

# Chapter 12

## GENERAL INTRODUCTION TO SORPTION PROCESSES

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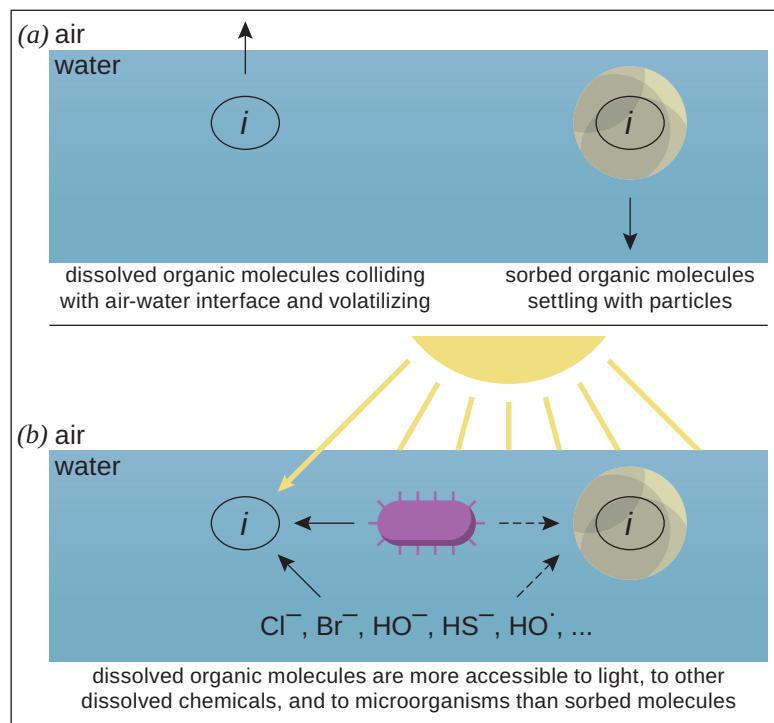
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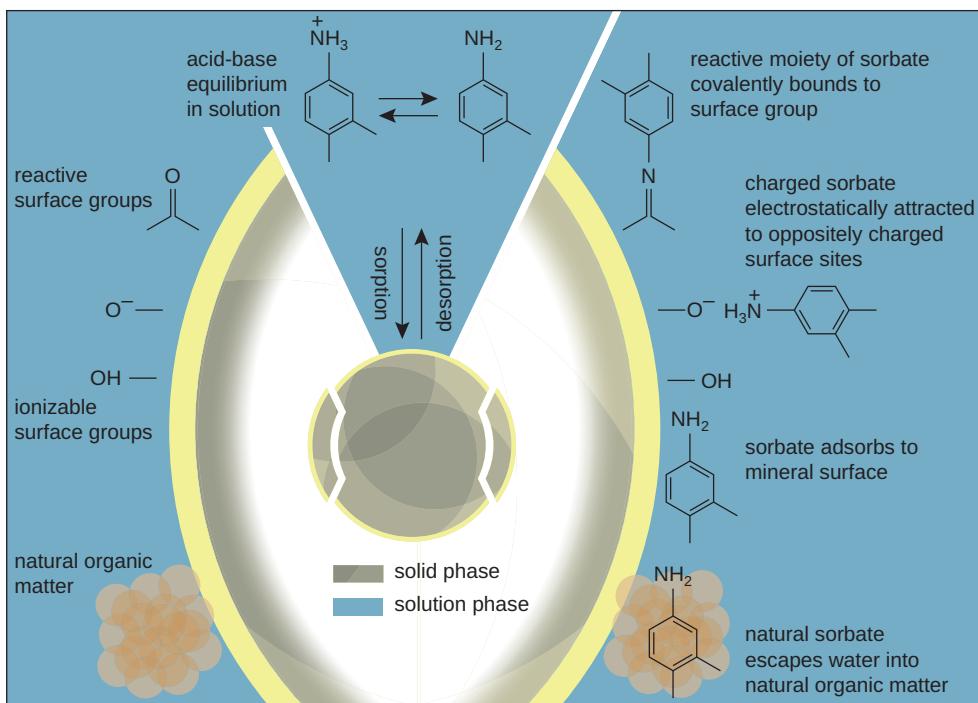
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## 12.1 Introduction

Based on our previous discussions of how molecular interactions affect partitioning, it makes sense that structurally identical molecules behave very differently if they are in the gas phase or surrounded by water molecules and ions, as opposed to clinging onto the exterior of solids or buried within a solid matrix. Therefore, sorption to condensed phases from water or air is extremely important because it can dramatically affect the fate and impacts of chemicals in the environment (see Fig. 12.1). For example, the environmental transport of water-borne molecules obviously differs from the movements of the same kind of molecules attached to particles that settle. Also, transport of a given compound in porous media such as soils, sediments, and aquifers is strongly influenced by the compound's tendency to sorb to the various components of the solid matrix. Additionally, only dissolved molecules are available to collide with the interfaces of other environmental compartments, such as the atmosphere; thus, phase transfers are controlled by the dissolved species of a chemical (Chapter 19). Similarly, since molecular transfer is a prerequisite for the uptake of organic pollutants by organisms, the *bioavailability* of a given compound and thus its rate of biotransformation or its toxic effect(s) are affected by sorption processes (Chapter 16). Furthermore, some sorbed molecules are substantially shaded from incident light. Therefore, these molecules may not experience direct photolysis processes (Chapter 24). Moreover, when present inside solid matrices, they may never come in contact with short-lived, solution-phase photooxidants like OH-radicals. Finally, since the chemical nature of aqueous solutions and solid environments differ greatly (e.g., pH, redox conditions), various chemical reactions including hydrolysis or redox reactions may occur at very



**Figure 12.1** Examples of environmental partitioning and reaction processes that depend on the phase in which the organic molecule is present. (a) Dissolved species may participate directly in air-water exchange while sorbed species may settle with solids. (b) Dissolved species may react at different rates as compared to their sorbed counterparts due to differential access of other dissolved and solid phase “reactants.”



**Figure 12.2** Various sorbent–sorbate interactions possibly controlling the association of a chemical (3,4-dimethylaniline) with natural solids present in an aquatic system.

different rates in the sorbed and dissolved states. Hence, we must understand solid–solution and solid–gas phase exchange phenomena before we can quantify virtually any other process affecting the fates of organic chemicals in the environment.

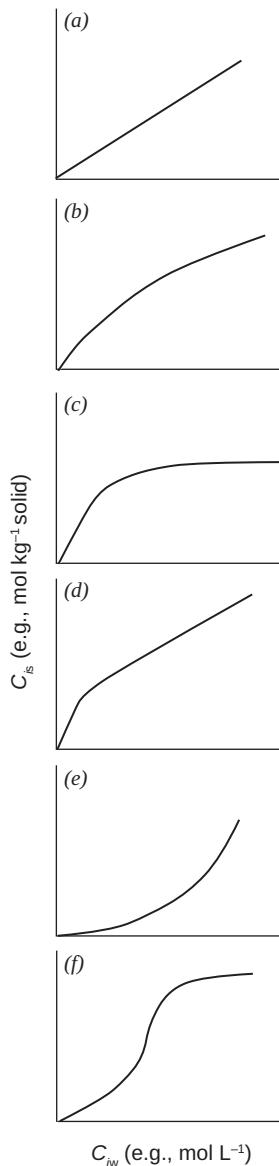
Unfortunately, when we are dealing with natural environments, sorption is often not an exchange between one homogeneous solution or vapor phase and a single, well-defined condensed medium, as we discussed in Part II. Rather, in a given environmental system, some combination of interactions governs the association of a particular chemical (called the *sorbate*) with any particular solid or mixture of solids (called the *sorbent(s)*). Consider the case of 3,4-dimethylaniline in an aquatic system (Fig. 12.2). This compound is a weak base with  $pK_{\text{ia}} = 5.28$ . As such, it reacts in aqueous solution to form some 3,4-dimethyl ammonium cations. For the fraction of molecules that remain uncharged, this organic compound may escape the water by penetrating the natural organic matter present in the system. Additionally, such a nonionic molecule may displace water molecules from the region near a mineral surface to a minor extent and be held there by London dispersive and polar interactions (see Chapter 11). These two types of sorption mechanisms are non-specific and will operate for any organic chemical and any natural solid. Additionally, since the sorbate is ionizable in the aqueous solution, then electrostatic attraction to specific surface sites exhibiting the opposite charge will promote sorption of the ionic species (Chapter 14). Finally, should the sorbate and the sorbent exhibit mutually reactive moieties (e.g., in Fig. 12.2 a carbonyl group on the sorbent and an amino group on the sorbate), some portion of the chemical may actually become bonded to the solid. All of these interaction mechanisms operate simultaneously, and the combination that dominates the overall solution–solid distribution depends on the structural properties of the organic sorbate and the solid sorbent of interest.

## 12.2

## Sorption Isotherms and the Solid–Water Equilibrium Distribution Coefficient ( $K_{id}$ )

### Qualitative Considerations

When we are interested in describing the *equilibrium* distribution of a chemical among the solids and solution present in any particular volume of an aquatic environment, we begin by considering how the total sorbed concentration of the chemical,  $C_{is}$  (e.g., mol kg<sup>-1</sup> solid), depends on its concentration in the solution,  $C_{iw}$  (e.g., mol L<sup>-1</sup>). The relationship of these two concentrations is commonly referred to as a *sorption isotherm*. The name “isotherm” indicates this sorption relationship only applies at a constant temperature. In the following discussion, we only consider sorption from aqueous solution, but we note that the same general considerations also hold for sorption from the gas phase, i.e., from air (one can just substitute the subscript “w” by “a”).



**Figure 12.3** Various types of observed relationships between concentrations of a chemical in the sorbed state,  $C_{is}$ , and the dissolved state,  $C_{iw}$ . Similar relationships apply to the sorption of gaseous compounds to solid sorbents (substitute  $C_{iw}$  by  $C_{ia}$ ).

Experimentally determined sorption isotherms exhibit a variety of shapes for different combinations of sorbates and sorbents (Fig. 12.3). As used in Chapter 11 when discussing adsorption to surfaces, the simplest case (Fig. 12.3a) is the one in which the affinity of the sorbate for the sorbent remains the same over the observed concentration range; thus, it is called the *linear* isotherm case. This case applies to situations where partitioning *into* a homogeneous organic phase is dominating the overall sorption or concentrations are sufficiently low so that the strongest adsorption sites are far from being saturated. The second type of isotherm behavior (Figs. 12.3b and c) reflects those situations in which at higher sorbate concentrations, less additional molecules sorb to the sorbent, such as when binding sites become filled or the remaining sites are less attractive to the sorbate molecules. In the extreme case (Fig. 12.3c), above some maximum  $C_{is}$  value, all sites are “saturated,” and no more additional sorption is possible. Isotherms of the type shown in Figs. 12.3b and c describe experimental studies of *adsorption* processes to organic (e.g., activated carbon) and inorganic (e.g., clay mineral) surfaces. Of course, in a soil or sediment, more than one important sorbent may be present. Therefore, the overall sorption isotherm may reflect the superposition of several individual isotherms that are characteristic for each specific type of sorbent. When such a mixed case involves an adsorbent exhibiting a limited number of sites with a high affinity for the sorbate that dominates the overall sorption at low concentrations (e.g., soot, clay mineral; type (c) isotherm), plus a partitioning process predominating at higher concentrations (e.g., into natural organic matter; type (a) isotherm), then a mixed isotherm best describes the data (Figs. 12.3b or d).

Another case encountered less frequently in experimental studies involves the situation in which previously sorbed molecules lead to a modification of the sorbent, which favors further sorption (Fig. 12.3e). Studies reporting such sorbent modifications usually involve anionic or cationic surfactants as sorbates. In some of these cases, a sigmoidal isotherm shape (Fig. 12.3f) has been observed, indicating that the sorption promoting effect only starts after a certain loading of the sorbent. In summary, depending on the composition of a natural bulk sorbent and on the chemical nature of the sorbate, multiple sorption mechanisms can act simultaneously, and the

resulting isotherms may have a variety of different shapes. However, it is not possible to prove a particular sorption mechanism applies from the shape of the isotherm. Instead, the isotherm type and its degree of nonlinearity must be consistent with the sorption mechanism(s) prevailing in a given situation.

### Quantitative Description of Sorption Isotherms

A very common mathematical approach for fitting experimentally determined sorption data using a minimum of adjustable parameters employs an *empirical* relationship known as the *Freundlich* isotherm:

$$C_{is} = K_{iF} C_{iw}^{n_i} \quad (12-1)$$

where  $K_{iF}$  is the Freundlich constant or capacity factor (e.g., with units in Eq. 12-1 of  $(\text{mol kg}^{-1})(\text{mol L}^{-1})^{-n_i}$ ) and  $n_i$  is the Freundlich exponent. For a correct thermodynamic treatment of Eq. 12-1, we would always have to use dimensionless partitioning constants of compound  $i$  in both the sorbed and aqueous phase in order to obtain a dimensionless  $K_{iF}$ . However, in practice,  $C_{is}$  and  $C_{iw}$  are expressed in a variety of concentration units. Therefore,  $K_{iF}$  is commonly reported in the corresponding units, which also means that for  $n_i \neq 1$ ,  $K_{iF}$  depends nonlinearly on the units in which  $C_{iw}$  is expressed.

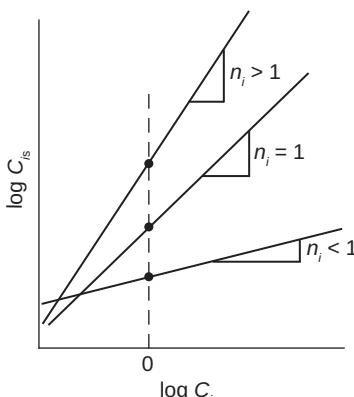
The relationship in Eq. 12-1 assumes that multiple types of sorption sites act in parallel, with each site type exhibiting a different sorption free energy and total site abundance. The Freundlich exponent is an index of the diversity of the free energies associated with the sorption of the solute by multiple components of a heterogeneous sorbent (Weber and Digiano, 1996). For the special case of  $n_i = 1$ , the isotherm is linear (Fig. 12.3a), and we denote constant sorption free energies at all sorbate concentrations with a concentration-independent distribution coefficient  $K_{id}$  (which is often also referred to as the partition coefficient and denoted as  $K_{ip}$ ):

$$C_{is} = K_{id} C_{iw} = K_{ip} C_{iw} \quad (12-2)$$

When  $n_i < 1$ , the isotherm is concave downward, and one infers that added sorbates are bound with weaker and weaker free energies (Fig. 12.3b). When  $n_i > 1$ , the isotherm is convex upward, and we infer that more sorbate present in the sorbent actually enhances the free energies of further sorption (Fig. 12.3e).

$K_{iF}$  and  $n_i$  can be deduced from experimental data by linear regression of the logarithmic form of Eq. 12-1 (Fig. 12.4):

$$\log C_{is} = n_i \log C_{iw} + \log K_{iF} \quad (12-3)$$



**Figure 12.4** Graphic representation of the Freundlich isotherm Eq. 12-3 for the three cases  $n_i > 1$ ,  $n_i = 1$ , and  $n_i < 1$ .  $n_i$  and  $\log K_{iF}$  are obtained from the slope ( $n_i$ ) and intercept ( $\log K_{iF}$  indicated by the points at  $\log C_{iw} = 0$ ) of the regression line.

The units of  $K_{iF}$  again depend on the units of  $C_{iw}$  and on the exponent  $n_i$  (Eq. 12-1). If a given isotherm is not well described by Eq. 12-3, then some assumption behind the Freundlich multi-site conceptualization is not valid. For example, if only a limited number of the total sorption sites become saturated (as in Fig. 12.3c), then  $C_{is}$  cannot

increase indefinitely with increasing  $C_{iw}$ . In this case, the *Langmuir* isotherm may be a more appropriate model:

$$C_{is} = \frac{\Gamma_{\max} K_{iL} C_{iw}}{1 + K_{iL} C_{iw}} \quad (12-4)$$

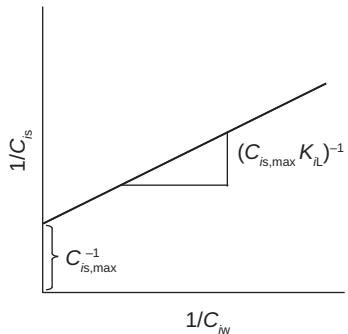
where  $\Gamma_{\max}$  represents the total number of surface sites per mass of sorbent. In the ideal case,  $\Gamma_{\max}$  would be equal for all sorbates. However, in reality,  $\Gamma_{\max}$  may vary somewhat between different compounds (e.g., because of differences in sorbate size). Therefore, it usually represents the maximum achievable surface concentration of a given compound  $i$  (i.e.,  $\Gamma_{\max} = C_{is,\max}$ , and thus has the same units). The constant  $K_{iL}$ , which is commonly referred to as the Langmuir constant, is defined as the equilibrium constant of the sorption reaction:



This approach using a constant  $K_{iL}$  implies a constant sorbate affinity for all surface sites exists. To derive  $K_{iL}$  and  $C_{is,\max}$  from experimental data, one can fit  $1/C_{iw}$  versus  $1/C_{is}$ :

$$\frac{1}{C_{is}} = \left( \frac{1}{C_{is,\max} K_{iL}} \right) \frac{1}{C_{iw}} + \frac{1}{C_{is,\max}} \quad (12-5)$$

and use the slope and intercept to extract estimates of the isotherm constants (Fig. 12.5).



**Figure 12.5** Graphic representation of the Langmuir isotherm Eq. 12-5.  $C_{is,\max}$  and  $K_{iL}$  can be derived from the slope and intercept of the regression line.

Many cases exist, such as type (d) and (f) isotherms in Fig. 12.3, in which the relationship between sorbed concentrations and dissolved concentrations covering a large concentration range cannot be described solely by a linear, a Freundlich, or even a Langmuir equation. In these cases, a combination of equations may need to be applied (e.g., Weber et al., 1992; Xia and Ball, 1999; Xing and Pignatello, 1997). Among these *distributed reactivity models*, the simplest case involves a pair of sorption mechanisms involving absorption (e.g., linear isotherm with partition coefficient,  $K_{ip}$ ) and site-limited adsorption (e.g., Langmuir isotherm), and the resultant combined equation is:

$$C_{is} = K_{ip} C_{iw} + \frac{C_{is,\max} K_{iL} C_{iw}}{1 + K_{iL} C_{iw}} \quad (12-6)$$

Another equation that fits data from sediments known to contain black carbon (e.g., soot) uses a combination of a linear and a Freundlich isotherm (Accardi-Dey and Gschwend, 2002):

$$C_{is} = K_{ip} C_{iw} + K_{iF} C_{iw}^{n_i} \quad (12-7)$$

These *dual-mode* models have been found to be quite good at fitting experimental data for natural sorbents that contain components exhibiting a limited number of

highly active adsorption sites in addition to components into which organic compounds may absorb (Huang et al., 1997; Xia and Ball, 1999; Xing and Pignatello, 1997). At low concentrations, the Langmuir or the Freundlich term may dominate the overall isotherm, while at high concentrations (e.g.,  $K_{iL}C_{iw} \gg 1$ ), the absorption term dominates.

### The Solid–Water Distribution Coefficient, $K_{id}$

To assess the extent to which a compound is associated with solid phases in a given system at equilibrium, we need to know the ratio of the compound's total equilibrium concentrations in the solids and in the aqueous solution. As mentioned earlier, we denote this solid–water “distribution” coefficient as  $K_{id}$  (e.g., in L kg<sup>-1</sup> solid):

$$K_{id} = \frac{C_{is}}{C_{iw}} \quad (12-8)$$

When writing these natural solid–water distribution or partition coefficients ( $K_{ip}$ ), we use a somewhat different subscript terminology than we introduced for air–water or organic solvent–water partitioning; that is, we do not indicate the involvement of a water or air phase by using a subscript “w” or “a”, respectively.

When dealing with nonlinear isotherms (i.e., if  $n_i$  in Eq. 12-1 is substantially different from 1), the value of this ratio may only apply at the given solute concentration. Inserting Eq. 12-1 into Eq. 12-8, we can see how  $K_{id}$  varies with the sorbate concentration:

$$K_{id} = K_{iF} C_{iw}^{n_i - 1} \quad (12-9)$$

For practical applications, one often assumes that  $K_{id}$  is constant over some concentration range. To examine how reasonable such a simplification is, we can differentiate  $K_{id}$  with respect to  $C_{iw}$  in Eq. 12-8 and rearrange the result to find:

$$\frac{dK_{id}}{K_{id}} = (n_i - 1) \frac{dC_{iw}}{C_{iw}} \quad (12-10)$$

Therefore, the assumption that  $K_{id}$  is constant is equivalent to presuming: (1) the overall process is either described by a linear isotherm ( $n_i - 1 = 0$ ), or (2) the relative concentration variation, ( $dC_{iw}/C_{iw}$ ), is sufficiently small, so that when multiplied by  $(n_i - 1)$ , the relative  $K_{id}$  variation, ( $dK_{id}/K_{id}$ ), is also small. For example, if the sorbate concentration range is less than a factor of 10, when multiplied by  $(n_i - 1)$  with an  $n_i$  value of 0.7, then the solid–water distribution coefficient would vary by less than a factor of 3.

*The Complex Nature of  $K_{id}$ .* The prediction of  $K_{id}$  for any particular combination of organic chemical and solids in the environment can be quite complicated, but, fortunately, many situations can be reduced to fairly simple limiting cases. We begin by emphasizing that the way we defined  $K_{id}$  means that we may have lumped together

several different “forms” of a given compound  $i$  in each phase. For example, referring again to Fig. 12.2, we recognize that the total concentration of the 3,4-dimethylaniline in the sorbed phase must combine the contributions of molecules in many different sorbed forms. Additionally, the solution even contains both a neutral and a charged species of this chemical. In a conceptual way, the distribution ratio for this case would have to be written as:

$$K_{id} = \frac{C_{ioc}f_{oc} + C_{imin}A_{surf} + C_{iex}\sigma_{surf\ ex}A_{surf} + C_{irxn}\sigma_{surf\ rxn}A_{surf}}{C_{iw,\text{neut}} + C_{iw,\text{ion}}} \quad (12-11)$$

where  $C_{ioc}$  is the concentration of sorbate  $i$  associated with the natural organic matter (expressed as organic carbon) present ( $\text{mol kg}^{-1}$  oc),

$f_{oc}$  is the weight fraction of solid which is natural organic matter (expressed as organic carbon, i.e.,  $\text{kg oc kg}^{-1}$  solid),

$C_{imin}$  is the concentration of sorbate  $i$  associated with the mineral surface ( $\text{mol m}^{-2}$ ),

$A_{surf}$  is the specific surface area of the relevant solid ( $\text{m}^2 \text{ kg}^{-1}$  solid),

$C_{iex}$  is the concentration of ionized sorbate drawn towards positions of opposite charge on the solid surface ( $\text{mol mol}^{-1}$  surface charges),

$\sigma_{surf\ ex}$  is the net concentration of suitably charged sites on the solid surface ( $\text{mol surface charges m}^{-2}$ ) for ion exchange,

$C_{irxn}$  is the concentration of sorbate  $i$  bonded in a reversible reaction to the solid ( $\text{mol mol}^{-1}$  reaction sites),

$\sigma_{surf\ rxn}$  is the concentration of reactive sites on the solid surface ( $\text{mol reaction sites m}^{-2}$ ),

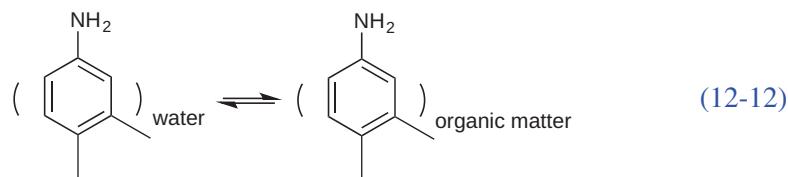
$C_{iw,\text{neut}}$  is the concentration of uncharged chemical  $i$  in solution ( $\text{mol L}^{-1}$ ), and

$C_{iw,\text{ion}}$  is the concentration of the charged chemical  $i$  in solution ( $\text{mol L}^{-1}$ ).

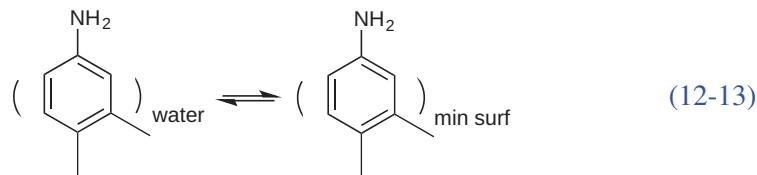
All terms in Eq. 12-11 may also warrant further subdivision. For example,  $C_{ioc}f_{oc}$  may reflect the sum of adsorption and absorption mechanisms acting to associate the chemical to a variety of different forms of organic matter (e.g., living biomass of microorganisms, partially degraded organic matter from plants, plastic debris from humans, etc.; see Chapter 13). Similarly,  $C_{imin}A_{surf}$  may reflect a linear combination of the interactions of several mineral surfaces present in a particular soil or sediment with a single sorbate (Chapters 11 and 14). Thus, a soil consisting of montmorillonite, kaolinite, iron oxide, and quartz mineral components may actually have  $C_{imin}A_{surf} = C_{imont}aA_{surf} + C_{ikao}bA_{surf} + C_{iron\ ox}cA_{surf} + C_{iquartz}dA_{surf}$  where the parameters  $a$ ,  $b$ ,  $c$ , and  $d$  are the area fractions exhibited by each mineral type. Similarly,  $C_{irxn}\sigma_{surf\ rxn}A_{surf}$  may reflect bonding to several different kinds of surface moieties, each with its

own reactivity with the sorbate (e.g., 3,4-dimethylaniline). For now, we work from the simplified expression of Eq. 12-11 primarily because little data is available allowing rational subdivisions of soil or sediment that differentially sorb organic chemicals beyond that reflected in this equation.

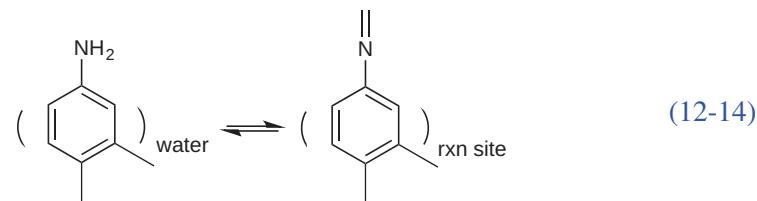
To properly apply Eq. 12-11, it is very important to realize that any one exchange process only involves particular combinations of species in the numerator and denominator. For example, in the case of sorption of dimethylaniline (DMA) to natural sorbents (Fig. 12.2), exchanges between the solution and the solid-phase organic matter reflect establishing the same chemical potential of the uncharged DMA species in the water and in the particulate natural organic phase:



As a result, a single free energy change and associated equilibrium constant applies to the sorption reaction depicted by Eq. 12-12. Similarly, the combination:

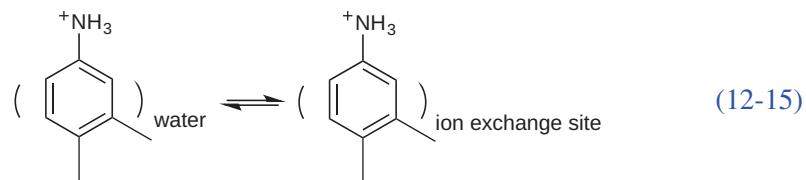


would indicate a simultaneously occurring exchange of uncharged aniline molecules from aqueous solution to the available mineral surfaces. Again, this exchange is characterized by a unique free energy difference reflecting the equilibria shown in Eq. 12-13. Likewise, the exchange of:



should be considered if it is the neutral sorbate which can react with components of the solid. Such specific binding to a particular solid phase moiety may prevent rapid desorption, and, therefore, such sorbate–solid associations may cause part or all of the sorption process to appear irreversible on some time scale of interest.

In addition to sorptive interactions in which only the uncharged DMA species is directly involved, the charged DMA species (i.e., anilinium ions) is involved in processes such as ion exchange:



Of course, the anilinium ion in solution is quantitatively related to the neutral aniline species via an acid-base reaction having its own equilibrium constant (see Chapter 4, Section 4.3). However, we emphasize that the solution–solid exchange shown in Eq. 12-15 has to be described using the appropriate equilibrium expression relating corresponding species in each phase.

The influence of each sorption mechanism is ultimately reflected by all these equilibria in the overall  $K_{id}$  expression, and each is weighted by the availability of the respective sorbent properties in the heterogeneous solid (i.e.,  $f_{oc}$ ,  $\sigma_{surf\ ex}$ ,  $\sigma_{surf\ rxn}$  or the various  $A$  values). By combining information on the individual equilibria (e.g., Eqs. 12-12 through 12-15) with these sorbent properties, we can develop versions of the complex  $K_d$  expression (Eq. 12-11) that take into account the structure of the chemical we are considering. In Chapters 13 to 15, we discuss these individual equilibrium relationships. Here, we strive to provide a first look at the effects of sorption on the speciation (sorbed versus dissolved or gaseous) and thus on some transport processes, including retardation in porous media and sedimentation from a water or air column.

## 12.3 Speciation (Sorbed versus Dissolved or Gaseous), Retardation, and Sedimentation

### Dissolved ( $f_{iw}$ ), Gaseous ( $f_{ia}$ ), and Sorbed Fractions ( $f_{is}$ ) of a Compound in a Given System

Let us start out by considering the speciation of a neutral organic compound in an environmental aqueous system containing only solids and water. We may evaluate what fraction of the compound is dissolved in the water,  $f_{iw}$ , for any volume:

$$f_{iw} = \frac{C_{iw}V_w}{C_{iw}V_w + C_{is}M_s} \quad (12-16)$$

where  $V_w$  is the volume of water (L) in the total volume  $V_t$ , and  $M_s$  is the mass of solids (kg) present in that same total volume. Now, if we substitute the product  $K_{id}C_{iw}$  from Eq. 12-8 for  $C_{is}$  in Eq. 12-16, we have:

$$f_{iw} = \frac{C_{iw}V_w}{C_{iw}V_w + K_{id}C_{iw}M_s} = \frac{V_w}{V_w + K_{id}M_s} \quad (12-17)$$

Finally, if we refer to the quotient,  $M_s/V_w$ , as the *solid-to-water phase ratio*,  $r_{sw}$  (e.g., kg L<sup>-1</sup>) in the environmental compartment of interest, we may describe the fraction of chemical in solution as a function of  $K_{id}$  and this ratio:

$$f_{iw} = \frac{1}{1 + (M_s/V_w) K_{id}} = \frac{1}{1 + r_{sw} K_{id}} \quad (12-18)$$

Such an expression clearly indicates that for substances exhibiting a great affinity for solids (and hence a large value of  $K_{id}$ ) or in situations having large amounts of solids per volume of water (large value of  $r_{sw}$ ), we predict that small fractions of the chemical remain dissolved in the water. Correspondingly, the fraction present in particulate form,  $f_{ip}$ , must be given by:

$$f_{ip} = (1 - f_{iw}) \quad (12-19)$$

since we assume that no other phases are present (e.g., air, other immiscible liquids).

The fraction of the total volume,  $V_t$ , that is not occupied by solids, the so-called porosity  $\phi$  (see also Box 5.4), is often used instead of  $r_{sw}$  to characterize the solid to water phase ratio in environmental systems like sediment beds or aquifers. In the absence of any gas phase,  $\phi$  is related to parameters previously discussed by:

$$\phi = \frac{V_w}{V_t} = \frac{V_w}{V_w + V_s} \quad (12-20)$$

where,  $V_s$ , the volume occupied by particles, can be calculated from  $M_s/\rho_s$ , (where  $\rho_s$  is the density of the solids and is typically near 2.5 kg L<sup>-1</sup> for many natural minerals). Thus, we find the porosity is also given by:

$$\phi = \frac{V_w}{V_w + M_s / \rho_s} = \frac{1}{1 + r_{sw} / \rho_s} \quad (12-21)$$

Some representative porosities encountered in the aquatic and terrestrial environment are given in Box 5.4. Solving for  $r_{sw}$  yields the relation:

$$r_{sw} = \rho_s \frac{1 - \phi}{\phi} \quad (12-22)$$

The definitions of the relevant quantities that are used to describe solid-water mixtures are summarized in Box 12.1, together with the approximations valid for ‘dilute’ systems such as the open water column in lakes and oceans. In the soil and ground-water literature, a third parameter, the bulk density  $\rho_b$ , is commonly used to describe systems:

$$\rho_b = \frac{M_s}{V_t} = \rho_s(1 - \phi) \quad (12-23)$$

Thus,  $r_{sw}$  is simply equal to  $\rho_b/\phi$ . It is a matter of convenience whether  $r_{sw}$ ,  $\phi$ , or  $\rho_b$  is used in discussions.

**Box 12.1 Definition of Concentrations in an Aqueous System with Solids**

$C_{ss}$	$(\text{kg}_s \text{ m}_{\text{tot}}^{-3})$	Concentration of (suspended) solids per bulk volume
$\rho_s$	$(\text{kg}_s \text{ m}_s^{-3})$	Density of solids
$\phi$	$(\text{m}_w^{-3} \text{ m}_{\text{tot}}^{-3})$	Porosity
$r_{sw}$	$(\text{kg}_s \text{ m}_w^{-3})$	Solid-to-water phase ratio: $r_{sw} = \rho_s \frac{1 - \phi}{\phi}$
$K_{id} = C_{is}/C_{iw}$	$(\text{kg}_s^{-1} \text{ m}_w^{-3})$	Solid–water distribution coefficient
$f_{iw}$	(–)	Fraction dissolved: $f_{iw} = \frac{1}{1 + r_{sw} K_{id}}$
$(1 - f_{iw})$	(–)	Fraction particulate: $1 - f_{iw} = \frac{r_{sw} K_{id}}{1 + r_{sw} K_{id}}$
$C_{it}$	$(\text{mol m}_{\text{tot}}^{-3})$	Total (dissolved and particulate) concentration per bulk volume
$C_{id} = f_{iw} C_{it}$	$(\text{mol m}_{\text{tot}}^{-3})$	Dissolved concentration per bulk volume
$C_{ip} = (1 - f_{iw}) C_{it}$	$(\text{mol m}_{\text{tot}}^{-3})$	Particulate concentration per bulk volume; $C_{it} = C_{id} + C_{is}$
$C_{iw}$	$(\text{mol m}_w^{-3})$	Dissolved concentration per water volume
$C_{is}$	$(\text{mol kg}_s^{-3})$	Concentration sorbed on solids

Approximations for small  $r_{sw}$  ('open water')

$$r_{sw} \sim C_{ss}; \phi \sim 1; f_{iw} \sim 1; (1 - f_{iw}) \sim r_{sw} K_{id}; C_{id} \sim C_{iw}$$

As compared to soils, aquifers, or sediments,  $r_{sw}$  in surface waters is much smaller (i.e.,  $10^{-5}$  to  $10^{-7}$  kg L<sup>-1</sup>), and, therefore,  $V_w \approx V_t$ . The same holds for the atmosphere ( $V_a \approx V_t$ ), where particle (aerosol) concentrations are even smaller, i.e.,  $10^{-10}$  to  $10^{-12}$  kg L<sup>-1</sup> (Table 5.2). In these cases,  $r_{sw}$  is simply given by the particle concentration, which is sometimes also denoted as  $S_w$  or  $S_a$  respectively.

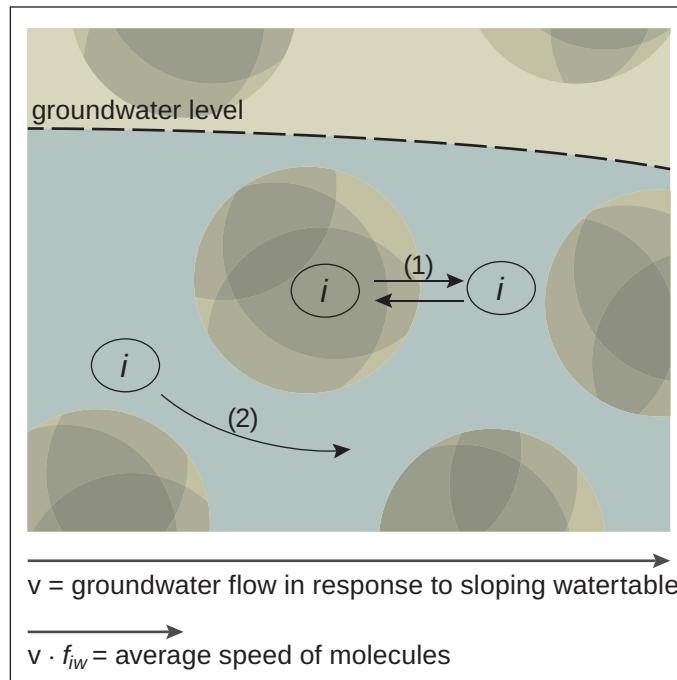
### Retardation in Porous Media

Let us now consider a typical groundwater situation: a chemical is released into flowing groundwater. The aquifer solids have a  $\rho_s$  of about 2.5 kg L<sup>-1</sup> (e.g., quartz

density is  $2.65 \text{ kg L}^{-1}$ ), and  $\phi$  of such porous media is often between 0.2 and 0.4. If in our particular groundwater situation  $\phi$  is 0.2, insertion of these values into Eq. 12-22 yields an  $r_{sw}$  value of  $10 \text{ kg L}^{-1}$ . Thus,  $f_{iw}$  as a function of  $K_{id}$  expressed in  $\text{L kg}^{-1}$  (Eq. 12-18) is:

$$f_{iw} = \frac{1}{1 + (10 \text{ kg L}^{-1})K_{id}} \quad (12-24)$$

We now apply this speciation information to a release of one of our companion compounds, the solvent tetrachloroethene (PCE, Chapter 3), into flowing groundwater. From experience, we know that the  $K_{id}$  value for PCE in this case happens to be in the order of  $1 \text{ L kg}^{-1}$  since the aquifer materials usually contain only very little organic matter, which is the main sorbent for this kind of compounds (see Chapter 13). Insertion of this  $K_{id}$  value into Eq. 12-24 then yields a  $f_{iw}$  of about 0.09. Therefore, we deduce that only one PCE molecule out of 11 will be in the moving groundwater at any instant (Fig. 12.6). This result has implications for the fate of the PCE in the subsurface environment. If PCE sorptive exchange between the aquifer solids and the water is fast relative to the groundwater flow and if sorption is reversible, we can conclude that all the PCE molecules move at one eleventh the rate of the water. The phenomenon of diminished chemical transport speed relative to the water seepage velocity is referred to as *retardation*. It is commonly described by the *retardation factor*,  $R_{fi}$ , which is simply equal to the reciprocal of the fraction of molecules capable



**Figure 12.6** Illustration of the retardation of the transport of an organic compound *i* in groundwater due to: (1) reversible sorptive exchange between water and solids, and (2) limiting transport of *i* to that fraction remaining in the flowing water. As dissolved molecules move ahead, they become sorbed and stop, while molecules sorbed at the rear return to the water and catch up. Thus, overall transport of *i* is slower than that of the water itself.

of moving with the flow at any instant,  $f_{iw}^{-1}$ :

$$R_{fi} = f_{iw}^{-1} = 1 + r_{sw}K_{id} \quad (12-25)$$

Hence,  $R_{f\text{ PCE}} = 11$ .

### Sedimentation

As already mentioned, in the water column of surface waters, for example in lakes,  $r_{sw}$  is in the order of  $10^{-6} \text{ kg L}^{-1}$ . In this case,  $f_{iw}$  is given by:

$$f_{iw} = \frac{1}{1 + (10^{-6} \text{ kg L}^{-1})K_{id}} \quad (12-26)$$

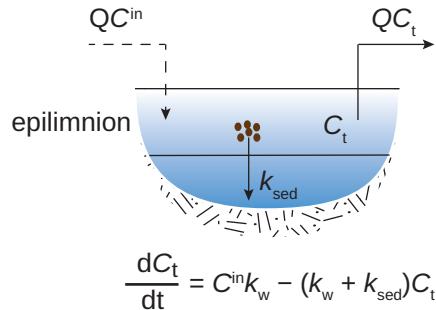
Since in lakes the organic matter content of the solids is commonly significantly higher than in aquifers (Chapter 5), for our companion compound PCE we may assume a  $K_{id}$  value of as large as  $100 \text{ L kg}^{-1}$  (see Chapter 13). However, even with this much larger  $K_{id}$ ,  $f_{iw}$  is  $1/1.0001 = 0.99990$ ; that is, virtually all PCE is present in a dissolved form in the water column of a lake. Only 0.1% will be sorbed to particles. From Eq. 12-26, we can easily see that we need a  $K_{id}$  of  $10^6$  in order to have 50% of the PCE molecules in a sorbed or particulate form ( $f_{ip} = 1 - f_{iw} = 0.5$ ).

Sedimentation, that is, the removal by sinking particles, can be an important process for a given organic pollutant in a water column. However, how large must the fraction of said pollutant be in particulate form,  $f_{ip}$ , in order for sedimentation to be of importance? To answer this question, we consider a well-mixed waterbody, such as the epilimnion of a lake, which can be described by the one-box model introduced in Chapter 6 (Section 6.2). We recall that, in this simple approach, we express all processes as first-order reactions characterized by a first-order reaction constant. By doing so, we can compare the different first-order rate constants to assess the relative importance of each process. Firstly, we note that a process that is equally important for all compounds is flushing or dilution, which we denote by the flushing rate constant  $k_w$ :

$$k_w = \frac{Q}{V} [\text{T}^{-1}] \quad (6-4)$$

where  $Q$  is the water flow rate (e.g., in  $\text{m}^3 \text{ d}^{-1}$ ) and  $V$  is the volume or the well-mixed waterbody (e.g., in  $\text{m}^3$ ). Here, we only further consider the first-order removal rate constant of sedimentation of the compound,  $k_{\text{sed}}$ , which we compare to  $k_w$  (see Fig. 12.7). We address all other processes in other respective chapters.

For our simple back-of-the-envelope calculation, we assume that we have a constant steady-state concentration of particles in the epilimnion, denoted as  $S_w$  (e.g., in  $\text{kg m}^{-3}$ ), and an average particle sinking velocity  $v_s$  (e.g., in  $\text{m d}^{-1}$ ). The flux  $F_s$  per unit area (e.g., in  $\text{kg m}^{-2} \text{d}^{-1}$ ) of particles out of our box (i.e., the epilimnion of the lake) is then



**Figure 12.7** Box model for Mystery Lake, Cleanland (see Chapter 6, Section 6.1) including removal of contaminant via the outlet ( $k_w$ ) and sedimentation ( $k_{\text{sed}}$ ). The model is used for some simple calculations assuming no water exchange between the epilimnion and the hypolimnion and all removal processes can be expressed as first-order reactions.

given by  $F_s = v_s S_w$ , which multiplied by the total surface area,  $A$ , of our waterbody yields the total flux of particles:

$$\text{total flux} = AF_s = Av_s S_w \quad (12-27)$$

which, divided by the volume, yields the first-order particle removal rate constant,  $k_s$  (e.g., in  $\text{d}^{-1}$ ):

$$k_s = \frac{A}{V} v_s = \frac{v_s}{h} \quad (12-28)$$

where  $h = A/V$  (e.g., in m) is the mean depth of the epilimnion. To now obtain the first-order removal rate constant of the compound,  $k_{\text{sed}}$ , we simply have to multiply Eq. 12-28 by the fraction in particulate form (note that we omit the subscript  $i$ ):

$$k_{\text{sed}} = k_s (1 - f_{iw}) = \frac{v_s}{h} (1 - f_{iw}) \quad (12-29)$$

For illustration, let us apply these equations to the epilimnion of Mystery Lake, Cleanland (Fig. 12.7), introduced in Chapter 6, Section 6.1. We assume a mean epilimnion depth  $h = 10 \text{ m}$  and a mean particle settling rate  $v_s = 1 \text{ m d}^{-1}$ , which yields a  $k_{\text{sed}} = 0.1 (1 - f_{iw}) \text{ d}^{-1}$ . The flushing rate constant of the epilimnion of Mystery Lake,  $k_w$ , is  $0.01 \text{ d}^{-1}$ . Therefore, in order to make sedimentation equally or more important than flushing ( $k_{\text{sed}} \geq k_w$ ), the value of  $(1 - f_{iw})$  has to be at least 0.1, that is, at least 10% of the compound has to be sorbed. When assuming a typical particle concentration of  $5 \times 10^{-6} \text{ kg L}^{-1}$  in a lake, only for compounds with  $K_{id}$  values equal or greater than  $22,000 \text{ L kg}^{-1}$  does sedimentation become an important process. Thus, for PCE with its  $K_{id}$  of  $100 \text{ L kg}^{-1}$ , sedimentation in the epilimnion can be completely neglected. In contrast, gas exchange with the atmosphere cannot be neglected, which we already predicted for PCE in Chapter 6 and which we further discuss in Chapter 19.

## 12.4 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 12.1

Give five reasons why it is important to know to what extent a given chemical is present in the sorbed form in a natural or engineered system.

#### Q 12.2

What are the most important natural sorbents and sorption mechanisms for (a) apolar compounds, (b) polar compounds, and (c) ionized compounds?

#### Q 12.3

What is a sorption isotherm? Which types of sorption isotherms may be encountered when dealing with sorption of organic compounds to natural sorbents? Does the shape of a sorption isotherm tell you anything about the sorption mechanism(s)? If yes, what? If no, why not?

#### Q 12.4

Write down the most common mathematical expressions used to describe sorption isotherms. Discuss the meaning of the various parameters and describe how they can be derived from experimental data.

#### Q 12.5

Which environmental parameters and compound properties determine the fraction in dissolved form of (a) a neutral organic compound and (b) an ionizable organic compound in an aquifer? How is the retardation factor of a compound in an aquifer defined, and what does it exactly describe?

#### Q 12.6

Which environmental parameters and compound properties determine the rate at which a compound is removed from a waterbody by sedimentation?

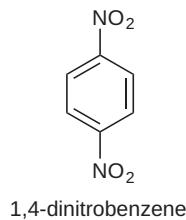
#### Q 12.7

Explain more explicitly how one gets from Eq. 12-28 to Eq. 12-29 and under which assumptions Eq. 12-29 may be used to describe sedimentation of organic chemicals in the water column.

### Problems

#### P 12.1\* Determining $K_{id}$ Values from Experimental Data

A common way to measure  $K_{id}$  values is to measure isotherms in *batch* experiments. To this end, the equilibrium concentrations of a given compound in the solid



$C_{iw}$ ( $\mu\text{mol L}^{-1}$ )	$C_{is}$ ( $\mu\text{mol kg}^{-1}$ )
0.06	97
0.17	241
0.24	363
0.34	483
0.51	633
0.85	915
1.8	1640
2.8	2160
3.6	2850
7.6	4240
19.5	6100
26.5	7060

phase ( $C_{is}$ ) and in the aqueous phase ( $C_{iw}$ ) are determined at various compound concentrations and/or solid/water ratios. Consider the adsorption of 1,4-dinitrobenzene (1,4-DNB) to the homoionic clay mineral,  $K^+$ -illite. 1,4-DNB forms electron donor-acceptor complexes with clay minerals. In a series of batch experiments, Haderlein et al., (1996) measured the data at pH 7.0 and 20°C given in the margin and plotted in the figure. Using this data, estimate the  $K_{id}$  values for 1,4-DNB for equilibrium concentrations of 1,4-DNB in the aqueous phase of 0.20  $\mu\text{M}$  and of 15  $\mu\text{M}$  respectively. Derive appropriate isotherms for estimating these  $K_{id}$  values.

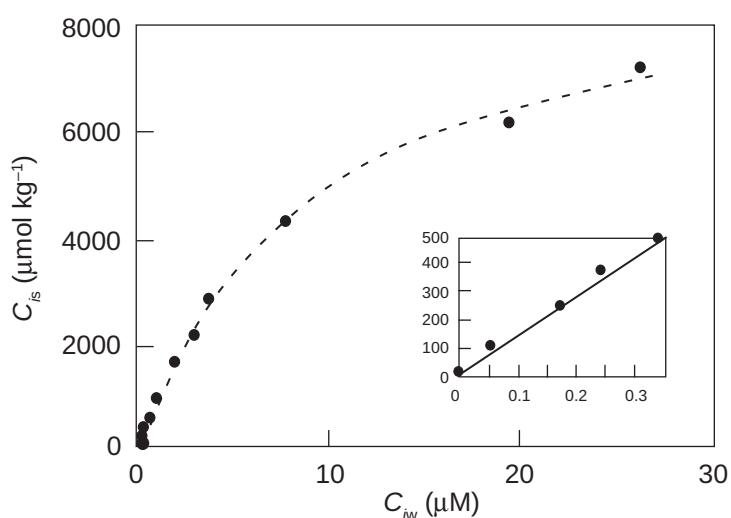


Figure. Adsorption of 1,4-DNB to  $K^+$ -illite

### P 12.2 Retardation of Phenanthrene in an Aquifer Containing Very Little Organic Material

Due to runoff from streets, a series of PAHs have been detected in drinking water originating from an aquifer containing very little organic carbon. Therefore, it can be assumed that primarily adsorption to mineral surfaces determines how fast these compounds are transported in the aquifer. Using the surface normalized  $K_{isurfw}$  values (Chapter 11, Eq. 11-15) given in the margin, estimate the retardation factor of our companion compound phenanthrene in this aquifer from which you have the following information: the average porosity is 0.3; the aquifer solids consist of 95% quartz (density 2.65  $\text{g mL}^{-1}$ ; surface area 1  $\text{m}^2 \text{ g}^{-1}$ ), 4% kaolinite (density 2.6  $\text{g mL}^{-1}$ ; surface area 10  $\text{m}^2 \text{ g}^{-1}$ ), and 1% iron oxides (density 3.5  $\text{g mL}^{-1}$ ; the surface area is 50  $\text{m}^2 \text{ g}^{-1}$ ); and organic carbon content is  $\ll 0.1\%$ . The average temperature is 10°C, and the pH is 7.0.

mineral	$\log K_{isurfw}$ (m) <sup>a</sup>
quartz	-7.2
kaolinite	-7.8
iron oxides	-7.3

<sup>a</sup>Data from the literature cited in Chapter 11, Fig. 11.8.

Values measured at 20°C.

### P 12.3 Elimination of PCB 153 from the Epilimnion of a Lake

After an accident in early summer, an unknown amount of our companion compound PCB 153 was introduced into the epilimnion of our model Mystery Lake, Cleanland. As the owner of an environmental analytical lab, you were offered the job to monitor the concentrations of this compound in the epilimnion of Mystery Lake during the summer. At the end of August, you look at your data and realize that after 46 days, the total concentration of PCB 153 had dropped to one fourth of its initial total concentration. A colleague of yours claims that the elimination of the compound was

only due to flushing. Is this person correct? If not, are there other significant elimination processes, and how important are they as compared to flushing? Since you have already read Chapter 6, you know that, unlike for PCE, gas exchange is not a major removal mechanism for this compound from the epilimnion of Mystery Lake. You also assume that, under the oxic conditions prevailing in the epilimnion, PCB 153 is quite persistent to any transformation reaction. Hence, only elimination by sedimentation could be important. Is this a reasonable assumption? Calculate the  $K_{id}$  value that would be necessary to account for the additional elimination by assuming the lake parameters used earlier (mean epilimnion depth  $h = 10$  m, flushing rate constant  $k_w = 0.01 \text{ d}^{-1}$ , and mean particle settling rate  $v_s = 1 \text{ m d}^{-1}$ ). Compare your result with an estimate of your colleague who has read Chapter 13 and who tells you that, for PCB 153, you should expect a  $K_{id}$  between  $10^4$  and  $5 \times 10^4 \text{ L kg}^{-1}$ .

*Hint:* You are dealing with case *a* in Box 6.2.

## 12.5

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