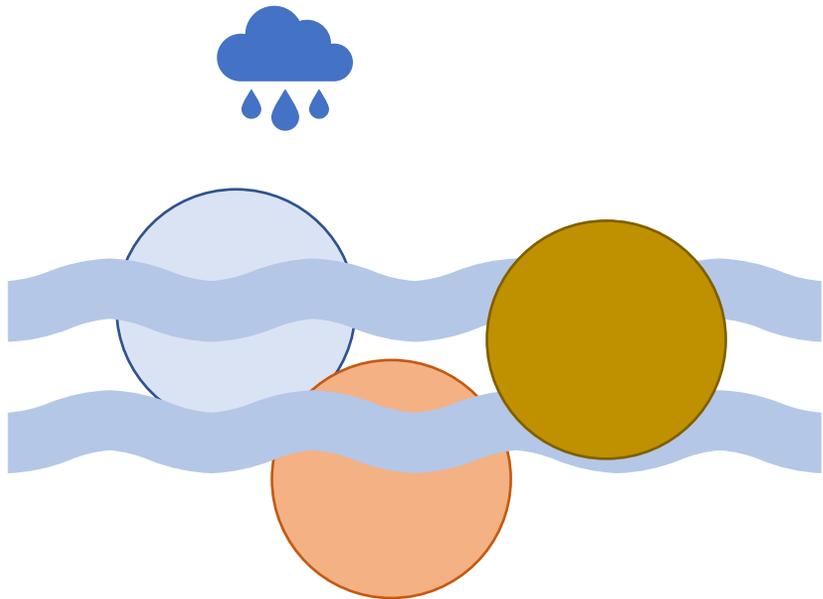


Mass-Transfer Mechanisms: Sorptions & Volatilization



Mass-transfer

1. Reflection: What is an important difference between toxic pollutants and conventional pollutants? How does this change modeling/remediation in your study water body?

2. Sorption

3. Isotherms

4. Fraction Sorbed

5. Estimatr of Partitioning Coeff

6. Sorption revisited (3rd phase)

Sorption

Sorption is a process whereby a dissolved substance is transferred to and becomes associated with solid material.

Adsorption: the accumulation of dissolved substances on the surface of solids

Absorption: the interpenetration or intermingling of substances with solids.

Sorbate: the substance is sorbed

Sorbent: the solid

Desorption: the process whereby a sorbed substance is released from a particle.

Sorption

For neutral organics, several mechanisms underlie the sorption process.

Hydrophobic effects cause the sorbate to associate with organic matter in the particulate phase (unfavorable free-energy cost of staying).

Weak surface interactions via van der Waals, dipole-dipole, induced dipole, and other weak intermolecular forces.

Surface reactions where the sorbate actually bonds to the solid.

Isotherms

An experiment to measure sorption starts by mixing a mass of solids in a well-stirred vessel with a quantity of dissolved chemical.

By adding different levels of contaminants and measuring the amount of chemical on the solids after centrifuging, one can obtain “ v ”, the concentration of contamination on the solids (mg m^{-3}), and “ c_d ” the dissolved concentration (mg m^{-3}).

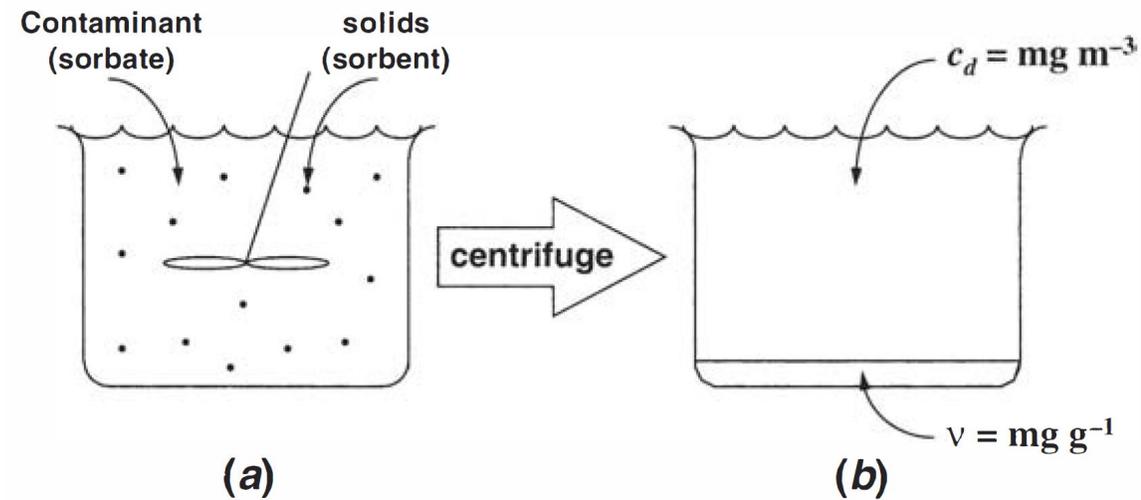


FIGURE 41.1

Isotherms

As the concentration increases, “ v ” increases until equilibrium is reached.

For most chemicals this is reached in minutes to hours.

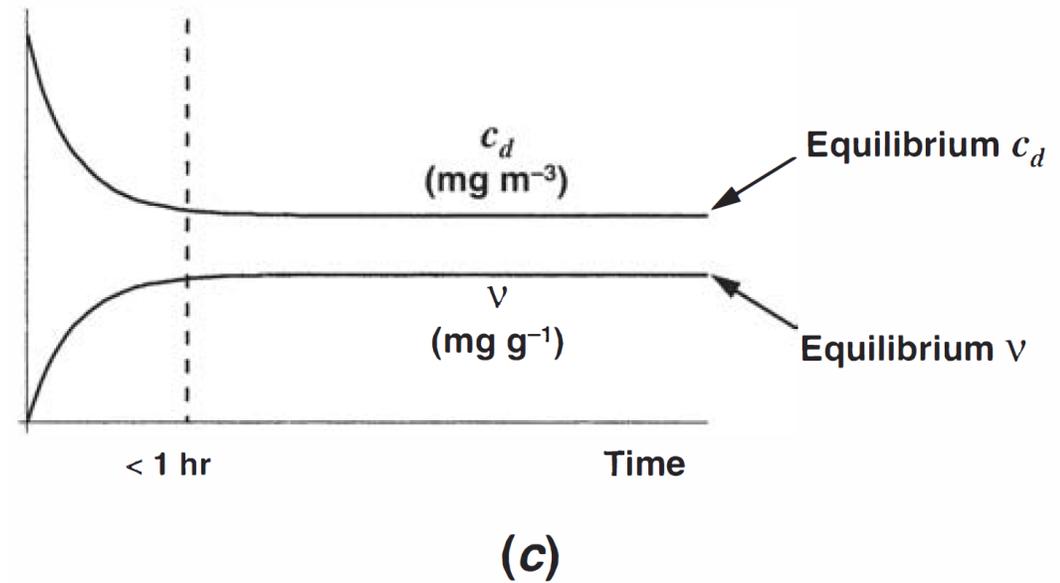


FIGURE 41.1

Experiment to determine sorption. (a) Solids and contaminant are mixed in a vessel. A sample is taken and centrifuged to separate the solids from the water. (b) The contaminant content of each phase is measured. The temporal progression of such an experiment is depicted in (c). An equilibrium is typically reached rapidly.

Isotherms

When the concentration of contamination on the solids (v) is plotted against the dissolved concentration (c_d), the result is called an *isotherm*.

The solid concentration increases with dissolved concentration until the available sites become saturated, at this point the curve levels off to a max (v_m ; mg g^{-1}).

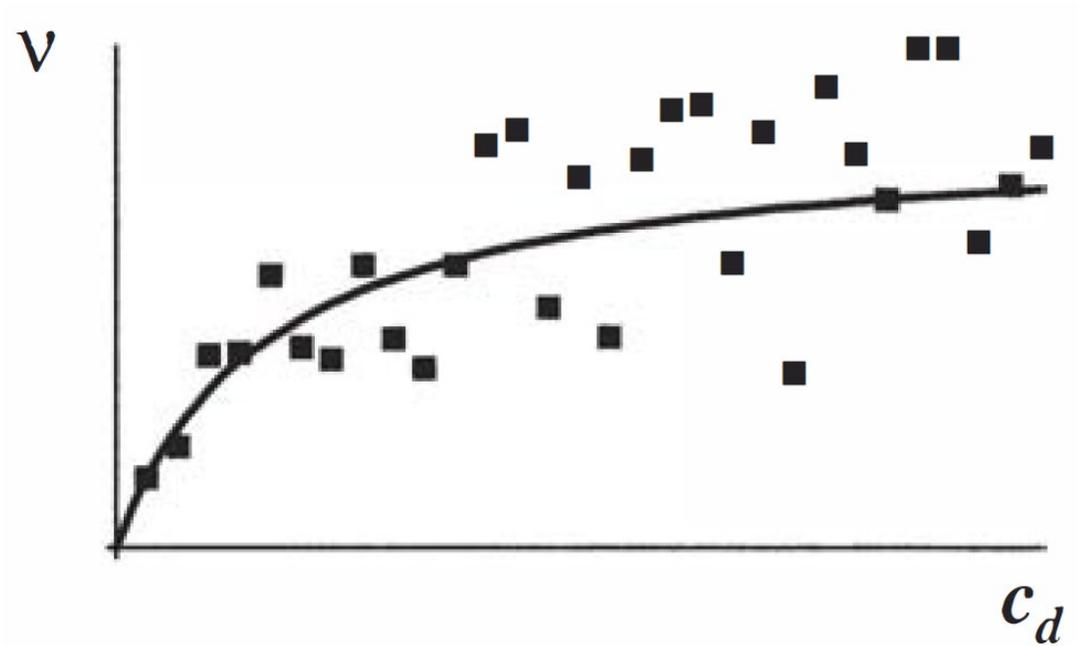


FIGURE 41.2

Sorption data and isotherm.

Isotherms

Some popular models to represent the isotherms mathematically:

$$v = \frac{v_m b c_d}{1 + b c_d} \quad (\text{Langmuir})$$

$$v = K_f c_d^{1/n} \quad (\text{Freundlich})$$

$$v = \frac{v_m B c_d}{(c_s - c_d)[1 + (B - 1)(c_d/c_s)]} \quad (\text{BET})$$

where b , B , c_s , K_f , and n are coefficients used to calibrate the curve.

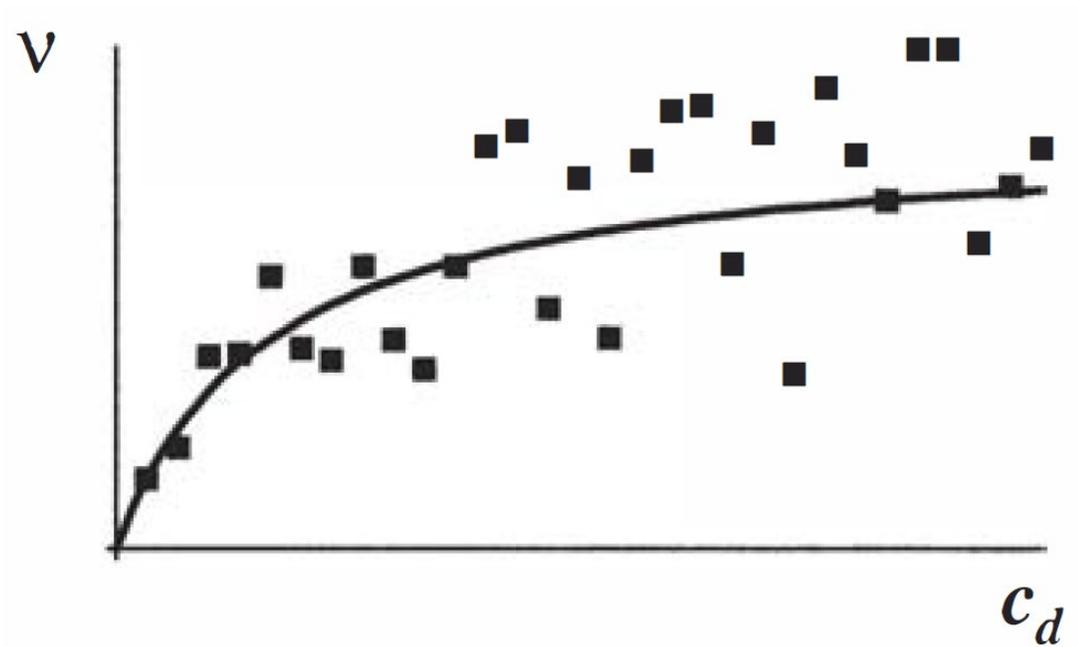


FIGURE 41.2

Sorption data and isotherm.

Isotherms

The Langmuir isotherm has utility and can be derived by recognizing that the sorption process represents an equilibrium between the rate of adsorption and desorption.

$$R_{ad} = R_{de}$$

where mass adsorbed per unit time, R_{ad} (mg s^{-1}) is represented as:

$$R_{ad} = k_{ad}M_s c_d (v_m - v)$$

here k_{ad} = mass-specific volumetric rate of adsorption [$\text{m}^3 (\text{mg s})^{-1}$], and M_s = mass of solids (g).

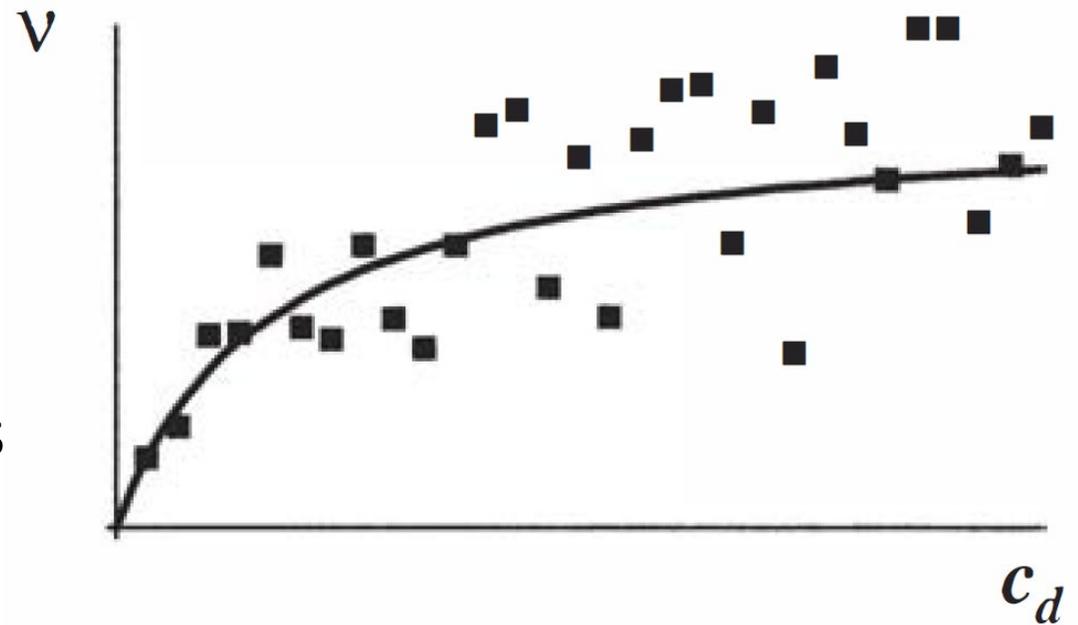


FIGURE 41.2
Sorption data and isotherm.

Isotherms

The mass desorbed per unit time, R_{de} (mg s^{-1}) is represented as:

$$R_{de} = k_{de}M_s v$$

where k_{de} = a first-order desorption rate (s^{-1}).

These equations substituted into ($R_{ad} = R_{de}$) yields:

$$v = \frac{v_m}{(k_{de}/k_{ad}) + c_d}$$

This is the general form of the Langmuir model.

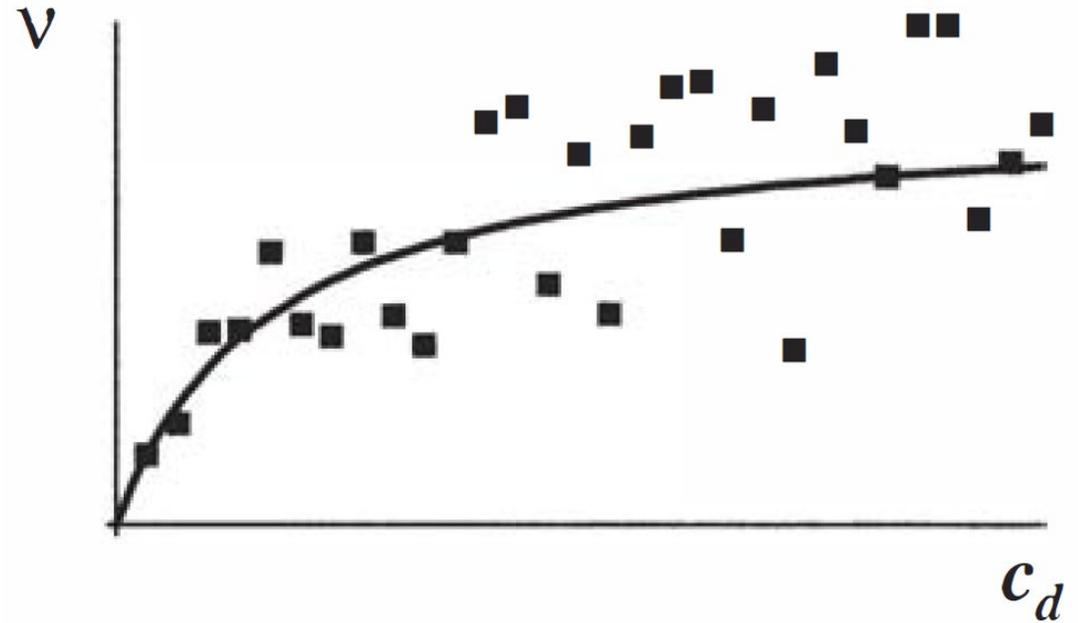


FIGURE 41.2
Sorption data and isotherm.

Isotherms

This equation ($v = \frac{v_m}{(k_{de}/k_{ad}) + c_d}$) is plotted in the graph.

For high levels of contaminants, the curve becomes zero-order. For low levels, the curve is first-order (linear). Most natural waters contain low toxicant concentrations.

This low region is modeled through ($v \ll v_m$):

$$R_{ad} = k_{ad} M_s c_d (v_m - v) \rightarrow k'_{ad} M_s c_d$$

where $k'_{ad} = k_{ad} v_m$ [$\text{m}^3(\text{g s})^{-1}$]. Adsorption is driven by the dissolved concentration.

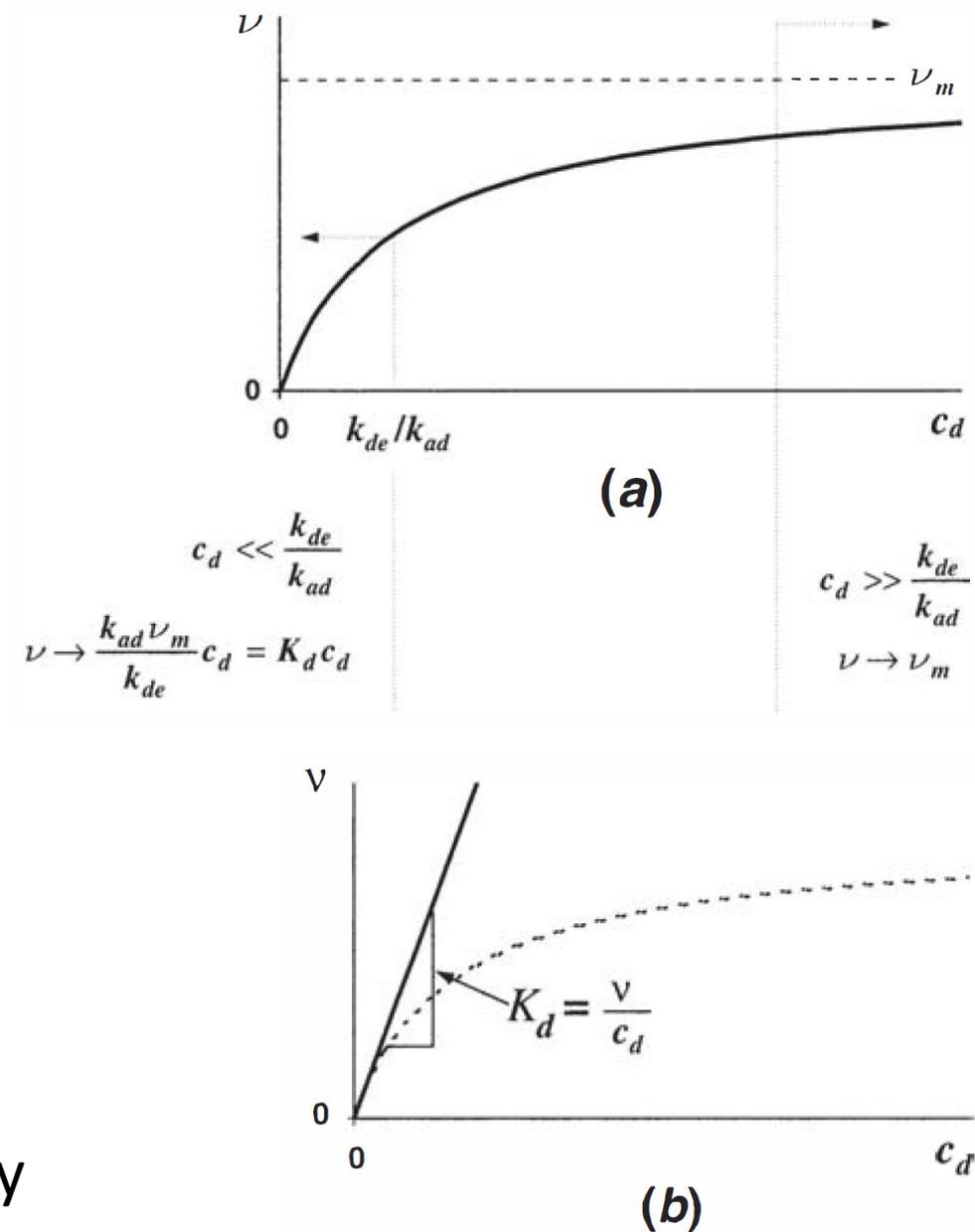


FIGURE 41.3

(a) A Langmuir isotherm indicating asymptotes.

(b) Linearization of isotherm.

Isotherms

When $(R_{ad} = k'_{ad}M_s c_d)$ is substituted with $(R_{de} = k_{de}M_s v)$ into $(R_{ad} = R_{de})$, the result is:

$$v = K_d c_d$$

where $K_d =$ partition coefficient $= k'_{ad}/k_{de}$ ($\text{m}^3 \text{g}^{-1}$). The partition coefficient represents the slope of the linear portion of the isotherm.

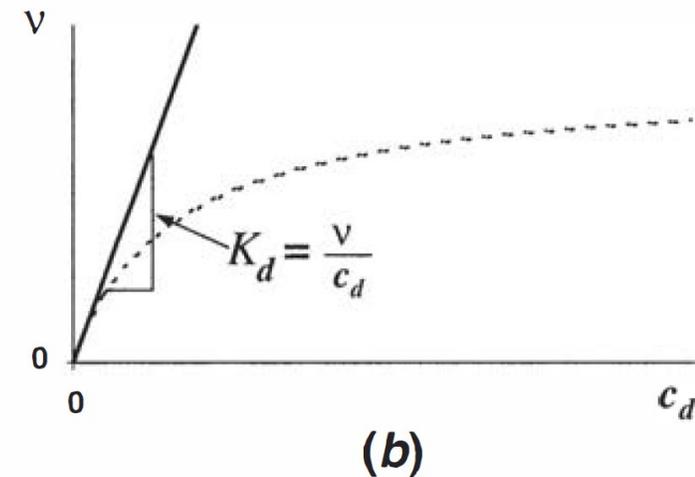
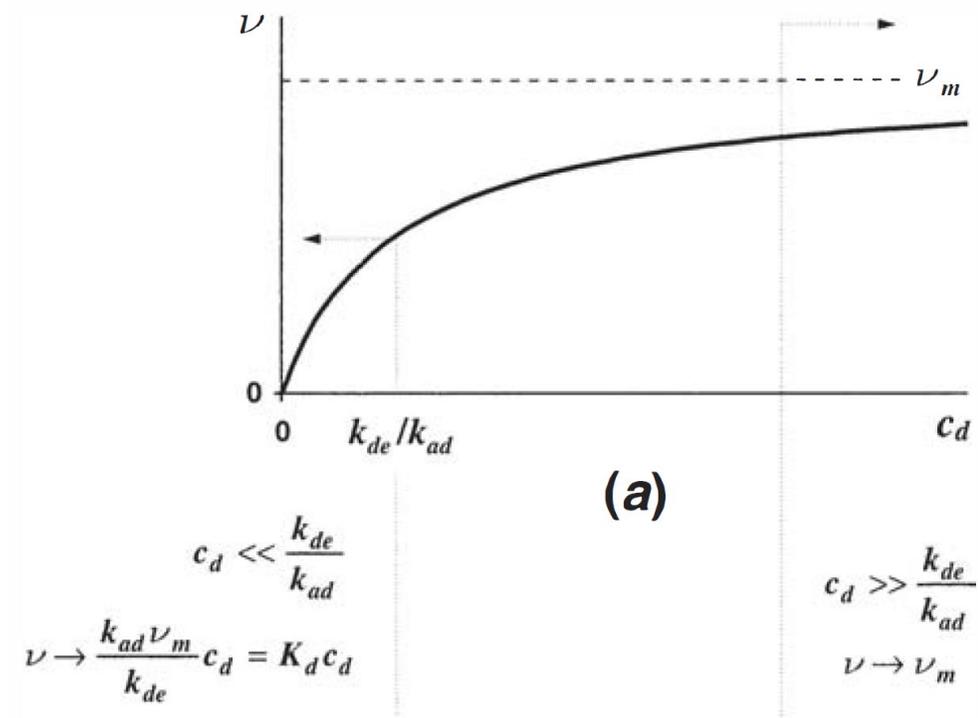


FIGURE 41.3

(a) A Langmuir isotherm indicating asymptotes.

(b) Linearization of isotherm.

Discussion

Which would you rather work on (difficulty/critical need)? What remediation strategies could you employ?

	Complexity	Critical Need	Remediation	
BOD				
Eutrophication	Sarah (many inputs/causes), Josh (plants, aquatic ecosystem), Amanda M (identifying sources)	Amanda C (impact drinking water); Algal blooms can become toxic; Case-by-case	BMP, natural rebounding Alternative fertilizers, transport; mitigation strategies, buffer zones, community action	
Toxics	Daniel (persistent in environment, human intervention)	Cielo, Evan (immediate consequences to health), methods need development	Drudging, adding coagulants, bioremediation (microorganisms), phytoremediation, chemical reaction, barriers; new methods needed	

Fraction Sorbed

We can now derive expressions relating the contaminant fraction in dissolved (F_d) and particulate (F_p) forms to the partition coefficient. Individual mass balances can be written for each fraction in CSTR. For dissolved:

$$V \frac{dc_d}{dt} = Q c_{d,in} - Q c_d + k_{de} M_s v - k'_{ad} M_s c_d$$

and for particulate:

$$V \frac{dc_p}{dt} = Q c_{p,in} - Q c_p - v_s A c_p - k_{de} M_s v + k'_{ad} M_s c_d$$

Fraction Sorbed

Because sorption kinetics are faster than other input-output terms, the previous equations can be added together to yield:

$$V \frac{dc}{dt} = Q c_{in} - Q c - v_s A c_p$$

where

$$c = c_d + c_p$$

and

$$c_{in} = c_{d,in} + c_{p,in}$$

Also recognize that the particulate concentration is related to suspended solids and mass-specific contaminant concentration (knowing that $v = K_d c_d$):

$$c_p = m v$$

where m = suspended solids concentration (g m^{-3}).

Fraction Sorbed

This equation ($c_p = mv$) can be combined with ($v = K_d c_d$) and ($c = c_d + c_p$) to yield:

$$c = c_d + mK_d c_d$$

which can be solved for:

$$c_d = F_d c$$

where

$$F_d = \frac{c_d}{c} = \frac{1}{1 + K_d m}$$

This can be substituted into ($c = c_d + c_p$) and the result solved for:

$$c_p = F_p c$$

where

$$F_p = \frac{c_p}{c} = \frac{K_d m}{1 + K_d m}$$

Estimation of Partition Coefficient

Relating partitioning to specific properties of the chemical has been the work of various investigators. For organic contaminants, the partitioning coefficient, K_d ($\text{m}^3 \text{g}^{-1}$) is assumed to be a function of the organic-carbon content of the solids:

$$K_d = f_{oc} K_{oc}$$

Where K_{oc} = organic-carbon partition coefficient [$(\text{mg gC}^{-1})(\text{mg m}^{-3})^{-1}$] and f_{oc} = weight fraction of the total carbon in the solid matter (gC g^{-1}).

The organic-carbon partition coefficient, K_{oc} , can be estimated by the contaminant's octanol-water partitioning coefficient K_{ow} [$(\text{mg m}^{-3}_{\text{octanol}})(\text{mg m}^{-3}_{\text{water}})$]:

$$K_{oc} = 6.17 \times 10^{-7} K_{ow}$$

And finally:

$$K_d = 6.17 \times 10^{-7} f_{oc} K_{ow}$$

Estimation of Partition Coefficient

Lastly the log of these values:

$$\log K_{ow} = 5.00 - 0.670 \log S'_w$$

where S'_w = solubility in μ mole L^{-1} which can be computed by:

$$S'_w = \frac{S_w}{M} \times 10^3$$

where S_w = solubility ($mg L^{-1}$) and M = molecular weight ($g mole^{-1}$).

Also another formula can be used if f_{oc} is assumed to be equal to 0.05, then the partitioning coefficient is:

$$K_d = 3.085 \times 10^{-8} K_{ow}$$

Estimation of Partition Coefficient

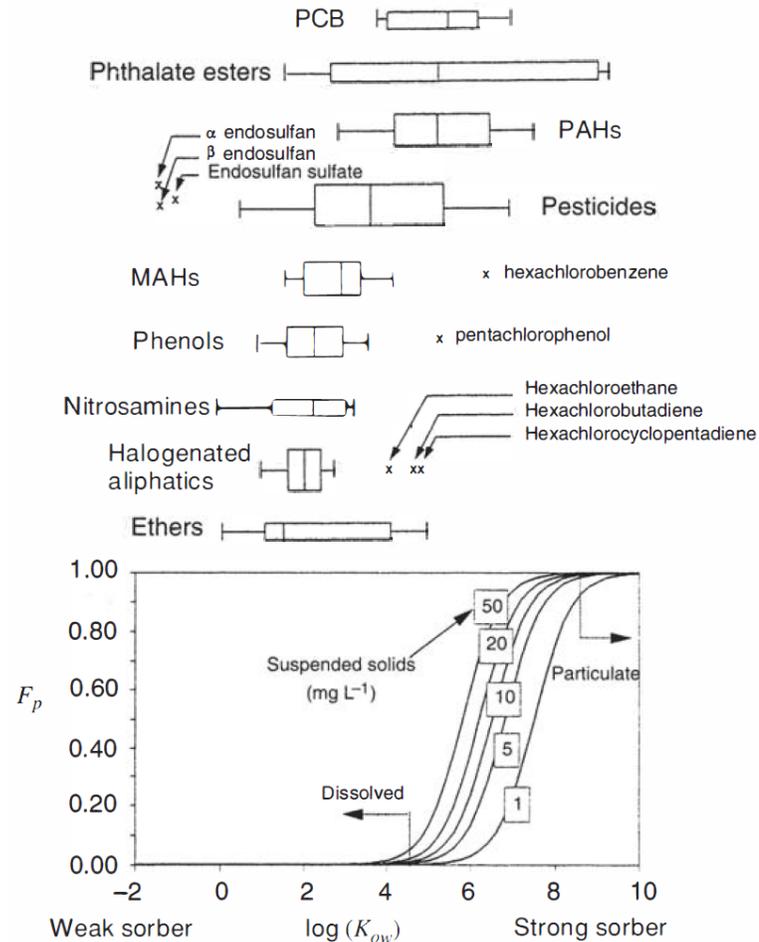


FIGURE 41.4 Plot of fraction dissolved, F_d , and fraction particulate, F_p , versus partition coefficients (Chapra 1991). Each curve represents a particular suspended solids concentration. Box-and-whisker diagrams (see Fig. 41.5) for nine classes of organic contaminants are drawn above the plot.

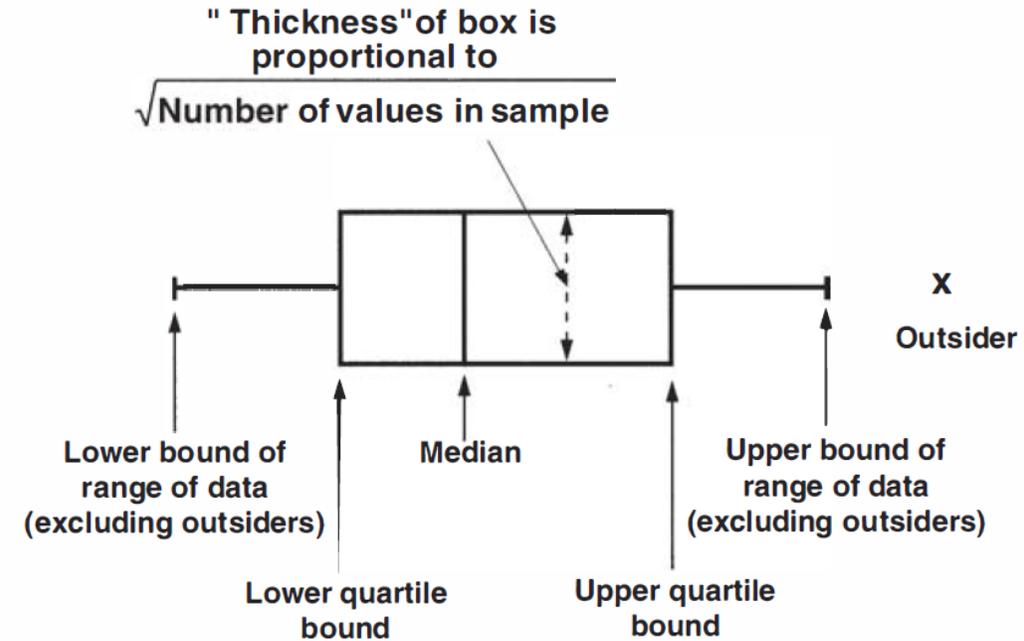


FIGURE 41.5 Tukey's (1977) box-and-whisker plot uses robust statistics such as the median and the interquartile range to summarize the distribution of a data set. In particular it provides a visual depiction of location, spread, skewness, tail length, and outlying data points (Hoaglin et al. 1983). As in the above diagram, an "outsider" refers to values that are far outside the normal range. Additional information on box-and-whisker plots and other interesting aspects of robust and exploratory data analysis can be found elsewhere (Tukey 1977, Hoaglin et al. 1983, Reckhow and Chapra 1983, etc.).

Estimation of Partition Coefficient

Once these values are plotted for a variety of major classes of toxicants, we can use box-and-whisker plots.

One simplification is:

$$\beta = \frac{Q}{Q + k_1 V_1 + v_v A F_{d1}}$$

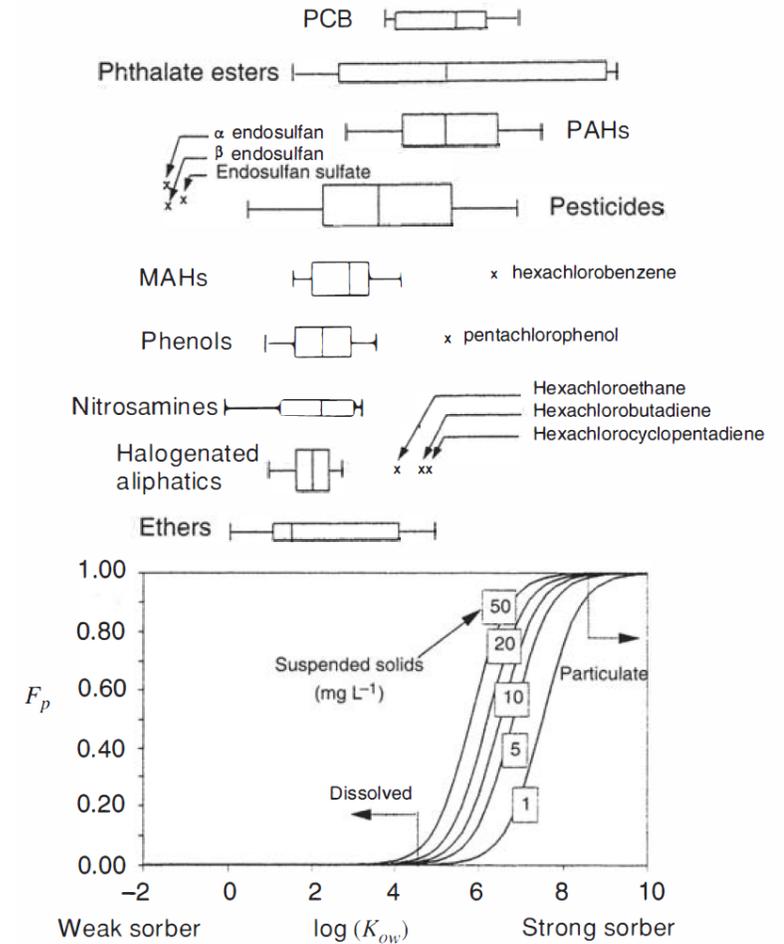


FIGURE 41.4 Plot of fraction dissolved, F_d , and fraction particulate, F_p , versus partition coefficients (Chapra 1991). Each curve represents a particular suspended solids concentration. Box-and-whisker diagrams (see Fig. 41.5) for nine classes of organic contaminants are drawn above the plot.

Sorption Revisited (The “Third-Phase” Effect)

From previous sections we have seen that suspended solids are categorized as allochthonous (drainage basin) and autochthonous (photosynthesis).

We expand in this section to include an approach to model particulate organic carbon (POC). Further, this perspective would have significant concentrations of dissolved (and colloidal) organic carbon (DOC). This DOC would be the “third phase” in addition to the particulate and dissolved phases.

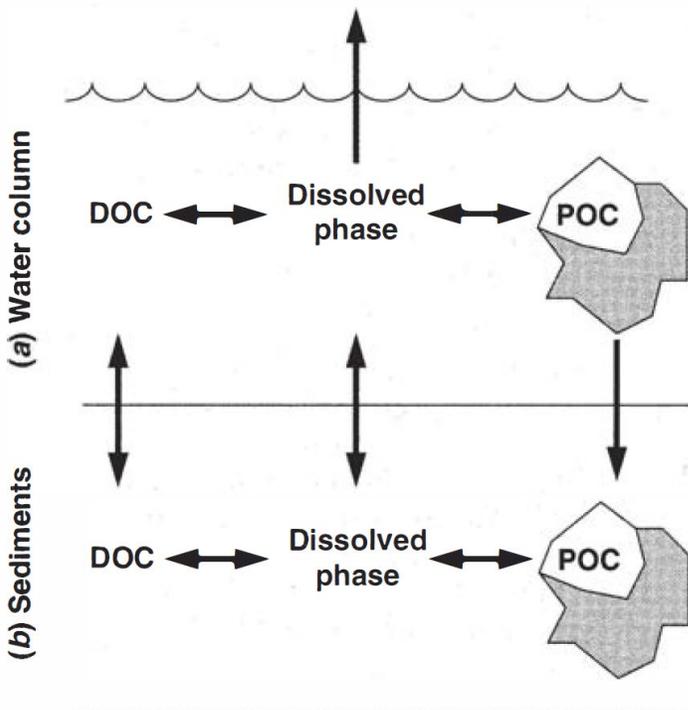


FIGURE 41.6
Depiction of how a DOC “third phase” competes with POC for dissolved toxicant in the (a) water and in the (b) sediments.

Sorption Revisited (The “Third-Phase” Effect)

To quantify this third phase recall the dissolved fraction is:

$$F_d = \frac{1}{1 + K_d m}$$

We have seen that the partitioning coefficient can be related to the octanol-water partition coefficient by:

$$K_d = 6.17 \times 10^{-7} f_{oc} K_{ow}$$

Thomann and Mueller (1987) have noted this can be approximated by:

$$K_d \approx (1 \times 10^{-6} K_{ow}) f_{oc}$$

Substituting this into above yields:

$$F_d = \frac{1}{1 + (1 \times 10^{-6} K_{ow}) f_{oc} m}$$

$$F_d = \frac{1}{1 + K_d m}$$

“Suspended
solids
basis”

$$K_{oc} f_{oc} m$$

$$K_{oc} POC$$

$$10^{-6} K_{ow} POC$$



$$F_d = \frac{1}{1 + 10^{-6} K_{ow} POC}$$

“Organic
carbon
basis”

Sorption Revisited (The “Third-Phase” Effect)

$$F_d = \frac{1}{1 + K_d m}$$

“Suspended solids basis”

$$K_{oc} f_{oc} m$$

$$K_{oc} POC$$

$$10^{-6} K_{ow} POC$$



$$F_d = \frac{1}{1 + 10^{-6} K_{ow} POC}$$

“Organic carbon basis”

$$F_d = \frac{1}{1 + (1 \times 10^{-6} K_{ow}) f_{oc} m}$$

recognizing that $POC = f_{oc} m$

$$F_d = \frac{1}{1 + (1 \times 10^{-6} K_{ow}) POC}$$

FIGURE 41.7

Depiction of how an organic-carbon basis has supplanted the original “suspended solids” basis employed in early water-quality models of toxic organic sorption.

Sorption Revisited (The “Third-Phase” Effect)

Assume that the toxicant associates with DOC, the third phase can be incorporated and three fractions derived:

$$F_d = \frac{1}{1 + K_d m}$$

“Suspended solids basis”

$$\underbrace{K_d m}_{K_{oc} f_{oc} m}$$

$$\underbrace{K_{oc} f_{oc} m}_{K_{oc} POC}$$

$$\underbrace{K_{oc} POC}_{10^{-6} K_{ow} POC}$$

↓

$$F_d = \frac{1}{1 + 10^{-6} K_{ow} POC}$$

“Organic carbon basis”

$$F_{d1} = \frac{1}{1 + (1 \times 10^{-6} K_{ow})(POC_1 + DOC_1)}$$

$$F_{p1} = \frac{(1 \times 10^{-6} K_{ow}) POC_1}{1 + (1 \times 10^{-6} K_{ow})(POC_1 + DOC_1)}$$

$$F_{o1} = \frac{(1 \times 10^{-6} K_{ow}) DOC_1}{1 + (1 \times 10^{-6} K_{ow})(POC_1 + DOC_1)}$$

where subscript 1 denotes water column and F_{d1} , F_{p1} , F_{o1} = dissolved, POC, DOC

Sorption Revisited (The “Third-Phase” Effect)

Similarly for fractions within the sediments:

$$F_d = \frac{1}{1 + K_d m}$$

“Suspended solids basis”

$$\underbrace{K_d m}_{K_{oc} f_{oc} m}$$

$$\underbrace{K_{oc} f_{oc} m}_{K_{oc} POC}$$

$$\underbrace{K_{oc} POC}_{10^{-6} K_{ow} POC}$$

↓

$$F_d = \frac{1}{1 + 10^{-6} K_{ow} POC}$$

“Organic carbon basis”

$$F_{dp2} = \frac{1}{\phi + (1 \times 10^{-6} K_{ow})(POC_2 + \phi DOC_{p2})}$$

$$F_{p2} = \frac{(1 \times 10^{-6} K_{ow}) POC_2}{\phi + (1 \times 10^{-6} K_{ow})(POC_2 + \phi DOC_{p2})}$$

$$F_{op2} = \frac{(1 \times 10^{-6} K_{ow}) DOC_{p2}}{\phi + (1 \times 10^{-6} K_{ow})(POC_2 + \phi DOC_{p2})}$$

where subscript 2 denotes sediments and F_{dp2} , F_{p2} , F_{op2} = dissolved in pore water, POC, dissolved in pore-water DOC. DOC_{p2} = dissolved organic carbon concentration in porewater ($gC\ m^{-3}$); POC_2 = particulate organic carbon on sediment ($gC\ m^{-3}$)

Sorption Revisited (The “Third-Phase” Effect)

It is often convenient to make the following substitution in these equations:

$$POC_2 = f_{oc,2}(1 - \phi)\rho$$

where $f_{oc,2}$ = dry-weight fraction of organic carbon in sediments (gC g^{-1}).

Higher DOC would detract from the volatilization and sedimentation mechanism because less toxicant would be associated with dissolved phase and settling particles.

$$F_d = \frac{1}{1 + K_d m}$$

“Suspended solids basis”

$$\underbrace{K_d m}_{K_{oc} f_{oc} m}$$

$$\underbrace{K_{oc} f_{oc} m}_{K_{oc} POC}$$

$$\underbrace{K_{oc} POC}_{10^{-6} K_{ow} POC}$$



$$F_d = \frac{1}{1 + 10^{-6} K_{ow} POC}$$

“Organic carbon basis”