

# Chapter 13

## SORPTION FROM WATER TO NATURAL ORGANIC MATTER (NOM)

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In Part II, we learned that the majority of nonionic organic pollutants tend to favorably partition from water into organic phases. The driving force of this partitioning is the tendency of the compound to leave the aqueous phase (its “hydrophobicity”), that is, the free energy gain associated with removing a compound from aqueous solution. Therefore, it makes sense that organic materials “dissolved” in water (i.e., truly dissolved or in colloidal form) or associated with solids (e.g., particles in the water column as well as constituents of sediments, soils, and aquifer materials) are often the dominating sorbents for organic chemicals dissolved in natural waters.

In this chapter, we discuss quantitative approaches for describing sorption equilibrium between such organic materials and water, with an emphasis on what is referred to as “natural organic matter” (NOM), which refers to all organic materials of natural origin. We also address the role of carbon-rich, combustion-derived materials from natural (e.g., forest fire chars) or anthropogenic (e.g., diesel soots) origins. These “black” carbon materials are important additional organic adsorbents, particularly for compounds such as PAHs and planar PCBs.

## 13.1 The Structural Diversity of Natural Organic Matter Present in Aquatic and Terrestrial Environments

### The Complex Nature of Natural Organic Matter (NOM)

*The Operational Size Fractions of NOM.* In a given environmental system, the NOM present is commonly operationally divided into a fraction that passes through a filter having a pore size near 1 μm (see also Chapter 5, Box 5.3), referred to as “dissolved” organic matter (DOM), and a “particulate” fraction (POM), sometimes also referred to as soil and sediment organic matter (SOM), which is withheld by the filter. DOM often represents a more diverse set of constituents than POM, as DOM encompasses small molecules (< 200 Da), aggregates of small and larger molecules, micelles, and colloids. Thus, the commonly studied NOM components of fulvic and humic acids (see Table 13.1) are considered part of DOM. Some of these “dissolved” organic water constituents may act as sorbents, while others are simply co-solutes or are too small to significantly sorb pollutants. For example, Remucal et al. (2012) showed that a significant fraction (36%) of Suwanee River fulvic acid (SRFA), which is frequently used as model DOM, is made up of constituents that pass a 100–500 molecular weight cutoff dialysis membrane.

The common analytical methods for determining the total organic carbon (TOC) present in a sample involve combusting (oxidizing) the sample and measuring the evolved CO<sub>2</sub>; the abundance of DOM in aqueous solution is usually expressed by the aqueous concentration of reduced carbon [DOC]:

$$[\text{DOC}] = \frac{\text{mass of organic carbon (e.g., kg oc)}}{\text{total volume (e.g., L)}} \quad (13-1)$$

**Table 13.1** Properties of Organic Components that May Act as Sorbents of Organic Compounds in the Environment<sup>a</sup>

Component	Mole Ratio				
	C	H	N	O	% Aromaticity
<i>Biogenic Molecules</i>					
Proteins	1.0	1.6	0.4	0.2	< 10
Collagen (protein)	1.0	1.7	0.19	0.31	< 10
Cellulose (polysaccharide)	1.0	1.7	< 0.01	0.84	< 10
Chitin (polysaccharide)	1.0	1.8	0.13	0.64	< 10
Lignin (alkaline extract)	1.0	1.1	< 0.01	0.40	28
Lignin (org. solvent extract)	1.0	0.98	< 0.01	0.33	34
<i>Diagenetic Materials</i>					
Fulvic acids					
soil leachate	1.0	1.04	< 0.1	0.53	36
brown lake water	1.0	0.88	< 0.1	0.55	35
river water	1.0	1.62	< 0.1	1.09	29
groundwater	1.0	1.04	< 0.1	0.51	24
Suwannee River	1.0	1.0	< 0.1	0.62	24
Humic acids					
brown lake water	1.0	0.80	< 0.1	0.54	40
river water	1.0	1.48	< 0.1	0.91	38
“average” soil	1.0	1.15	0.07	0.50	
Aldrich (AHA)	1.0	0.90	0.02	0.40	45
Suwannee River	1.0	1.9	0.02	1.1	31
Pahokee peat	1.0	1.0	0.06	0.48	47
Humin	1.0	0.4 to 1		0.05 to 0.3	
<i>Combustion-Derived Materials</i>					
NIST diesel soot	1.0	0.1	0.016		~100
BC <sup>b</sup> from Boston Harbor sediment	1.0	1.0	0.07		

<sup>a</sup>Data from Oser (1965); Brownlow (1979); Chin et al. (1994); Xing et al. (1994); Zhou et al. (1995); Schulten and Schnitzer (1997); Arnold et al. (1998); Haitzer et al. (1999); Accardi-Dey and Gschwend (2002); Niederer et al. (2007); Bronner and Goss (2011a).

<sup>b</sup>BC = black carbon.

The abundance of POM (or SOM) is described by the weight fraction of organic carbon present in a given solid matrix,  $f_{oc}$ :

$$f_{oc} = \frac{\text{mass of organic carbon (e.g., kg oc)}}{\text{total mass of solid sorbent (e.g., kg solid)}} \quad (13-2)$$

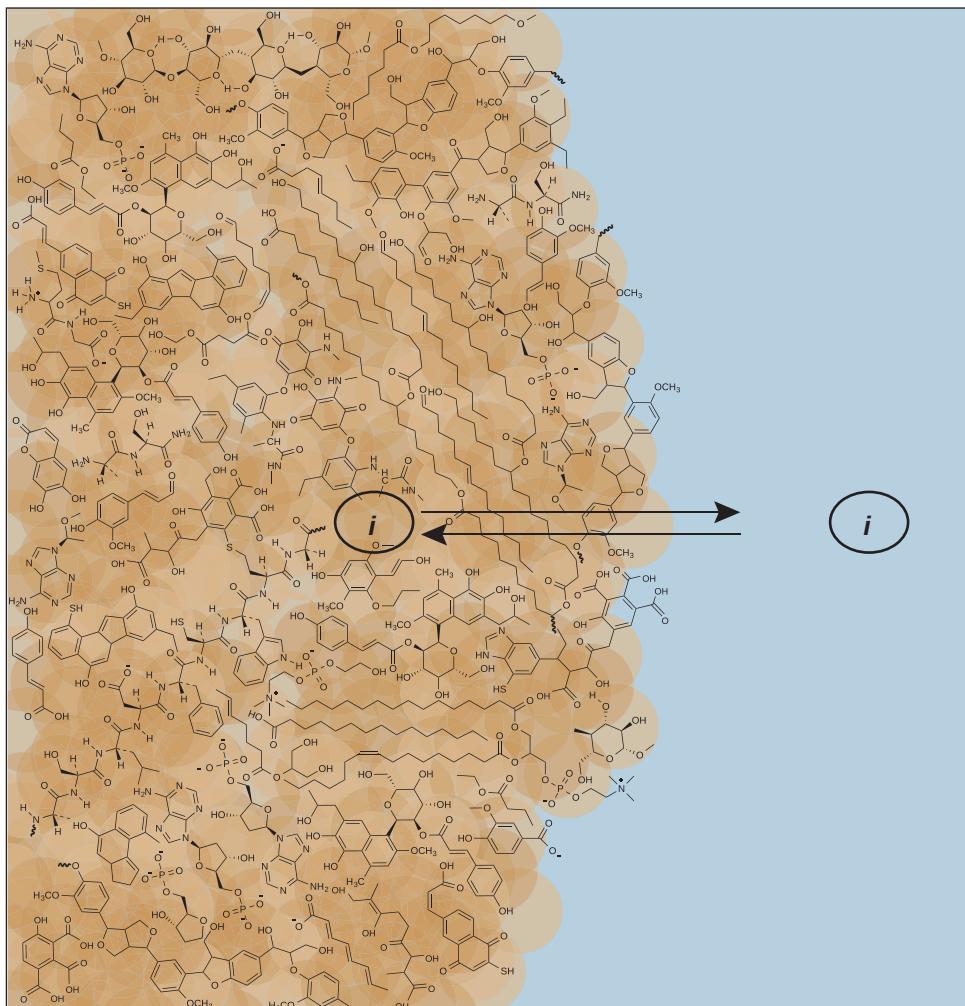
Since NOM is typically made up of about half (40 to 60%) carbon, [DOM] (e.g., kg om L<sup>-1</sup> water) equals approximately 2 [DOC], and  $f_{om}$  is approximately  $2f_{oc}$ .

This purely operationally size division of the total organic matter present in a sample into DOM and POM is often misleading from a process-oriented point of view. For example, if we consider a porous medium such as lake sediment or aquifer stratum, we may be interested in the fraction of NOM that is mobile and thus may transport sorbed organic pollutants. This mobile fraction is not necessarily represented by a DOM measurement; POM may also be mobile. Conversely, POM may not include all the organic material settling in the water column of a lake or in the ocean. Finally, when we consider the bioavailability of a compound in aqueous solution, both POM and DOM may be important sorbents, but not all of the DOM may represent a “separate phase” that can act as a sorbent.

*The Structural Composition of NOM.* In the past 10 years, the number of studies focused on determining the structural composition of NOM and its dynamics in aquatic and terrestrial environments has grown exponentially. The growth stems from increased interest in local, regional, and global carbon cycles coupled with increasingly powerful analytical tools such as modern spectroscopy (see Simpson and Simpson, 2012; Nebbioso and Piccolo, 2013; Abdulla and Hatcher, 2014; Minor et al., 2014). However, despite these enormous research efforts, only modest progress has been made in characterizing NOM from various origins, especially with respect to its properties as a sorbent for organic pollutants.

What we do know, from work conducted many years ago (e.g., Thurman, 1985; Schulten and Schnitzer, 1997; Hayes, 1998), is that NOM present in soils, sediments, groundwater, surface waters, atmospheric aerosols, and wastewater comprises recognizable biochemicals like proteins, nucleic acids, lipids, cellulose, and lignin (addressed in more detail in Chapter 16; structures in Fig. 16.2). NOM also contains a menagerie of micro- and macromolecular residues generated by *diagenesis*, i.e., the reactions of partial degradation, rearrangement, and recombination of the original molecules formed in *biogenesis* (see Table 13.1). In the past, this mixture of residues in NOM was postulated to exist in high molecular weight polymeric structures, particularly in the “persistent” fractions (e.g., Schulten and Schnitzer, 1997). The current view of the structural composition of NOM is that of a supramolecular association of a diversity of much smaller molecules (schematically depicted in Fig. 13.1, see Sutton and Sposito, 2005; Kleber and Johnson, 2010; Schmidt et al., 2011; Nebbioso and Piccolo, 2013; Drosos et al., 2014; Lehmann and Kleber, 2015).

These supramolecular associations are characteristic in both the DOM and POM fractions of NOM and can form structurally distinct sorptive phases. In solution, dissolved (macro)molecules may form organic phases relevant for sorption by aggregation facilitated by complexing cations (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ), which act as intermolecular bridges. The formation and stability of such aggregates is dependent on the concentration of the respective metal cation and on pH (Mouvenchery et al., 2012; Kloster et al., 2013). At mineral surfaces, molecules exhibiting numerous bipolar groups such as polyphenols (Bentley and Payne, 2013), sugars (Petridis et al., 2014), or fulvic acids (Armanious et al., 2014) tend to form self-assembled organic layers. Subsequently, other molecules may adsorb to these layers, thus forming a stable supramolecular assembly held together by electrostatic, H-bonding, and vdW interactions (Petridis



**Figure 13.1** Schematic picture of the supramolecular associations of a diversity of “small” biogenic molecules and their breakdown products that form natural organic matter.

et al., 2014). Such POM assemblies formed in soils can persist because of the impenetrability of light and microbes (see Mayer, 2004; Schmidt et al, 2011). However, when these assemblies reach surface waters, photochemical and microbial processes can readily degrade or transform them (Rossel et al., 2013; Guenet et al., 2014; Hotchkiss et al., 2014; Marin-Spiotta et al., 2014). Particularly NOM exposed to photochemical transformation processes tends to exhibit smaller *aromaticities* as compared to the source material, which was observed in the terrestrially-derived components of marine NOM (Bianchi, 2011).

Whether we consider DOM or POM as the bulk sorbent or “solvent” for organic pollutants in a given system, we are faced with a spatially and structurally heterogeneous matrix; a variety of organic phases of different sizes (volumes) exhibit different polar (reflected primarily by the O/C ratio) and apolar (reflected by the H/C ratio and the % aromaticity) moieties, creating different microenvironments into which organic compounds may partition. Depending on the organic material considered, the number of polar groups might vary quite significantly. Highly polar fulvic acids may have O/C ratios of near 0.5 (Table 13.1), while more mature organic matter

have ratios of around 0.2 to 0.3; these evolve towards coal values below 0.1 (Brownlow, 1996). Furthermore, evidence exists that some NOM consists of both flexible (“rubbery”) molecules and materials with more rigid (“glassy”) character. Rigid domains are often present in the POM of soils and sediments, and contain nanopores that are accessible only by diffusion (Leboeuf and Weber, 1997; Xing and Pignatello, 1997; Xia and Ball, 1999; Cornelissen et al., 2000; Latao et al., 2012; Pignatello, 2012). In summary, the chemical composition and the physical characteristics of this complex mixture of organic phases in a given environmental setting depend on the types of the biological source materials and on the physical, chemical, and biological processes to which they have been exposed. *From a process-oriented point of view, we should envision NOM as a continuum of dissolved, colloidal, particulate, and solid surface-bound organic phases of different sizes (volumes) and chemical compositions.*

### Black Carbon and Other Organic Sorbents

In addition to the NOM found in the environment due to biogenesis and diageneisis, other identifiable organic sorbents, mostly derived from human activities, can be present and so be included in a TOC measurement. Examples include combustion products (soots, fly ash, biochars), tars and asphalt, plastics and rubbers, wood, and nonaqueous phase liquids. The most important among these sorbents are the various forms of “black” carbon (BC) engendered from incomplete combustion (Goldberg, 1985). The myriad descriptors of these materials, such as soot, smoke, black carbon, carbon black, charcoal, spheroidal carbonaceous particles, elemental carbon, graphitic carbon, charred particles, high surface area carbonaceous material, reflect either the formation processes or the operational techniques employed for their characterization. BC particles are ubiquitous in sediments and soils, often contributing up to 10% or even more of TOC (Gustafsson and Gschwend, 1998; Cornelissen et al., 2005; Lohmann et al., 2005; Koelmans et al., 2006). Such particles can be quite porous and exhibit a rather apolar and aromatic surface (Table 13.1). Consequently, BC has a high affinity for many organic pollutants, particularly for planar aromatic compounds. Therefore, at low pollutant concentrations where these sorptive sites are not saturated, significantly higher apparent partition coefficient values may be observed as compared to values that would be predicted from simple partitioning models considering only NOM (Gustafsson et al., 1997; Naes et al., 1998; Karapanagioti et al., 2000; Lohmann et al., 2005; Koelmans et al., 2006). Capitalizing on this high sorptive affinity, activated carbon or biochars are increasingly used to amend soils and sediments as a means of remediation via immobilization of pollutants (see Ghosh et al., 2011; Oen et al., 2012; Ahmad et al., 2014).

Another identifiable organic sorbent in natural systems are synthetic polymers, such as plastics (Andrade, 2011; Lambert et al., 2014); rubber (Kim et al., 1997); and wood, as found in the wood chips or sawdust used as fills at industrial sites (Severton and Banerjee, 1996; Mackay and Gschwend, 2000). If such materials are present in a soil, sediment, or waste of interest, then they will serve as part of the organic sorbent mix. We further discuss sorption to such sorbents when addressing bioaccumulation in Chapter 16.

Finally, special organic sorbents that may be of importance, particularly when dealing with contamination in the subsurface, are nonaqueous phase liquids (NAPLs, see also Section 10.4). These liquids may be immobilized in porous media and serve as absorbents for passing nonionic organic compounds (Mackay et al., 1996). In such cases, we may apply partition coefficients as discussed in Chapter 10 for organic solvents; in the special case of phases such as coal tar, one may describe sorption equilibrium using the data reported by Endo et al. (2008a). We should keep in mind, however, that the chemical composition of the absorbing NAPL evolves with time.

## 13.2

### Quantifying Natural Organic Matter–Water Partitioning of Neutral Organic Compounds

#### The Organic Carbon–Water Partition Coefficient ( $K_{iocw}$ )

Sorption of neutral organic chemicals to the organic matter present in a given environmental system may involve partitioning into, as well as adsorption onto, a wide variety of different organic substances. Thus, in general, we cannot expect linear isotherms over the whole concentration range, and we should be aware that predictions of overall organic matter–water partition coefficients may have rather large errors if some of the important organic materials present are not recognized (Kleineidam et al., 1999; Lohmann et al., 2005; Koelmans et al., 2006). Conversely, with appropriate site-specific information, reasonable estimates of representative, generally applicable organic carbon–water partition coefficients,  $K_{iocw}$ , are often possible using:

$$K_{iocw}(\text{e.g., L kg}^{-1} \text{ oc}) = \frac{C_{ioc}(\text{e.g., mol kg}^{-1} \text{ oc})}{C_{iw}(\text{e.g., mol L}^{-1})} \quad (13-3)$$

where  $C_{ioc}$  and  $C_{iw}$  are the concentrations of  $i$  per mass organic carbon and per volume of water respectively.

Historically, the vast majority of  $K_{iocw}$  values were determined for soil and sediment organic matter (SOM), primarily by equilibrium batch experiments with slurries or in columns (Chiou et al., 1979; Karickhoff et al., 1979; Schwarzenbach and Westall, 1981).  $K_{iocw}$  is calculated by dividing the experimentally determined  $K_{id}$  ( $= C_{is}/C_{iw}$ ) value by the fraction of organic carbon,  $f_{oc}$ , of the sorbent investigated:

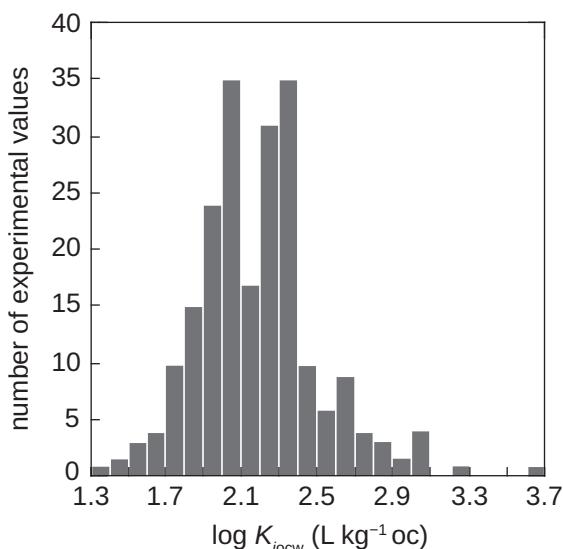
$$K_{iocw}(\text{e.g., L kg}^{-1} \text{ oc}) = \frac{K_{id}(\text{e.g., L kg}^{-1} \text{ solid})}{f_{oc}(\text{e.g., kg oc kg}^{-1} \text{ solid})} \quad (13-4)$$

Of course, a meaningful  $K_{iocw}$  value is only obtained if sorption to the natural organic material is the dominant process. This may be particularly problematic for sorbents exhibiting very low organic carbon contents (i.e.,  $f_{oc} < 0.001$ ) (Schwarzenbach and Westall, 1981). Also, care must be taken to ensure that equilibrium is established and the analyzed aqueous phase does not contain any colloids (Gschwend and Wu, 1985).

Various techniques have been developed to measure DOM–water partition coefficients, as the organic phase cannot be easily separated from the aqueous phase. Examples include dialysis techniques (e.g., Aeschbacher et al., 2012), solubility enhancement measurements (e.g., Wei-Haas et al., 2014), fluorescence quenching techniques (e.g., Hur et al., 2009), direct solid–phase microextraction (SPME) (e.g., Doll et al., 1999), and passive dosing (e.g., Gouliarmou et al., 2012). However, despite all these method developments, compared to SOM, the available data for DOM–water partitioning is still rather scarce, particularly with respect to the range of compounds investigated. By far, the most studies have been conducted with PAHs (e.g., ter Lak et al., 2005; Hafka et al., 2010; Kim and Kwon, 2010;) and, to a lesser extent, with polyhalogenated aromatic compounds, including PCBs (e.g., Durjava et al., 2007) and PBDEs (Wei-Haas et al., 2014), as model pollutants.

Let us now look at the variability in  $K_{i\text{ocw}}$  values reported for a given compound for partitioning to SOM and DOM of different origins. For most organic compounds, organic carbon–water partition constants are primarily determined by the “desire” of the compound to escape the water. In thermodynamic terms,  $K_{i\text{ocw}}$  mostly depends on the aqueous activity coefficient (Chapter 10, Eq. 10.2 and Fig. 10.1). When considering soil or sediment organic matter (SOM) from different origins, the variability in  $K_{i\text{ocw}}$  of a given compound is not too large, often being within a factor of 2 to 3, as shown for our companion compound atrazine in Fig. 13.2 (see other examples in Gerstl, 1990; Nguyen et al., 2005; Bronner and Goss, 2011a). Larger variability of up to an order of magnitude or even more in reported SOM  $K_{i\text{ocw}}$  values, also seen in Fig. 13.2, are likely due to experimental artifacts or the nonlinearity of isotherms (Endo et al., 2008b).

As DOM often contains a more diverse set of materials as compared to SOM, we may expect that the differences in DOM- $K_{i\text{ocw}}$  of a given compound between DOM of different origins will be larger than SOM- $K_{i\text{ocw}}$ . For example, for sorption to Aldrich humic acid as compared to Suwannee River fulvic acid, 5 and 10 times higher  $K_{i\text{ocw}}$



**Figure 13.2** Frequency diagram illustrating the variability in the  $\log K_{i\text{ocw}}$  values determined for our companion atrazine for 217 different soil and sediment samples. The majority of  $\log K_{i\text{ocw}}$  values are within 0.3–0.5 log units. Data compiled by Gerstl (1990).

values have been reported for phenanthrene and benzo(a)pyrene respectively (Kim and Kwon, 2010). Also, as not all of the components of DOM are large enough to act as sorbents, DOM- $K_{i\text{ocw}}$  values are often smaller than those of SOM- $K_{i\text{ocw}}$ . Suwannee River fulvic acid, for instance, is a poorer sorbent as compared to average values reported for SOM.

### LFER Modeling Approaches to Estimate Organic Carbon–Water Coefficients

*sp-LFER Approach to Estimate  $K_{i\text{ocw}}$ .* The most widely used method for estimating  $K_{i\text{ocw}}$  of a given compound is still to estimate it from its octanol–water partition constant,  $K_{i\text{ow}}$ , using the sp-LFER:

$$\log K_{i\text{ocw}} = a \log K_{i\text{ow}} + b \quad (13-5)$$

As discussed in Chapters 7 and 10, such sp-LFERS work best for structurally closely related compounds. Severe limitations are seen when pooling compounds exhibiting different molecular interactions, particularly when pooling apolar with bipolar compounds (Nguyen et al., 2005). Furthermore, they are strictly applicable only for the range of  $K_{i\text{ow}}$  values for which they were derived.

Table 13.2 summarizes some sp-LFERS derived from experimental NOM- $K_{i\text{ocw}}$  values for various compound classes. As can be seen from the  $r^2$  values, good

**Table 13.2** sp-LFERS (Eq. 13-5) Relating NOM–Water Partition Coefficients,  $K_{i\text{ocw}}$  and Octanol–Water Partition Constants,  $K_{i\text{ow}}$ , at 20 to 25°C for Some Sets of Neutral Organic Compounds<sup>a</sup>

NOM Type	Set of Compounds <sup>b</sup>	<i>a</i>	<i>b</i>	log $K_{i\text{ow}}$ range <sup>c</sup>	$r^2$	<i>n</i> <sup>d</sup>
SOM	Alkylated benzenes	0.81	-0.22	2.2 – 4.0	0.96	10
SOM	PAHs	1.12	-0.86	3.4 – 6.1	0.95	11
SOM	Chlorinated benzenes and PCBs	0.94	-0.43	2.8 – 7.2	0.98	24
SOM	Chlorinated phenols (neutral species)	0.89	-0.15	2.2 – 5.3	0.97	10
SOM	All phenylureas	0.49	1.05	0.5 – 4.2	0.62	52
SOM	Only alkylated and halogenated phenylureas, phenyl-methylureas, and phenyl-dimethylurea	0.59	0.78	0.8 – 2.9	0.87	27
SOM	Only alkylated and halogenated phenylureas	0.62	0.84	0.8 – 2.8	0.98	13
Aldrich humic acid	PAHs	1.20	-0.81	4.6 – 6.8	0.98	7
Suwannee River fulvic acid	Chlorinated benzenes and PCBs	0.82	0.31	4.6 – 6.8	0.93	8

<sup>a</sup> $K_{i\text{ocw}}$  in L kg<sup>-1</sup> oc: slopes (*a*) and intercepts (*b*) of Eq. 13-5.

<sup>b</sup>Data compiled from Schellenberg et al. (1984); Sabljic et al. (1995); Chiou et al. (1998); Poole and Poole (1999); Nguyen et al. (2005); Durjava et al. (2007); Kim and Kwon (2010); Gouliarmou et al. (2012).

<sup>c</sup>Range of experimental values for which LFER has been established.

<sup>d</sup>Number of compounds used for LFER.

correlations are found for structurally closely related sets of compounds, except for the group of 52 phenylureas. For the alkylated benzenes, chlorinated benzenes, PCBs, PAHs, and chlorinated phenols, the sp-LFERs were derived from averaged  $K_{\text{iocw}}$  values representing, in general, quite a large number of measurements. For these classes of compounds, predictions within a factor of 2 to 3 should be possible (Nguyen et al., 2005). Since the 52 phenylureas represent quite a different structural diversity, the correlation is much weaker but improves significantly for subsets of structurally more similar compounds (Table 13.2).

From the differences in the various sp-LFERs given in Table 13.2, it is, however, difficult to draw any mechanistic conclusions. What can be seen is that, compared to octanol, partitioning from water to SOM increases somewhat more with size for the PAHs (slope  $> 1$ ), whereas, for the substituted benzenes and PCBs, the increase is somewhat smaller (slope  $< 1$ ), and is smallest for the bipolar phenylureas (slope  $\ll 1$ ). A final insight from Table 13.2 is that Aldrich humic acid represents a sorbent that is much more similar to SOM as compared to most DOM in the environment, which is reflected in very similar or even larger  $K_{\text{iocw}}$  found for Aldrich humic acid as compared to average values reported for SOM (e.g., for PAHs).

*pp-LFER Approach to Estimate  $K_{\text{iocw}}$ .* As with predicting partition constants for organic solvent–water partitioning (Chapter 10), pp-LFERs are generally applicable tools for predicting  $K_{\text{iocw}}$  values. Few pp-LFERs derived from experimental NOM–water partitioning data have been reported in the literature to date. However, these still provide some important insights into the variability of NOM and the prominent intermolecular interactions at play during sorption.

As discussed in Chapter 7, two types of pp-LFERs are commonly used that differ primarily in the way in which the vdW-interactions are expressed. Thus, pp-LFERs for NOM–water partitioning may also take two forms, one using the solute descriptor of the excess molar refraction ( $E_i$ ) and the other using  $\log K_{\text{ihexadecane-air}}$  ( $L_i$ ), which incorporates size (Eqs. 13-6 and 13-7). Table 13.3 summarizes the coefficients of the pp-LFERs, as compiled in the UFZ-LSER database (Endo et al., 2014).

$$\log K_{\text{iocw}} = v_{\text{ocw}} V_i + e_{\text{ocw}} E_i + s_{\text{ocw}} S_i + a_{\text{ocw}} A_i + b_{\text{ocw}} B_i + c \quad (13-6)$$

$$\log K_{\text{iocw}} = v_{\text{ocw}} V_i + l_{\text{ocw}} L_i + s_{\text{ocw}} S_i + a_{\text{ocw}} A_i + b_{\text{ocw}} B_i + c \quad (13-7)$$

Both Eqs. 13-6 and 13-7 are well suited to fit the reported experimental data (Bronner and Goss, 2011b; Neale et al., 2012). However, as with all pp-LFERs, one must use caution when applying these equations to solutes exhibiting different intermolecular interactions than the compounds used for the calibration regression. For example, the data sets used to calibrate the pp-LFERs in Table 13.3 did not contain groups of compounds that exhibit unusually small vdW properties, such as polyfluorinated compounds or siloxanes (see Chapter 7). Additionally, because of the heterogeneity of NOM (Section 13.1), the coefficients derived from a multi-parameter regression analysis of the experimental data depend on, to even greater degree than well-defined organic solvents, the range and structural diversity of the set of calibration compounds used. Therefore, a mechanistic interpretation of the system

**Table 13.3** pp-LFERs for Some NOM–Water Systems ( $\log K_{i\text{ocw}}(\text{Lkg}_{\text{oc}}^{-1}) = v_{\text{ocw}}V_i + e_{\text{ocw}}E_i + s_{\text{ocw}}S_i + a_{\text{ocw}}A_i + b_{\text{ocw}}B_i + c$  and  $\log K_{i\text{ocw}}(\text{Lkg}_{\text{oc}}^{-1}) = v_{\text{ocw}}V_i + l_{\text{ocw}}L_i + s_{\text{ocw}}S_i + a_{\text{ocw}}A_i + b_{\text{ocw}}B_i + c$ ) at 25°C or 15°C<sup>a</sup>

NOM Type	Eq.	$v_{\text{ocw}}$	$l_{\text{ocw}}$	$e_{\text{ocw}}$	$s_{\text{ocw}}$	$a_{\text{ocw}}$	$b_{\text{ocw}}$	$c$	$r^2$	n <sup>b</sup>	S.D.
SOM <sup>c</sup>	13-8	+2.28		+1.10	-0.72	+0.15	-1.98	+0.14	0.98	75	
Pahokee peat <sup>d</sup>	13-9	+2.99		+0.81	-0.61	-0.21	-3.44	-0.29	0.92	79	0.25
Pahokee peat(low conc) <sup>e</sup>	13-10	+3.71		+0.31	+1.27	-0.10	-3.94	-1.04	0.91	51	0.34
Pahokee peat (high conc) <sup>e</sup>	13-11	+3.51		+0.43	+0.19	+0.02	-3.83	-0.82	0.90	51	0.34
Aldrich humic acid <sup>f</sup>	13-12	+3.94		+0.29	-0.52	+0.36	-3.40	-0.85	0.97	52	0.29
Swannee River fulvic acid <sup>f</sup>	13-13	+2.86		+0.63	-0.63	+0.05	-2.48	-1.21	0.85	34	0.24
Pahokee peat <sup>d</sup>	13-14	+1.20	+0.54		-0.98	-0.42	-3.34	+0.02	0.93	79	0.24
Aldrich humic acid <sup>f</sup>	13-15	+2.65	+0.40		-0.72	+0.49	-3.42	-0.92	0.97	51	0.32
Aldrich humic acid(dry) <sup>g</sup>	13-16	+1.81	+0.45		-1.25	-0.40	-2.31	-0.16		74	
Swannee River fulvic acid <sup>f</sup>	13-17	+1.54	+0.34		-0.69	+0.02	-2.43	-0.82	0.82	34	0.26
Swannee River fulvic acid(dry) <sup>g</sup>	13-18	+3.68	+0.05		-0.96	-0.11	-3.51	-0.79		87	

<sup>a</sup>Contain solute descriptors for the size of the compound ( $V_i$ ), the excess molar refraction ( $E_i$ ) or the log  $K_{i\text{hexadecane-air}}$  ( $L_i$ ), the H-donor property ( $A_i$ ), the H-acceptor property ( $B_i$ ), and a “dipolarity/polarizability” parameter ( $S_i$ ), plus the complementary fitted system descriptors characterizing the NOM phases involved (lower case letters).

<sup>b</sup>Number of compounds used for LFER.

<sup>c</sup>Data from Nguyen et al. (2005);  $\log K_{i\text{ocw}}$  range: 1 to 7.

<sup>d</sup>Data from Bronner and Goss (2011b);  $\log K_{i\text{ocw}}$  range: 1 to 4.5.

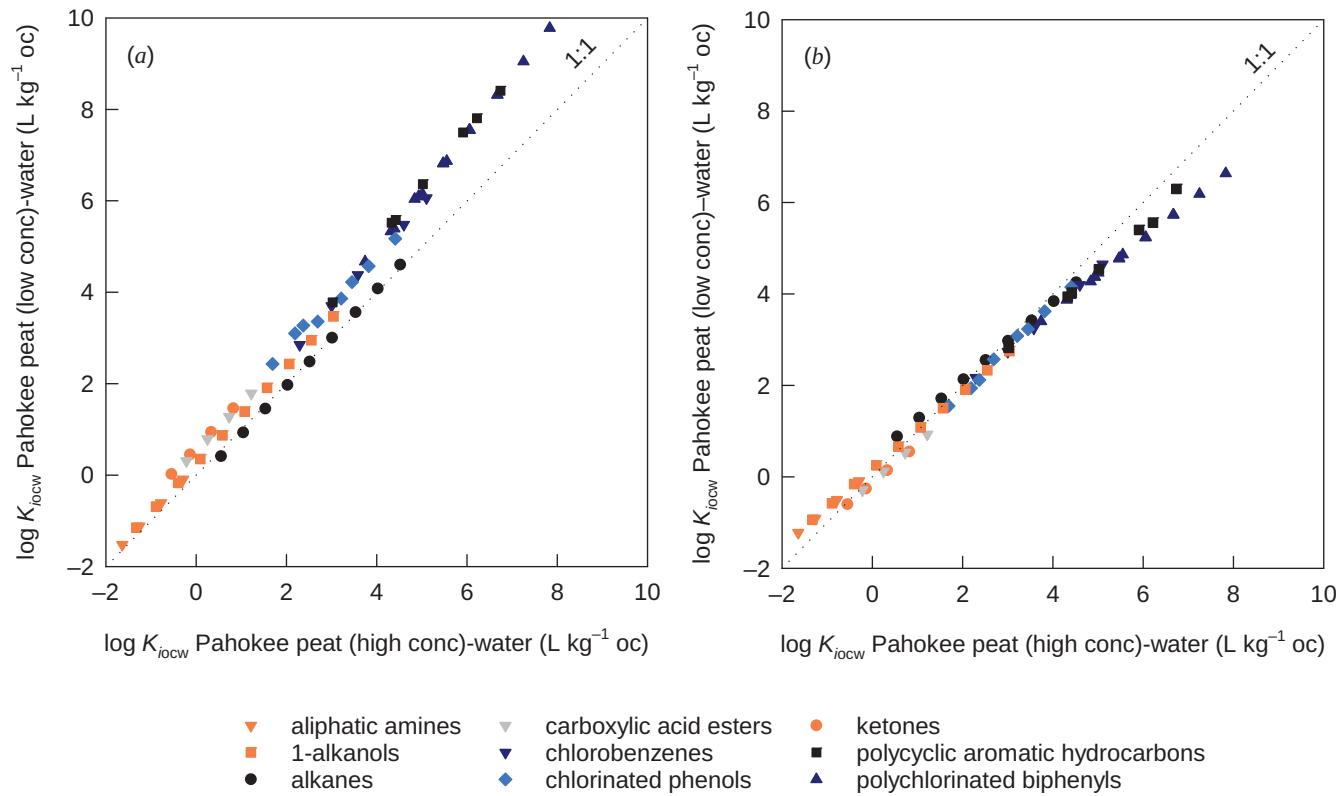
<sup>e</sup>Data from Endo et al. (2009);  $\log K_{i\text{ocw}}$  range: 1 to 6. low conc = 4.3 mg kg<sup>-1</sup>oc, high conc = 430 mg kg<sup>-1</sup>oc.

<sup>f</sup>Data from Neale et al. (2012); Aldrich:  $\log K_{i\text{ocw}}$  range: 2 to 7; Suwannee River:  $\log K_{i\text{ocw}}$  range: 1 to 4.

<sup>g</sup> $K_{i\text{ocw}}$  calculated at 15°C using Eq. 13-19 with pp-LFER for OC–air partitioning from Niederer et al. (2007) and pp-LFER for air–water partitioning from Goss (2006). dry = partially hydrated state (RH = 98%).

descriptors in Eqs. 13-8 through 13-18 is rather difficult. The only general conclusions are that, similar to the octanol–water system (Chapters 7 and 10),  $a_{\text{ocw}}$  is commonly rather small, implying NOM is “electron rich” and thus a good H-acceptor, and that  $b_{\text{ocw}}$  is strongly favoring the aqueous phase, suggesting NOM does not supply protons as well as bulk water. Finally, we should note that, as for the sp-LFERs previously discussed, the pp-LFERs are strictly applicable for the range of  $K_{i\text{ocw}}$  values for which they were derived (see Table 13.3).

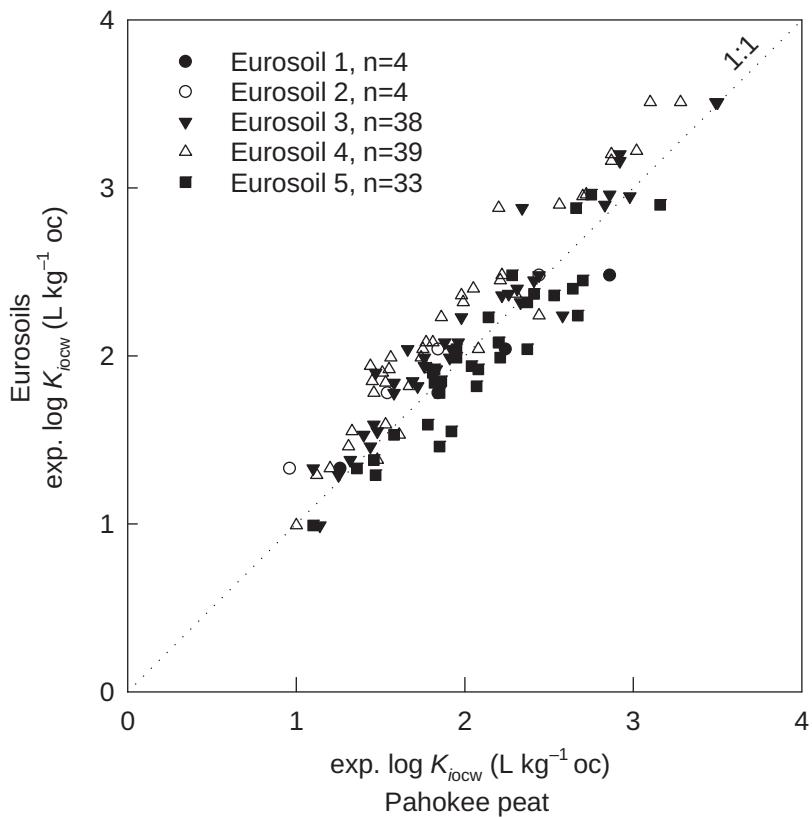
As the equations for different types of NOM depend significantly on the set of calibration compounds from which they were derived, we compare them instead by calculating the respective partition coefficients of our test set of apolar, monopolar, and bipolar compounds (introduced in Chapter 7 and in the following referred to as test set). Looking at the Pahokee peat data, Endo et al. (2009) used two concentrations of solute to probe for high affinity sorption sites leading to nonlinearity of isotherms at low concentrations. Figure 13.3a shows that, particularly for the highly hydrophobic



**Figure 13.3** Plots of calculated  $\log K_{i\text{ocw}}$  values for our test set (without polyfluorinated compounds and siloxanes) for Pahokee peat (a) at different solute concentrations; Pahokee peat (low conc) (Eq. 13-10) versus Pahokee peat (high conc) (Eq. 13-11) (Endo et al., 2009) and (b) derived using a wider sorbate concentration range (Eq. 13-9) than Pahokee peat (high conc) (Eq. 13-11).

planar PAHs and PCBs, much higher  $K_{i\text{ocw}}$  values (more than an order of magnitude) are predicted for low solute concentrations (Eq. 13-10), which is in line with experimental evidence. Hence, Eq. 13-10 reflects both sorption to high affinity sites and partitioning, whereas Eq. 13-11 can be assumed to describe primarily partitioning. Figure 13.3b shows that  $K_{i\text{ocw}}$  values calculated for Pahokee peat with Eq. 13-11 are in good agreement with those using Eq. 13-9 derived by Bronner and Goss (2011b), even below and somewhat above the  $K_{i\text{ocw}}$  range for which they were derived. Only for the highly hydrophobic compounds are there noticeable deviations, in that Eq. 13-11 predicts significantly larger  $K_{i\text{ocw}}$  values.

In subsequent discussions, we use Pahokee peat (Eqs. 13-9 or 13-14, respectively) as a representative SOM for estimating SOM–water partition coefficients for several reasons. First, as shown by Fig. 13.4, Pahokee peat seems to be reasonably representative for SOM originating from different soil environments (factor of 2 for  $\log K_{\text{oc}}$  ranging from 1 to 4). Also, compared to all other reported pp-LFERS, the calibration data set used to derive Eq. 13-9 for Pahokee peat represents a much larger structural diversity than in Eq. 13-8 for SOM. Furthermore, Eq. 13-8 and earlier data by Poole and Poole (1999; data not shown) represent composites of literature values of quite varying quality. Finally, Eq. 13-9 and the equivalent Eq. 13-14, respectively, have been validated for a large number of complex molecules, including pesticides and pharmaceuticals.

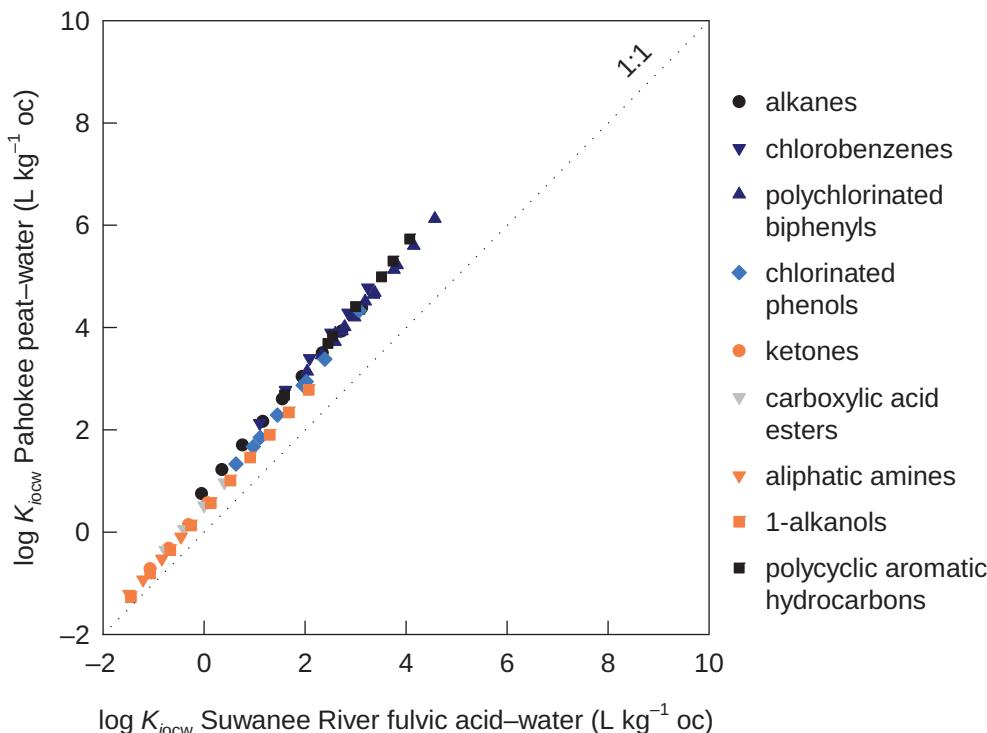


**Figure 13.4** Comparison of experimental  $K_{iocw}$  values for standard soils (Eurosoil 1-5) to experimental  $K_{iocw}$  values for Pahokee peat at 25°C. Data from Bronner and Goss (2011a).

For *DOM–water partitioning*, to date, only two pp-LFERs are available that are based on direct measurements: Eqs. 13-12 and 13-15 for Aldrich humic acid and Eqs. 13-13 and 13-17 for Suwannee River fulvic acid, both from Neale et al. (2012). However, for *DOM–air partitioning*, Niederer et al. (2007) have reported pp-LFERs for 10 fulvic and humic acids at 98% relative humidity. These DOMs cover a wide range of sorbents exhibiting different polarities and aromaticities. Among these DOMs, the strongest sorbents for partitioning from air are the least polar humic acids tested, including Leonardite and Aldrich humic acid (C/O ratio > 1.7; aromaticity > 45%). These sorbents exhibit  $K_{ioca}$  values that are up to one order of magnitude larger than the weakest sorbents, including the most polar fulvic acids such as Suwannee River, Elliot Soil, and Wakish Peat fulvic acids (C/O ratio < 1.3; aromaticity < 36%). Assuming that the thermodynamic cycle approach (Section 7.1) is valid, from these data, we can calculate the corresponding *DOM–water partition coefficient* by multiplying  $K_{ioca}$  with the air–water partition constant,  $K_{iaw}$ :

$$K_{iocw} = K_{ioca} K_{iaw} \quad (13-19)$$

In the same vein, we can predict  $K_{iocw}$  values using a pp-LFER derived by adding the one reported for air–water partitioning (Eq. 9-18) to the corresponding one for *DOM–air*. Comparison of the resulting equations for Aldrich humic acid (Eq. 13-16) and Suwannee River fulvic acid (Eq. 13-18) with the ones for the immersed acids, Eqs. 13-15 and 13-17, shows that quite different system descriptors parameters are



**Figure 13.5** Plot of calculated  $\log K_{i\text{ocw}}$  values for our test set (without polyfluorinated compounds and siloxanes) for Pahokee peat versus Suwannee River fulvic acid.

obtained. Again, a mechanistic interpretation of these differences is ambiguous. However, we would expect that the characteristics of any NOM sorbent would be different in a partially hydrated state (“dry” state, RH = 98%) as compared to being completely immersed (“dissolved”) in water. We conclude that using Eq. 13-19 to calculate  $K_{i\text{ocw}}$  from  $K_{i\text{oca}}$  or vice versa may lead to significant under- or overestimation of these values, and should therefore be applied with caution.

Instead, we can use NOM-air partitioning data to assess upper and lower limits for the  $K_{i\text{ocw}}$  of a given compound. In other words, we can identify those NOMs that we can expect to be the strongest and weakest sorbents. The strongest sorbents include humic materials such as the lignite derived Leonardite humic acid, and also Pahokee peat, which we use as a representative SOM. The weakest bulk sorbents are surface water DOMs including fulvic acids, such as Suwannee River fulvic acid, which we use to estimate the lower limit of  $K_{i\text{ocw}}$  values. Figure 13.5 shows the differences that we may expect between SOM- $K_{i\text{ocw}}$  and DOM- $K_{i\text{ocw}}$  values typical for surface waters. The disparity grows with increasing hydrophobicity of the compounds and may become larger than one order of magnitude.

### Effect of Temperature and Solution Composition on $K_{i\text{ocw}}$

**Temperature.** As with organic solvent–water partition constants (Eqs. 10-15 and 10-18), we may express the temperature dependence of  $K_{i\text{ocw}}$  by:

$$\ln K_{i\text{ocw}} = -\frac{\Delta_{\text{ocw}}H_i}{R} \cdot \frac{1}{T} + \text{constant} \quad (13-20)$$

with the change in enthalpy as:

$$\Delta_{\text{ocw}}H_i = H_{\text{ioc}}^{\text{E}} - H_{\text{iw}}^{\text{E}} \quad (13-21)$$

$H_{\text{ioc}}^{\text{E}}$  and  $H_{\text{iw}}^{\text{E}}$  are the excess enthalpies of the compound in the NOM considered and in water respectively. A negative  $\Delta_{\text{ocw}}H_i$  means that  $K_{\text{iocw}}$  decreases with increasing temperature. As we have seen in Chapter 9 (Table 9.2),  $H_{\text{iw}}^{\text{E}}$  values are in the order between  $-20 \text{ kJ mol}^{-1}$  and, at maximum,  $+30 \text{ kJ mol}^{-1}$ . Furthermore, as is the case with organic solvents, for NOM–water partitioning,  $H_{\text{ioc}}^{\text{E}}$  can be assumed to be generally rather small (i.e.,  $\pm 10 \text{ kJ mol}^{-1}$ ). For example, Haftka et al. (2010) reported  $\Delta_{\text{ocw}}H_i$  values of between  $-15$  and  $-25 \text{ kJ mol}^{-1}$  for partitioning of a series of PAHs to DOMs of various origins.

However, since  $H_{\text{ioc}}^{\text{E}}$  represents the average excess enthalpy of the compound for the various organic sorbents present, it may, in some cases, depend on the concentration range considered. Particularly for SOM, where at low concentrations sorption to specific sites may dominate the overall  $K_{\text{iocw}}$ ,  $H_{\text{ioc}}^{\text{E}}$  may be somewhat larger as compared to higher concentrations where partitioning is the major process. This effect is not so significant for apolar and weakly polar compounds as  $H_{\text{iw}}^{\text{E}}$  was found to primarily determine  $\Delta_{\text{ocw}}H_i$  for adsorption to hydrophobic surfaces, including surfaces of black carbon materials (Bucheli and Gustafsson, 2000). For polar compounds that may undergo H-bond interactions with specific sites present in SOM, however,  $\Delta_{\text{ocw}}H_i$  may be concentration dependent. For example, for sorption of diuron and other phenylurea herbicides to soils,  $\Delta_{\text{ocw}}H_i$  is between  $-50$  and  $-60 \text{ kJ mol}^{-1}$  at very low concentrations and between  $-20$  and  $0 \text{ kJ mol}^{-1}$  at high concentrations (Spurk, 1995). Hence, as for organic solvent–water partition constants (see Table 10.3), NOM–water partition coefficients are usually rather insensitive to temperature, whereas adsorption coefficients may vary by about a factor of two with a ten degree change in temperature.

*pH and Ionic Strength.* For sorption of neutral compounds to SOM over the ambient pH range, we may assume, in general, that pH will not have a significant altering effect, as has been demonstrated for Pahokee peat (Bronner and Goss, 2011a). We may also assume that the sorbent properties of SOM will not be heavily influenced by ionic strength (Means, 1995), but we may have to take into account the effect of salt on the activity coefficient of the compound in the aqueous phase (see Section 9.4) and thus on  $K_{\text{iocw}}$ . Similar to air–water or organic solvent–water partitioning, we may quantify this effect simply by:

$$K_{\text{iocw, salt}} = K_{\text{iocw}} 10^{+K_i^s[\text{salt}]_{\text{tot}}} \quad (13-22)$$

$K_i^s$  values can be estimated using Eq. 9-33. For example, for the companion compound phenanthrene,  $K_i^s = 0.3$  (Table 9.6) and  $[\text{salt}]_{\text{tot}} = 0.5 \text{ M}$  for seawater, meaning that the presence of the salt from seawater will increase  $K_{\text{iocw}}$  by a factor of about 1.4.

Because particularly polar DOMs such as Suwannee River fulvic acid exhibit a rather large number of acidic (e.g., carboxylic, phenolic; see Table 13.1) and other polar

groups that may dissociate or form complexes with metal ions (e.g.,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Al^{3+}$ ), pH and major ion composition of the solution may affect their sorption characteristics. When carboxyl groups are ionized, their electrostatic repulsions cause the DOM to spread out in solution. When divalent cations like calcium are bound to such functional groups, they enable bridging of like-charged groups and, therefore, cause the macromolecules to coil. The results of the limited number of relatively old studies on this subject demonstrate that these effects may be quite complex (Schlautman and Morgan, 1993; Ragle et al., 1997). Depending on the nature of the DOM constituents, changes in pH and ion composition may or may not have a significant impact on the number of hydrophobic and hydrophilic domains that are relevant for sorption of a given neutral organic compound. Consequently, based on the still very limited data available, it is not possible to predict quantitatively the effect of solution composition on the  $K_{iocw}$  value of a given compound for such DOMs. Nevertheless, a few general comments on trends and magnitudes of such effects can be made.

First, when considering the effect of pH,  $K_{iocw}$  values of apolar and weakly polar compounds exhibit a general decreasing trend with increasing pH, with the trend more pronounced for larger as compared to smaller compounds. For DOMs, the largest effects of pH are found for those consisting primarily of smaller sized, highly polar constituents, such as fulvic acids. For example,  $K_{iocw}$  values for large PAHs and such DOMs vary up to a factor of 2 to 3 between pH 4 and 10 (Schlautman and Morgan, 1993). We can rationalize these findings by envisioning an increase in the number of negatively charged functional groups with increasing pH; these may lead to the destruction of hydrophobic DOM domains (e.g., by uncoiling of macromolecules or by disaggregation of DOM components). However, since these effects are particularly pronounced at low pH (<5), we often neglect the effect of pH on  $K_{iocw}$  of neutral organic compounds within the pH range typically encountered in natural waters (i.e., pH 6 to 9).

At low to moderate ionic strengths (i.e.,  $I < 0.1$  M), as a first approximation, we can neglect the effect of dissolved salts on  $K_{iocw}$  for apolar and weakly polar compounds on DOM. Since little data is available for higher ionic strengths, it is not possible to draw any general conclusions for solutions such as seawater, except for the salting-out phenomena as described for SOM (Eq. 13-22).

### Nonlinearity of Sorption Isotherms Due to the Presence of Black Carbon (BC) in Soils and Sediments

So far, we have primarily considered those cases in which partitioning into NOM is the dominant sorption mechanism, that is, in which  $K_{id}$  is linearly related to  $K_{iocw}$ :

$$K_{id} = f_{oc} K_{iocw} \quad (13-23)$$

However, in numerous experiments with soils and sediments, nonlinear isotherms have been observed with apparent  $K_{id}$  values at low sorbate concentrations of up to one or even two orders of magnitude higher than would have been predicted from Eq. 13-23 using estimated SOM  $K_{iocw}$  values (Gustafsson et al., 1997; Xia and Ball,

1999; Accardi-Dey and Gschwend, 2002 and 2003; Lohmann et al., 2005; Cornelissen et al., 2005; Koelmans et al., 2006; Sobek et al., 2009). If a natural soil or sediment matrix includes hydrophobic solids on which the chemical of interest may adsorb, the overall  $K_{id}$  value for sorption to organic matter must reflect both absorption into natural organic matter and adsorption onto these surfaces. Since quantifying all the different surfaces and sites available for adsorption of organic pollutants is difficult, sorption isotherms are often simply approximated by a dual-mode model that expresses the concentration of the sorbed compound on a per unit mass basis. The model is a combination of a linear absorption (Eq. 13-23; to represent the sorbate's partitioning into natural organic matter) and a Freundlich equation (Eq. 12-1; as seen for adsorption to any hydrophobic surfaces or pores of solids like activated carbons):

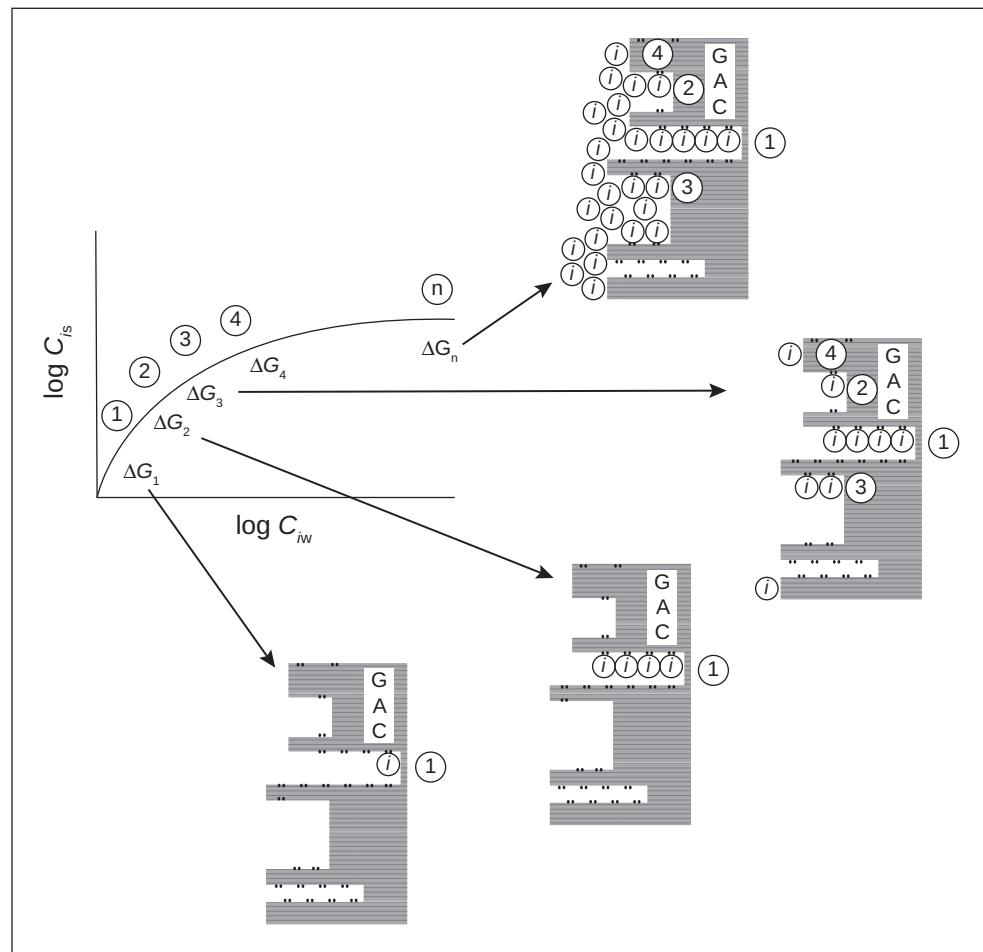
$$C_{is} = f_{oc} K_{iocw} C_{iw} + K_{iF} C_{iw}^{n_i} \quad (13-24)$$

where  $K_{iF}$  is the Freundlich constant or capacity factor (e.g., in  $(\text{mol kg}^{-1})(\text{mol L}^{-1})^{n_i}$ ) and  $n_i$  is the Freundlich exponent. The value of  $K_{iF}$  is not really well understood. However, for practical purposes, it can be related to the quantity of adsorbent present (e.g., the fraction of carbonaceous materials such as "black carbon" in a solid matrix,  $f_{bc}$ ) and the particular compound's black carbon-normalized adsorption coefficient (e.g.,  $K_{ibcw}$ ). In a first approximation, we can write:

$$C_{is} = f_{oc} K_{iocw} C_{iw} + f_{bc} K_{ibcw} C_{iw}^{n_i} \quad (13-25)$$

Values of  $n_i$  measured to date vary from 0.4 to 1.0. Modelers often use an average value of 0.7, but the data are still quite limited. The smaller the  $n_i$ , the sooner linear absorption predominates and adsorption at higher concentrations is less important. Recent work using known forms of black carbon (BC) has begun to elucidate the intermolecular interactions that influence their capabilities to act as sorbents by applying pp-LFER approaches (see Plata et al., 2015). Since, depending on their origin, these BC solids exhibit quite different surface characteristics. Furthermore, as schematically depicted in Fig. 13.6, a given BC solid offers an array of sorption sites. Therefore, one can expect the sorbate:sorbent interaction energies will vary with surface coverage, which, together with the variability of BC phases present in a given soil or sediment (e.g., coal dust, soots, chars, or highly metamorphosed organic matter such as kerogen), renders rather difficult the derivation of more generally applicable predictive tools for quantifying adsorption to BC. Nevertheless, the pp-LFER approaches reported so far show a promising first step in this direction.

The highly planar aromatic surfaces of BC materials are particularly attractive for planar, highly hydrophobic sorbates, which can maximize the molecular contact with these surfaces. Therefore, it is not surprising that planar compounds including PCDFs, PCDDs, non *ortho*-substituted PCBs and PBDEs, and particularly PAHs have been found to exhibit very large  $K_{ibc}$  values that are up to two orders of magnitude larger than the corresponding  $K_{iocw}$  values (see Koelmans et al., 2006). For other than these strongly adsorbing compounds, rather little experimental data is available. We may, however, assume that for smaller apolar or more polar compounds, adsorption to carbonaceous materials is less important (Xia and Ball, 1999 and 2000; Plata et al., 2015). We also note that for polar compounds, other high affinity sites present in SOM may



**Figure 13.6** Conceptualization of varying affinity sorption sites for a BC (granular activated carbon, GAC) exhibiting microporosity (i.e., pores on nanometer scales) such that sorbates may interface with different sorbent surface areas. Such varying degree of contact results in diminishing energies of interaction as a function of sorbent coverage and thus cause the adsorption isotherm's slope to decline with increasing sorbate concentration. Figure from Shih and Gschwend (2009).

be the cause of some nonlinearities of sorption isotherms (Spurlock, 1995; Sposito et al., 1996; Chiou and Kile, 1998).

In summary, we should realize that, when applying  $K_{iow}$  values determined at high concentrations or derived from LFERs such as those given in Tables 13.2 and 13.3, we might underestimate equilibrium sorption at low concentrations (i.e., below 1% of the compound's solubility) by a factor of 2 or even more. Due to competition with other sorbates present in a natural system, the effect of specific adsorption could, however, be significantly attenuated (Chiou et al., 2000; Oen et al., 2012). Furthermore, the abundance of specific adsorption sites may be rather low in certain environments. In cases in which the effect can be expected to be moderate and in which we only need to get an order of magnitude estimate of  $K_{iow}$ , we may decide to neglect the nonlinearity of the isotherm. For planar, hydrophobic compounds such as the PAH, however, adsorption to carbonaceous materials or other high affinity sorbents present in significant abundances should be taken into account. Finally, we should also note that in those cases where specific adsorption to surfaces plays a role,  $\Delta_{\text{surf}w} H_i$  can be in the order of  $-50$  to  $-60$   $\text{kJ mol}^{-1}$  (e.g., Spurlock, 1995), and, therefore, the corresponding adsorption coefficient will decrease/increase by a factor of about two with a temperature increase/decrease of  $10^\circ\text{C}$ .

### 13.3

## Sorption of Organic Acids and Bases to Natural Organic Matter

### Effect of Charged Moieties on Sorption: General Considerations

As shown in Chapter 3, numerous important organic pollutants such as pesticides and pharmaceuticals exhibit acidic (e.g., carboxylic, phenolic) and basic (e.g., amino) groups. Depending on their  $pK_{ia}$  values, organic acids and bases may be partially or even fully ionized at ambient pH (Chapter , Section 4.3). When considering the sorption of ionized species, in addition to vdW and hydrogen bonding interactions, we also have to take into account electrostatic interactions with charged species present in natural sorbents including NOM and inorganic surfaces (Fig. 12.2). Furthermore, some acid and base functionalities may also form chemical bonds with certain sorbent moieties (see Fig. 12.2 and Eq. 12-14). In these cases, quantification of sorption in soils and sediments may become even more complicated because the abundances and reactivities of such sorptive sites need to be quantified. We address this issue of chemical bonding to sorption sites later in Chapter 14. Here, we focus on the mostly reversible sorption of organic acids and bases to NOM, which we describe with an overall sorption *distribution ratio*,  $D_{iocw}$ , since more than one dissolved and sorbed species may exist.

At ambient pH values, NOM exhibits an overall negative charge, primarily due to the presence of carboxylic acid and phenolic groups. Therefore, bulk NOM primarily acts as a cation exchanger, and we may expect that, in general, negatively charged organic species will sorb more weakly to NOM than their neutral counterparts. Nevertheless, situations exist in which sorption of the anionic species to NOM is appreciable. For positively charged species, on the other hand, we may expect a stronger association with NOM constituents as compared to the neutral compound.

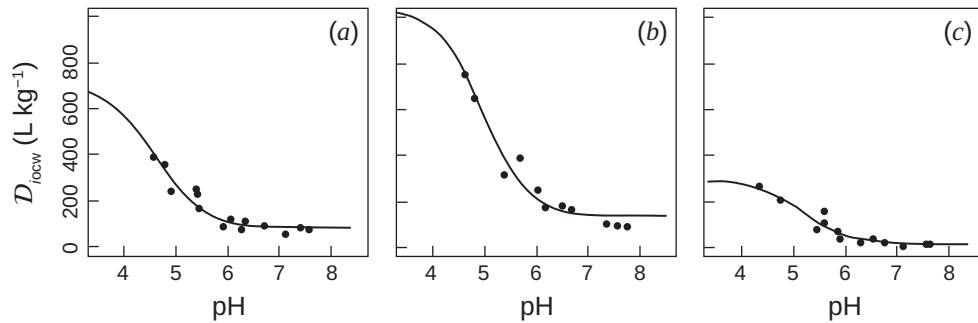
### Sorption to NOM of Compounds Forming Anionic Species (Organic Acids)

Although the available data on the pH-dependence of the sorption of organic acids to NOM is rather scarce, we can still make a few general statements. For *weak acids* (e.g., compounds exhibiting a carboxylic or phenolic moiety) that exhibit only one acidic group, we may describe  $D_{iocw}$  using the following simple approach (Gundersen et al, 1997; Jafvert, 1990; Lee et al., 1990; Schellenberg et al., 1984; Severtson and Banerjee, 1996; Tülp et al., 2009):

$$D_{iocw} = \frac{[HA]_{oc} + [A^-]_{oc}}{[HA]_w + [A^-]_w} = \alpha_{ia} K_{iocw}^{HA} + (1 - \alpha_{ia}) K_{iocw}^{A^-} \quad (13-26)$$

where  $K_{iocw}^{HA} = [HA]_{oc}/[HA]_w$  and  $K_{iocw}^{A^-} = [A^-]_{oc}/[A^-]_w$  are the (apparent) sorption coefficients for the neutral and the charged species, respectively, *which are assumed to be pH-independent*, and  $\alpha_{ia}$  and  $(1 - \alpha_{ia})$  are the fractions of the compound in the

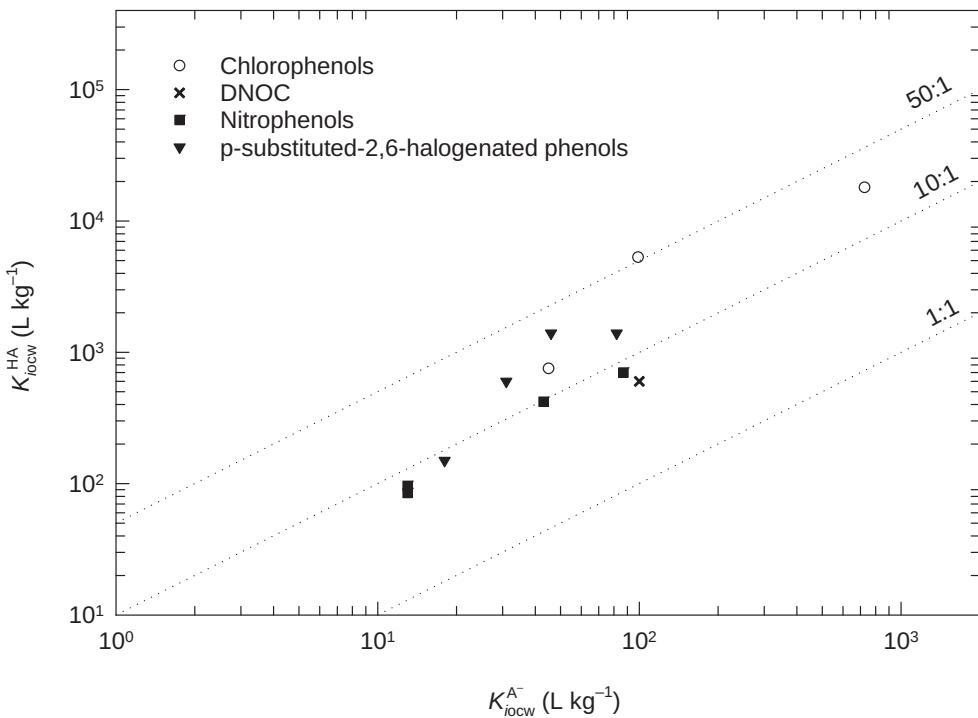
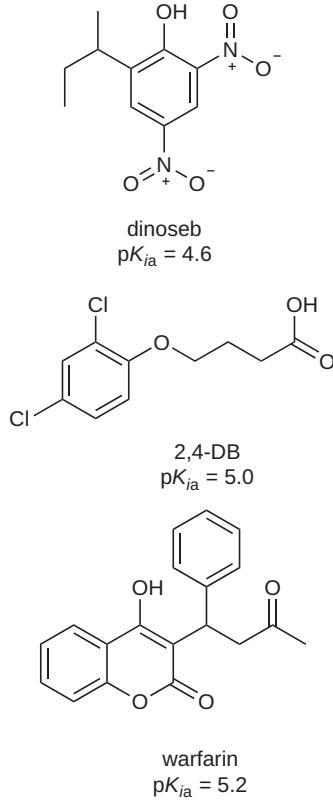
**Figure 13.7** Plots of experimental  $D_{locw}$  (in  $\text{L kg}^{-1}$  oc) versus pH for sorption to Pahokee peat for (a) dinoseb, (b) 4-(2,4-dichlorophenoxy) butanoic acid (2,4-DB), and (c) warfarin (see structures in margin) at  $T = 25^\circ\text{C}$ ; 10 mM  $\text{CaCl}_2$ . The line is the fit using Eq. 13-26. Data from Tülp et al. (2009).



neutral and dissociated form, respectively, in the aqueous phase. As introduced in Eq. 4-59,  $\alpha_{ia}$  is given by:

$$\alpha_{ia} = \frac{1}{1 + K_{ia}/\{\text{H}^+\}} = \frac{1}{1 + 10^{p\text{H}-pK_{ia}}} \quad (13-27)$$

Using a liquid chromatographic technique, Tülp et al. (2009) investigated the pH-dependence of the sorption of a diverse set of organic acids to Pahokee peat, our representative SOM (see Section 13.2). As illustrated in Fig. 13.7 for three compounds, the simple model of Eq. 13-26 fit the experimental data for 20 acids reasonably well. Depending on the structure of the compound, the neutral species were found to sorb between 5 and 60 times stronger as compared to the anionic species, as shown in Fig. 13.8 for a set of substituted phenols. The smallest differences in sorption (factor  $\leq 10$ ) were observed for the nitrophenols, which can be rationalized



**Figure 13.8** Relationship between  $\log K_{locw}^{\text{HA}}$  and  $\log K_{locw}^{\text{A}^-}$  for a variety of substituted phenols at  $T = 25^\circ\text{C}$ ; 10 mM  $\text{CaCl}_2$ . Data from Tülp et al. (2009).

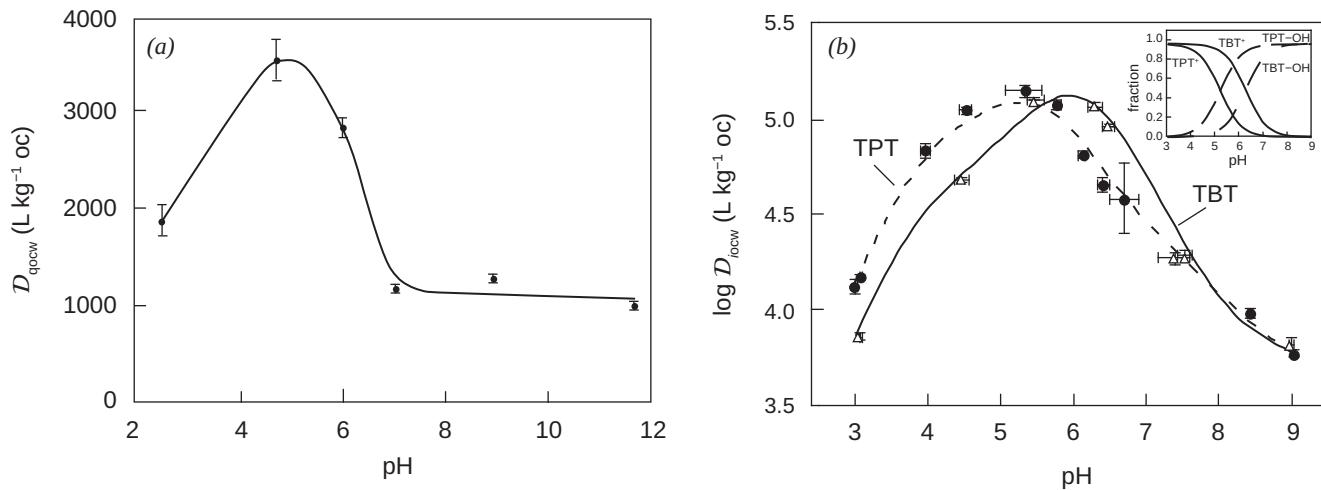
by the delocalization of the negative charge (see Chapter 4; Fig. 4.5) leading to a “smeared” charge. The anion can thus be better accommodated in the NOM as compared to compounds carrying a more localized charge, such as some of the chlorinated phenols. Furthermore, Tülp et al. (2009) found that for sorption to Pahokee peat at pH 5.9, independent of the structure of the acid, the influence of cations such as  $\text{Ca}^{2+}$  had a moderate effect (i.e., a factor of 2 to 3 increase in  $K_{\text{icw}}^{\text{A}^-}$  between 1 and 100 mM). The possibility of ion pair formation with the anionic sorbate forming a neutral or even cationic species more inclined to sorb can explain this increasing sorption found with increasing concentration of positively charged cations (e.g.,  $\text{Ca}^{2+}$ ). Also, such cations may complex with the anionic moieties of the NOM, reducing the negative charge and the electrostatic repulsion of the anionic sorbate (Westall et al., 1999).

We should point out that when describing the sorption of an organic anion over a large pH-range, the pH dependence of  $K_{\text{icw}}^{\text{A}^-}$  has to be taken into account (Jafvert, 1990), particularly for highly acidic, amphiphilic compounds that are present exclusively as anions at ambient pH. A prominent example involves the linear alkylbenzene sulfonates (LASs) that are widely used detergents (see Chapter 3). For these compounds, sorption to sediments (primarily to the organic matter present) decreased by almost an order of magnitude between pH 5 and 10 (Westall et al., 1999). Furthermore, sorption isotherms were nonlinear ( $n_i < 1$  in Eq. 12-1). These results make sense when considering that many NOM constituents (as well as other surface sites, see Chapter 14) become increasingly negatively charged with increasing pH, thus making it more difficult to accommodate a negatively charged sorbate. Furthermore, nonlinear sorption of the anion may be explained by the limited number of sites for accommodation of negatively charged species as well as the increasing electrostatic repulsion with increasing sorbate concentration.

As such, many factors need to be considered when dealing with the sorption of anionic species. Nevertheless, for practical purposes, we may use Eq. 13-26 to describe the sorption of weak organic acids to SOM over the ambient pH-range and for typical bivalent cation concentrations encountered in freshwater environments (e.g., 10 mM). Furthermore, for compounds that do not form strong complexes with cations, we may assume that the sorption coefficient of the anion is a factor of 10 to maximally 100 smaller than for the corresponding neutral species (Tülp et al., 2009). Finally, although little data on the sorption of organic anions to polar NOMs such as fulvic acids is available, in many cases we may neglect anion sorption to such sorbents in light of the fact that the neutral species already exhibit rather small sorption coefficients.

### Sorption to NOM of Compounds Forming Cationic Species (Organic Bases)

Sorption of the cationic form of an organic base to negatively charged sites on NOM can dominate the overall sorption of the compound, at least over a certain pH range. Examples of such cases include sorption on NOM of aliphatic and aromatic amines (e.g., Davis 1993; Lee et al., 1997; Sibley and Pedersen, 2008; Richter et al., 2009; Droege and Goss, 2012 and 2013), N-heterocyclic compounds (Brownawell et al., 1990; Nielsen et al., 1997; Zachara et al., 1986), and triorganotin compounds (Arnold et al., 1998; Berg et al., 2001). Because of the limited number of cation exchange sites present in NOM, sorption isotherms of the cationic species will be nonlinear and competition with other cations present may occur (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ).

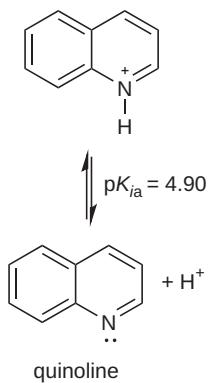


**Figure 13.9** Sorption of organic bases to Aldrich Humic Acid at various pH values. (a) Plot of  $D_{qocw}$  of quinolone versus pH with fit with Eq. 13-28 above pH 7 and Eq. 13-29 below pH 7; data from Nielsen et al. (1997). (b)  $D_{iocw}$  of TBT and TPT as a function of pH. The lines were calculated using the model described by Arnold et al. (1998). The insert shows the speciation of TBT and TPT as a function of pH.

Furthermore, the number of negatively charged sites present in a NOM is strongly pH-dependent. Hence, the quantitative description of sorption of organic cations to NOM and other natural sorbents is a rather complex task, so, here, we confine ourselves only to some qualitative observations. Some more quantitative considerations will be given in Chapter 14 (Section 14.3).

Consider the pH-dependence (Fig. 13.9a) of the sorption of quinoline (subscript q, see margin for structure) to Aldrich humic acid. In this case, the  $D_{qocw}$  value shows a maximum at around pH 5, corresponding to the  $pK_{ia}$  of the compound as well as to the  $pK_a$ s of the carboxyl groups present in Aldrich humic acid. At high pHs (i.e.,  $\text{pH} > 7$ ), when virtually all of the quinoline is in its nonionic form, the overall sorption is primarily determined by partitioning of this neutral species ( $Q$ ) to Aldrich humic acid:

$$D_{qocw} \cong \frac{[Q]_{\text{oc}}}{[Q]_w} = K_{qocw} \quad \text{at high pHs} \quad (13-28)$$

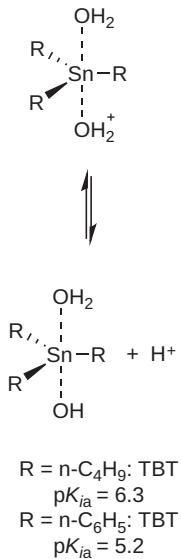


With decreasing pH, the fraction of the cationic form of quinoline ( $\text{QH}^+$ ) increases and the sorbed cations increase too. However, at the same time, the number of negatively charged moieties in Aldrich humic acid decreases, leading to the observed sorption maximum at pH 5. Now, the partitioning reflects:

$$D_{qocw} \cong \frac{[Q]_{\text{oc}} + [\text{QH}^+]_{\text{oc}}}{[Q]_w + [\text{QH}^+]_w} \quad \text{at pH below 7} \quad (13-29)$$

In this case, due to electrostatic interactions, the maximum  $D_{qocw}$  is about a factor of 4 larger than the  $K_{qocw}$  for partitioning of the neutral species.

An even more pronounced case of pH-dependence involves the sorption to Aldrich humic acid of the two biocides, tributyltin (TBT) and triphenyltin (TPT). Because



of their high toxicity to aquatic organisms, TBT and TPT are of considerable environmental concern (Fent, 1996). Again, sorption varies strongly with pH (Fig. 13.9b). As the pH increases, the  $D_{\text{icw}}$  increases by more than a factor of 10 as compared to the neutral species (TBTOH, TP TOH). In fact, even at pH 8, where the abundance of  $\text{TBT}^+$  or  $\text{TPT}^+$  is very small, sorption of the cation was still found to dominate the overall sorption (Arnold et al., 1998).

These findings concerning the sorption of triorganotin biocides on NOM can be rationalized by postulating the formation of an inner sphere complex (i.e., by ligand exchange of a water molecule) between the tin atom of the charged species and negatively charged ligands (i.e., carboxylate, phenolate groups) present in the humic acid. For more details, we refer to Arnold et al. (1998). Other examples illustrating the domination of cation binding to NOM include the sorption of the antimicrobials clarithromycin to Elliot humic acid (Sibley and Pedersen, 2008) and sulfathiazole to Leonardite humic acid (Richter et al., 2009).

We conclude this section by noting that sorption of charged species to NOM is generally fast and reversible, provided that no real chemical reactions take place that lead to the formation of covalent bonds (i.e., to “bound residues”). This conclusion is based on experimental data and on the assumption that in aqueous solution more polar sites on NOM are more easily accessible as compared to more hydrophobic domains. Therefore, for charged species we may assume that equilibrium is established within relatively short time periods. Hence, in the case of TBT and TPT, contaminated sediments may represent an important source for these highly toxic compounds in the overlying water column (Berg et al., 2001).

## 13.4

### Questions and Problems

Special note: Problem solutions are available on the book’s website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

#### Questions

##### Q 13.1

- (a) Why is natural organic matter (NOM) such an important sorbent for the majority of organic pollutants in aquatic as well as in terrestrial systems?
- (b) What is the general make-up of NOM and what are its most important properties with respect to the sorption of organic compounds? What is (are) the driving force(s) for sorption to NOM from water? From air?
- (c) What is the difference between dissolved organic matter (DOM) and particulate organic matter (POM), e.g., soil and sediment organic matter (SOM)? Does it make sense to strictly distinguish between POM and DOM?
- (d) What properties of NOM may lead to nonlinear sorption isotherms?

**Q 13.2**

Besides NOM, which other organic sorbents may play an important role in soils and sediments? aquifers? surface waters? Which of these sorbents may lead to nonlinear sorption isotherms? Why?

**Q 13.3**

How is the  $K_{iocw}$  value of a given neutral organic compound defined? How large is the variability its  $K_{iocw}$  for (a) different SOMs and (b) different DOMs? Which are the major (structural) factors of SOM or DOM that cause this variability? Which NOM can be used as a representative SOM when discussing sorption properties?

**Q 13.4**

Kile et al. (1995) reported numerous  $K_{iocw}$  values of 1,2-dichlorobenzene determined for uncontaminated soil–water and sediment–water partitioning in the range between 300 and 500 L kg<sup>-1</sup> oc. However, for heavily contaminated soils and sediments, these authors found significantly higher  $K_{iocw}$  values (700 – 3000 L kg<sup>-1</sup> oc), although isotherms were linear over a wide concentration range. Try to explain these findings.

**Q 13.5**

How do (a) pH, (b) ionic strength, and (c) temperature affect the sorption of *neutral* organic compounds to dissolved and particulate organic matter? Give examples of compound–organic phase combinations in which you expect (i) a minimum and (ii) a maximum effect.

**Q 13.6**

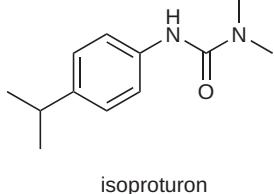
Why is it more difficult to interpret the coefficients of the pp-LFERs derived for NOM–water partitioning (Table 13.3) as compared to organic solvent–water partitioning discussed in Chapter 10?

**Q 13.7**

What is the major difference between the sorption of neutral and the sorption of charged organic species to NOM? Describe qualitatively the pH-dependence of the NOM–water partitioning of (a) an organic acid and (b) an organic base.

**Problems****P 13.1 Estimating the  $K_{iocw}$  Value of Isoproturon from  $K_{iocw}$ 's of Structurally Related Compounds**

Urea-based herbicides are widely used despite the concern that they may contaminate groundwater of agricultural regions (Johnson et al., 1998). You have been asked to evaluate the sorption behavior of the herbicide Isoproturon ( $V_i = 1.78$ ,  $E_i = 1.20$ ,  $S_i = 1.54$ ,  $A_i = 0.39$ ,  $B_i = 0.88$ ) in soils.



As you are unable to find the  $K_{i\text{ocw}}$  of this specific compound, you collect data on some structurally related compounds:

	$\log K_{i\text{ow}}$	$\log K_{i\text{ocw}}$ (L kg <sup>-1</sup> oc)
4-methyl	1.33	1.51
3,5-dimethyl	1.90	1.73
4-chloro	1.94	1.95
3,4-dichloro	2.68	2.40
3-fluoro	1.37	1.73
4-methoxy	0.83	1.40

Using the collected data, estimate a  $K_{i\text{ocw}}$  for Isoproturon. Did you use all the compounds for deriving an sp-LFER? Why or why not? Compare this value with the one estimated by using the pp-LFER Eq. 13-9 in Table 13.3.

### P 13.2\* What Fraction of Atrazine is Present in Dissolved Form?

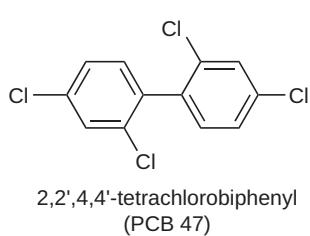
Our companion compound atrazine is still one of the most widely used herbicides. Estimate the fraction of total atrazine present in truly dissolved form (a) in lake water exhibiting 2 mg POC L<sup>-1</sup>, (b) in marsh water containing 100 mg solids L<sup>-1</sup>, if the solid's organic carbon content is 20%, and (c) in an aquifer exhibiting a porosity of 0.2 by volume, a density of the minerals present of 2.5 kg L<sup>-1</sup>, and an organic carbon content of 0.5%. Assume that partitioning to NOM is the major sorption mechanism. You can find  $K_{i\text{ocw}}$  values for atrazine in Fig. 13.2. Comment on which values you select for your calculations.

### P 13.3 Is Sorption to Dissolved Organic Matter Important for the Environmental Behavior of Phenanthrene and Benzo(a)pyrene?

Somebody claims that for our companion compounds phenanthrene and benzo(a)pyrene (see structures in Table 3.1 and Abraham parameters in Table 7.3 or Appendix C), sorption to DOM is generally unimportant in the environment. Is this statement correct? Use Eq. 13-17 (Table 13.3) to estimate  $K_{i\text{ocw}}$  for sorption to DOM. Comment on your assumptions.

### P 13.4 Assessing the Speciation of a PCB-Congener in a Sediment–Pore Water System

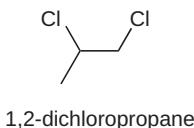
Consider a surface sediment exhibiting a porosity  $\phi = 0.8$ , solids with average density  $\rho_s = 2.0 \text{ kg L}^{-1}$  solid, a particulate organic carbon content of 5%, and a DOC concentration in the pore water of 20 mg DOC L<sup>-1</sup>. Estimate the fractions of the total 2,2',4,4'-tetrachlorobiphenyl (PCB 47,  $V_i = 1.81$ ,  $L_i = 8.23$ ,  $S_i = 1.48$ ,  $A_i = 0$ ,  $B_i = 0.15$ ) present in truly dissolved form in the porewater and associated with the



pore water DOM. Assume that absorption into the organic material is the major sorption mechanism. Estimate the  $K_{i\text{ocw}}$  values using the respective pp-LFER given in Table 13.3, i.e., Eqs. 13-14 (SOM) and 13-17 (DOM).

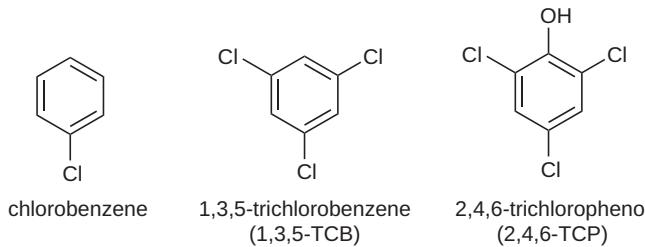
### P 13.5 Evaluating the Transport of 1,2-Dichloropropane in Groundwater

A group of investigators from the USGS recently discovered a large plume of the soil fumigant 1,2-dichloropropane (DCP) ( $\log K_{i\text{ow}} = 2.28$ ; Montgomery, 1997;  $V_i = 0.776$ ,  $L_i = 2.84$ ,  $S_i = 0.63$ ,  $A_i = 0$ ,  $B_i = 0.17$ ) in the groundwater flowing away from an airfield. The aquifer through which the DCP plume is passing has been found to have a porosity of 0.3. The aquifer solids consist of 95% quartz (density  $2.65 \text{ g mL}^{-1}$ ; surface area  $0.1 \text{ m}^2 \text{ g}^{-1}$ ), 4% kaolinite (density  $2.6 \text{ g mL}^{-1}$ ; surface area  $10 \text{ m}^2 \text{ g}^{-1}$ ), 1% iron oxides (density  $3.5 \text{ g mL}^{-1}$ ; surface area  $50 \text{ m}^2 \text{ g}^{-1}$ ), and organic carbon content of 0.2%. What retardation factor [ $(R_{fi} (f_{iw}^{-1}, \text{ see Eq. 12-18})$ ] do you expect at minimum (assumption that only SOM is responsible for sorption) for DCP transport in the plume assuming that sorptive exchanges are always at equilibrium?



### P 13.6 Estimating the Retardation of Organic Compounds in an Aquifer from Breakthrough Data of Tracer Compounds

Using tritiated water as conservative tracer, an average retardation factor,  $R_{fi} (f_{iw}^{-1}, \text{ see Eq. 12-18})$  of about 10 was determined for chlorobenzene in an aquifer. (a) Assuming this retardation factor only reflects absorption to the aquifer solids' POM, what is the average organic carbon content ( $f_{oc}$ ) of the aquifer material if its minerals have a density of  $2.5 \text{ kg L}^{-1}$  and if the porosity is 0.33? (b) Estimate the  $R_{fi}$  values of 1,3,5-trichlorobenzene (1,3,5-TCB) and 2,4,6-trichlorophenol (2,4,6-TCP) in this aquifer ( $\text{pH} = 7.5$ ,  $T = 10^\circ\text{C}$ ) by assuming that absorption into the SOM present is the major sorption mechanism. Why can you expect to make a better prediction of  $R_{fi}$  for 1,3,5-TCB compared to 2,4,6-TCP? You can find all relevant information in Appendix C (website). Comment on all assumptions that you make.



### P 13.7\* Evaluating the Concentration Dependence of Phenanthrene Sorption to Soils and Sediments Containing Black Carbon (BC)

Huang et al. (1997) measured sorption isotherms for our companion phenanthrene ( $K_{i\text{ow}} = 4.57$ ; use sp-LFER in Table 13.2 to estimate  $K_{i\text{ocw}}$ ) for 21 soils and sediments. All isotherms were nonlinear with Freundlich exponents  $n_i$  between 0.65 and 0.9. For example, for a top soil (Chelsea I) and for a lake sediment (EPA-23), interpolating their isotherm data yields the following “observed” sorbed concentrations,

$C_{is}$ , in equilibrium with dissolved concentrations,  $C_{iw}$ , of  $1 \mu\text{g L}^{-1}$  and  $100 \mu\text{g L}^{-1}$ , respectively:

$C_{iw} (\mu\text{g L}^{-1})$	$C_{is} (\mu\text{g kg}^{-1} \text{ solid})$	
	Chelsea-I	EPA-23
1	3,200	1,700
100	91,000	51,000

For Chelsea I soil,  $f_{oc}$  was measured as  $0.056 \text{ kg oc kg}^{-1} \text{ solid}$ , and for the EPA-23 lake sediment as  $0.026 \text{ kg oc kg}^{-1} \text{ solid}$ . The  $f_{bc}$  values were not measured, but in sediment samples, it is typically between 1 and 10% of the  $f_{oc}$  (Gustafsson and Gschwend, 1998). Use the full range of 1 to 10% for both cases to see the possible impact of adsorption to black carbon, i.e.,  $f_{bc} = 0.00056$  to  $0.0056 \text{ kg bc kg}^{-1} \text{ solid}$ . Use an  $n_i$  value of 0.7 in Eq. 13-25. Finally, for estimating  $K_{ibcw}$  values for planar compounds use the relationship that can be derived from data published by Xia and Ball, (1999) and Bucheli and Gustafsson, (2000):

$$\log K_{ibcw} (\text{L kg}^{-1} \text{bc}) \approx 1.6 \log K_{iow} - 1.4 \quad (r^2 = 0.98; n = 9)$$

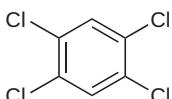
### P 13.8 Evaluating the Concentration Dependence of Equilibrium Sorption of 1,2,4,5-Tetrachlorobenzene (TeCB) to an Aquitard Material

Xia and Ball (1999) measured sorption isotherms for a series of chlorinated benzenes and PAHs for an aquitard material ( $f_{oc} = 0.015 \text{ kg oc kg}^{-1} \text{ solid}$ ) from a formation believed to date from the middle to late Miocene. Therefore, compared to soils or recent sediment POM, the organic matter present in this aquitard material can be assumed to be fairly mature and/or contain char particles from prehistoric fires. A nonlinear isotherm was found for TeCB (fitting Eq. 12-3) and the following Freundlich parameters were reported:  $K_{TeCBF} = 128 \text{ (mg g}^{-1} \text{ solid)(mg mL}^{-1}\text{)}^{-n_{TeCB}}$  and  $n_{TeCB} = 0.80$ . For partitioning of TeCB to this material (linear part of the isotherm at higher concentrations), the authors found a  $K_{TECBocw}$  value of  $4.2 \times 10^4 \text{ L kg}^{-1} \text{ oc}$ .

(a) Calculate the apparent  $K_{TECBocw}$  values of TeCB for the aquitard material for aqueous TeCB concentrations of  $C_{iw} = 1, 10, \text{ and } 100 \mu\text{g L}^{-1}$  using the Freundlich isotherm previously given. Compare these value of the  $K_{TECBocw}$  values previously given for POM–water partitioning. Comment on the result.

(b) At what aqueous TeCB concentration ( $\mu\text{g L}^{-1}$ ) would the contribution of adsorption to the overall  $K_{TECBocw}$  be equal to the contribution of absorption, (partitioning)?

*Note:* When using Freundlich isotherms, be aware that the numerical value of  $K_{TECB}$  F depends nonlinearly on the unit in which the concentration in the aqueous phase is expressed. Hence for solving this problem, you may first convert  $\mu\text{g L}^{-1}$  to  $\text{mg mL}^{-1}$



1,2,4,5-tetrachlorobenzene  
(TeCB)

or you may express the Freundlich equation using, for example,  $\mu\text{g kg}^{-1}$  and  $\mu\text{g L}^{-1}$ , respectively:

$$\begin{aligned} K_{\text{TeCBF}} &= 128(10^6 \mu\text{g kg}^{-1})(10^6 \mu\text{g L}^{-1})^{-0.8} \\ &= 128 \times 10^6 \times 10^{4.8} (\mu\text{g kg}^{-1})(\mu\text{g L}^{-1})^{-0.8} \\ &= 2030(\mu\text{g kg}^{-1})(\mu\text{g L}^{-1})^{-0.8} \end{aligned}$$

## 13.5

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