. LITERATURE

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