Mass-transfer

1. Reflection: From this last section of the course: (a) what concept should be understood (b) what types of equations should be mastered?

2. Peer Review / Final Project
3. Workshop
4. Volatilization
5. Parameter Estimation
6. Toxicant-Loading Concept

Volatilization

Many toxic substances move across a lake’s surface by volatilization. The flux of a gas across the air-water interface can be modeled as:

$$J = v_v \left(\frac{p_g}{H_e} - c_l \right)$$

where J = mass flux (mole m^{-2} yr^{-1})

v_v = net transfer velocity across the air-water interface (m yr^{-1})

p_g = partial pressure of gas in the air over the water (atm)

H_e = Henry’s constant (atm m^3 $mole^{-1}$)

c_l = concentration of the gas in the water (mole m^{-3})

Volatilization

The transfer velocity can be calculated based on two film theory:

$$v_v = K_l \frac{H_e}{H_e + RT_a(K_l/K_g)}$$

Contaminant-specific

Environment-specific

where K_l and K_g = mass-transfer coefficient liquid, gas film (m yr^{-1})

R = universal gas constant [8.206×10^{-5} atm m^3 $(\text{K mole})^{-1}$]

T_a = absolute temperature (K)

Volatilization

The transfer coefficients can be computed based on more fundamental parameters. For stagnant systems (e.g. lakes):

$$K_l = \frac{D_l}{z_l} \qquad K_g = \frac{D_g}{z_g}$$

where D_l and D_g = diffusion coefficients for toxicant in liquid, gas film

z = the stagnant film thickness

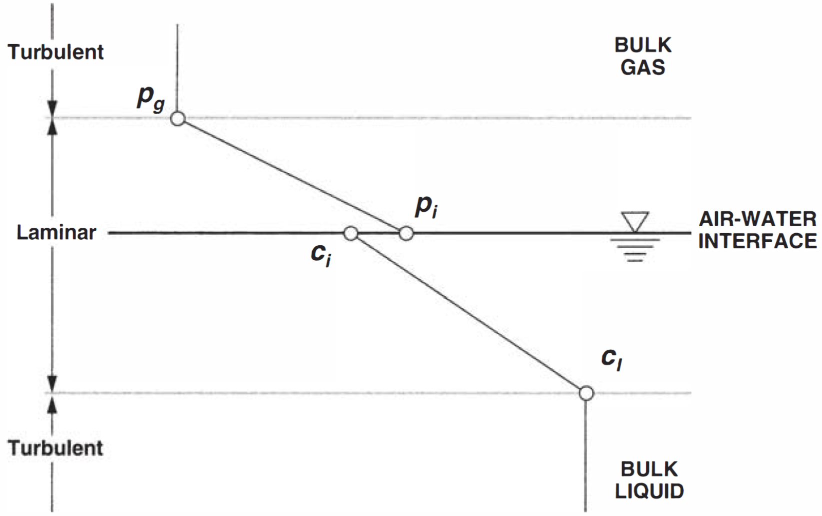


FIGURE 20.2
Schematic representation of Whitman's two-film theory of gas transfer. Liquid and gas concentration at the interface are assumed to be at an equilibrium as defined by Henry's law. Gradients in the films control the rate of gas transfer between the bulk fluids.

Volatilization

For rivers, the liquid flow is turbulent:

$$K_l = \sqrt{r_l D_l} \qquad K_g = \sqrt{r_g D_g}$$

where the r’s are the renewal rates.

The volatilization model can be integrated into a mass-balance by multiplying the flux ($J = v_v \left(\frac{p_g}{H_e} - c_l\right)$) by surface area to give:

$$V\frac{dc}{dt} = v_v A_s \left(\frac{p_g}{H_e} - c_d\right)$$

where *V* = volume of the water being modeled (m^3) and *A_s* = surface area. The subscript for c denotes “dissolved”.

Volatilization

The result could be simplified for oxygen:

$$V\frac{do}{dt} = K_l A_s(o_s - o)$$

where o_s = saturation concentration related to partial pressure of oxygen in the atmosphere (g m^3) and o = concentration of oxygen in the water in mass units (g m^{-3}).

Since not abundant in gaseous concentration ($J = v_v\left(\frac{p_g}{H_e} - c_l\right)$) becomes:

$$J = -v_v c_d$$

Multiplied by the lake surface area and toxic substance's molecular weight:

$$V\frac{dc}{dt} = -v_v A_s c_d$$

Parameter Estimation

Now the key to representing volatilization hinges on estimating v_v. This means we must estimate values for Henry's constant and the liquid, gas-film-transfer coefficients.

Molecular weight and Henry's constant.

Of priority pollutants, molecular weights range from low (50.6) for halogenated aliphatic chloromethane to high (430) for the pesticide toxaphene.

The lightest groups (<200): halogenated aliphatics, phenols, monocyclic aromatics, ethers, and nitrosamines

Heaviest: pesticides, followed by phthalate esters and PCBs (>200). The PAHs intermediate.

Parameter Estimation

The diagram shows three classes of compounds: highly insoluble (halogenated aliphatics, phenols, monocyclic aromatics, PCBs).

Relative solubility

Moderately insoluble.

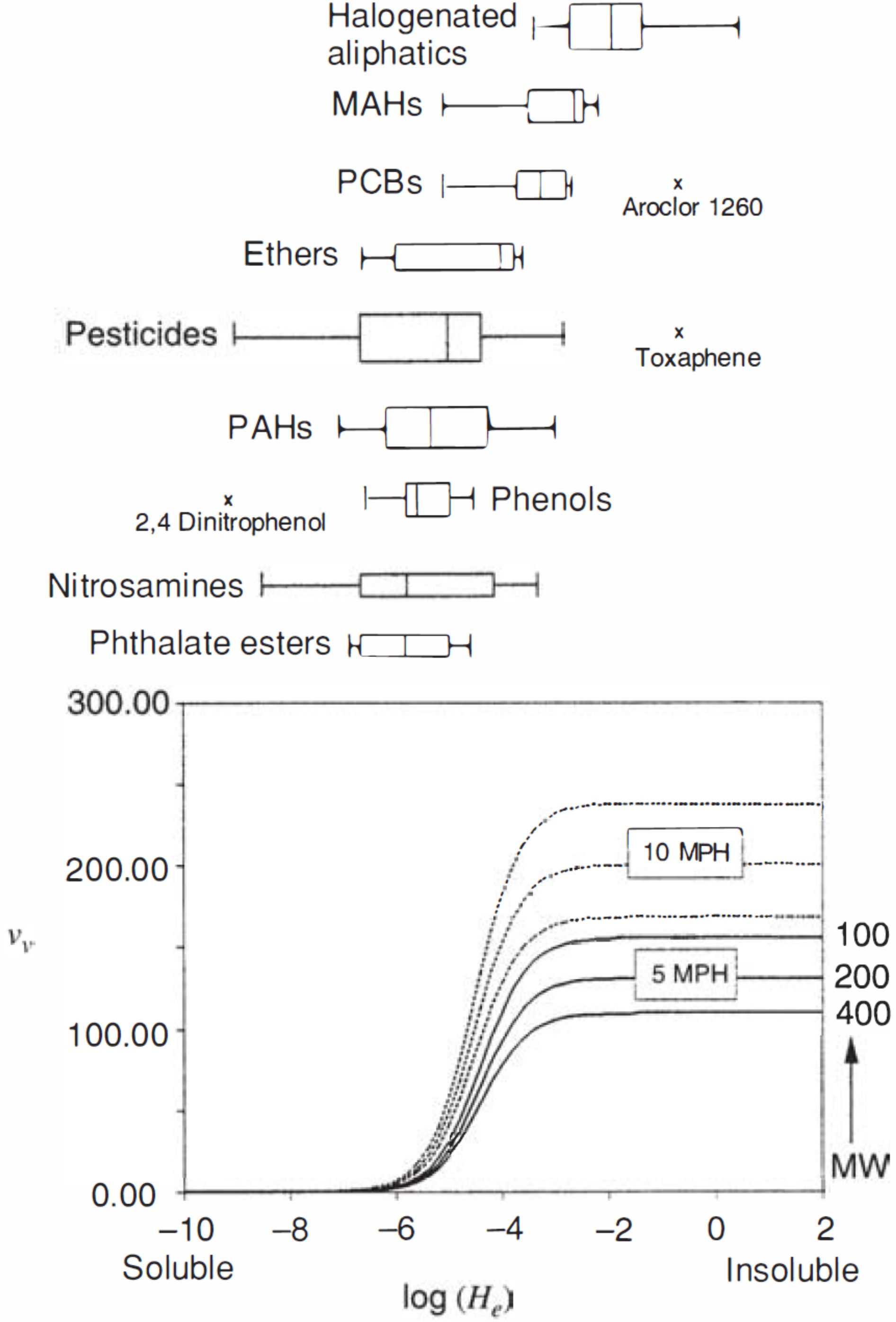


FIGURE 41.9 Plot of volatilization transfer coefficient v_v versus Henry's constant H_e (Chapra 1991). Each curve represents a particular molecular weight. Box-and-whisker diagrams (see Fig. 41.5) for nine classes of organic contaminants are drawn above the plot.

Parameter Estimation

Film-transfer coefficients:

Transfer coefficients are commonly correlated to other studied transfer processes.

Liquid-film coefficient correlated with dissolved oxygen transfer coefficient. From Lecture 20, the liquid-film mass transfer coefficient can be related to the oxygen-transfer coefficient K_L by:

$$K_l = K_{l,O_2}\left(\frac{32}{M}\right)^{0.25}$$

M = molecular weight , $K_{l,O2}$ = oxygen transfer coefficient.

Gas-film coefficient correlated with evaporative transport of water vapor. Gas-film rate:

$$K_g = 168\, U_w\, \left(\frac{18}{M}\right)^{0.25}$$

where U_w = wind speed (mps), based on gas-film transfer coefficient for water vapor.

Discussion

Ideas: How can we get started with modeling?

Individual: Empirical data around region, practice calculating; find one and get hands-on exposure; papers looking at model, see how they use and employ model, get direct feedback; tutorials online; manuals

Roadblock: person to reference during learning; lack of resources for self-learning

Course: Modeling example problems that are local (internalize issues); demos (simple exercise) in a programming language (python,R); tutorials online; manuals

Roadblock: complicated/time-intensive; too-much energy for mastering in one semester; different programming language preferences (might need basis before starting class); homework dedicated to a program (QUAL2K/E) on their own; struggle during assignment

EXAMPLE 41.1. KINETIC PARAMETER ESTIMATION FOR PCB. Estimate (*a*) the sorption coefficient and (*b*) the volatilization mass-transfer velocity for high-molecular-weight PCBs (> 250 gmole). Note that parameters for these compounds can be summarized as

Toxicant	**MW**	log (K_{ow})	log (H_e)
Aroclor 1016	257.9	5.58	−3.48
Aroclor 1242	266.5	5.29	−2.42
Aroclor 1248	299.5	5.97	−2.45
Aroclor 1254	328.4	6.14	−2.84
Aroclor 1260	375.7	6.99	−0.60
Mean	305.6	5.99	−2.358

Assume that the wind speed is approximately 10 mph (= 4.47 m s^{-1}) and that the temperature is 10°C (= 283 K).

Toxic-Loading Concept

To assess the big picture of toxic substance's transport and fate in natural waters we must incorporate sorption and volatilization into a simple toxicant loading model using the two-layer sediment-water model.

Recall the mass balance for water and sediment layer of a well-mixed lake yields:

$$c_1 = \frac{Qc_{in}}{Q + v_T A}$$

$$c_1 = \frac{Qc_{in}}{Q + k_1 V_1 + v_v A F_d + (1 + F_r')(v_s F_{p1} + v_d F_{d1})A}$$

where F_r' = ratio of recycle sediment purging to total sediment purging.

$$F_r' = \frac{v_r + v_d F_{d2}}{v_r + v_b + v_d F_{d2} + k_2 H_2}$$

Toxic-Loading Concept

This model depends on 14 independent parameters. In order to solve we need some simplifying assumptions and some manipulations to make it more manageable. First we express F_r' in terms of F_r:

$$v_r = F_r v_{sb}$$

and

$$v_b = (1 - F_r) v_{sb}$$

where v_{sb} = a scaled settling velocity.

$$v_{sb} = \frac{m}{(1-\phi)\rho} v_s$$

Using these terms, F_r' becomes:

$$F_r' = \frac{v_r + v_d F_{d2}}{v_r + v_b + v_d F_{d2} + k_2 H_2} \qquad F_r' = \frac{F_r v_{sb} + v_d F_{d2}}{v_{sb} + v_d F_{d2} + k_2 H_2}$$

Toxic-Loading Concept

Now instead of interdependent variables, v_r, v_b, it is expressed in terms of the single parameter F_r.

Two more simplifying assumptions:

1. **Decay reactions are negligible (i.e. $k_1 = k_2 = 0$)**, this ignores removal mechanisms (hyrdrolysis, photolysis, biodegradation) creating upper bound.

2. **Water sorption is equal to sediment sorption (i.e. $K_{d1} = K_{d2}$)**. Meaning diffusive sediment-water transfer will be negligible, creating upper bound.

Toxic-Loading Concept

This reduces the equation to:

$$c_1 = \frac{Qc_{in}}{Q + v_T A}$$

where v_T = net toxicant loss rate (m yr^{-1}), which represents all purging mechanism aside from flushing.

Sorption

$$v_T = v_v F_{d1} + (1 - F_r) v_s F_{p1}$$

Volatilization

Sediment
interactions

This approach presents a way to separate the lake-specific flushing from the toxicant-specific mechanisms. Here we can use the top equation to see how different values of v_T affect concentration with different level of flushing.

Toxic-Loading Concept

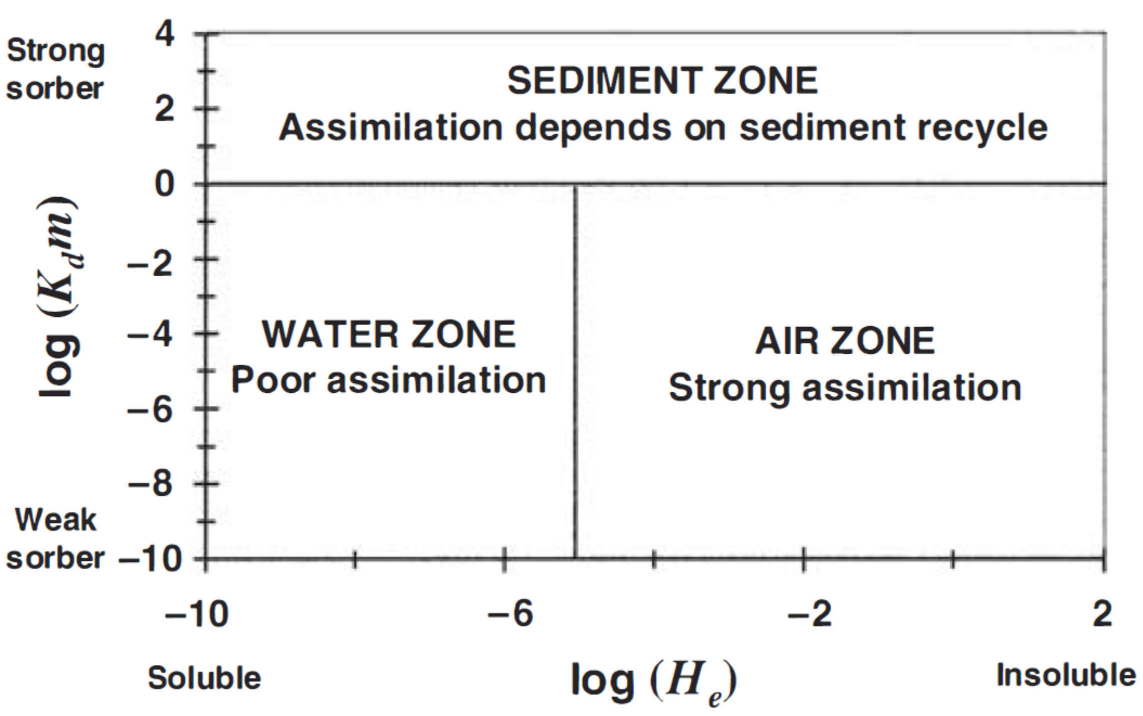


FIGURE 41.11
Three regions on a logarithmic space defined by sorption ($K_d m$) versus volatilization (H_e).

The impact of sorption and volatilization on v_T can be assessed by mapping on a logarithmic space defined by sorption ($K_d m$) and volatilization (H_e).

We assume at T_a =283 K, M = 200 g gmole^{-1}, U_w = 2.235 m s^{-1}, and v_s =91.25 m yr^{-1}.

Thus three distinct regions can be studied:

Air zone (insoluble weak sorbers): High removal rates, dissolved and volatilized

Water Zone (soluble weak sorbers): low removal rates, dissolved and not volatilized

Sediment Zone (strong sorbers): not dissolved, removal depends on sediment-water interactions, based on resuspension.

Toxic-Loading Concept

Here we plot organic priority pollutants on the sorption/volatilization space. We specify the suspended solids concentration (5 g m^{-3}) to indicate a mildly eutrophic lake condition.

A significant portion of the 114 organic priority pollutants rapidly purge due to volatilization.

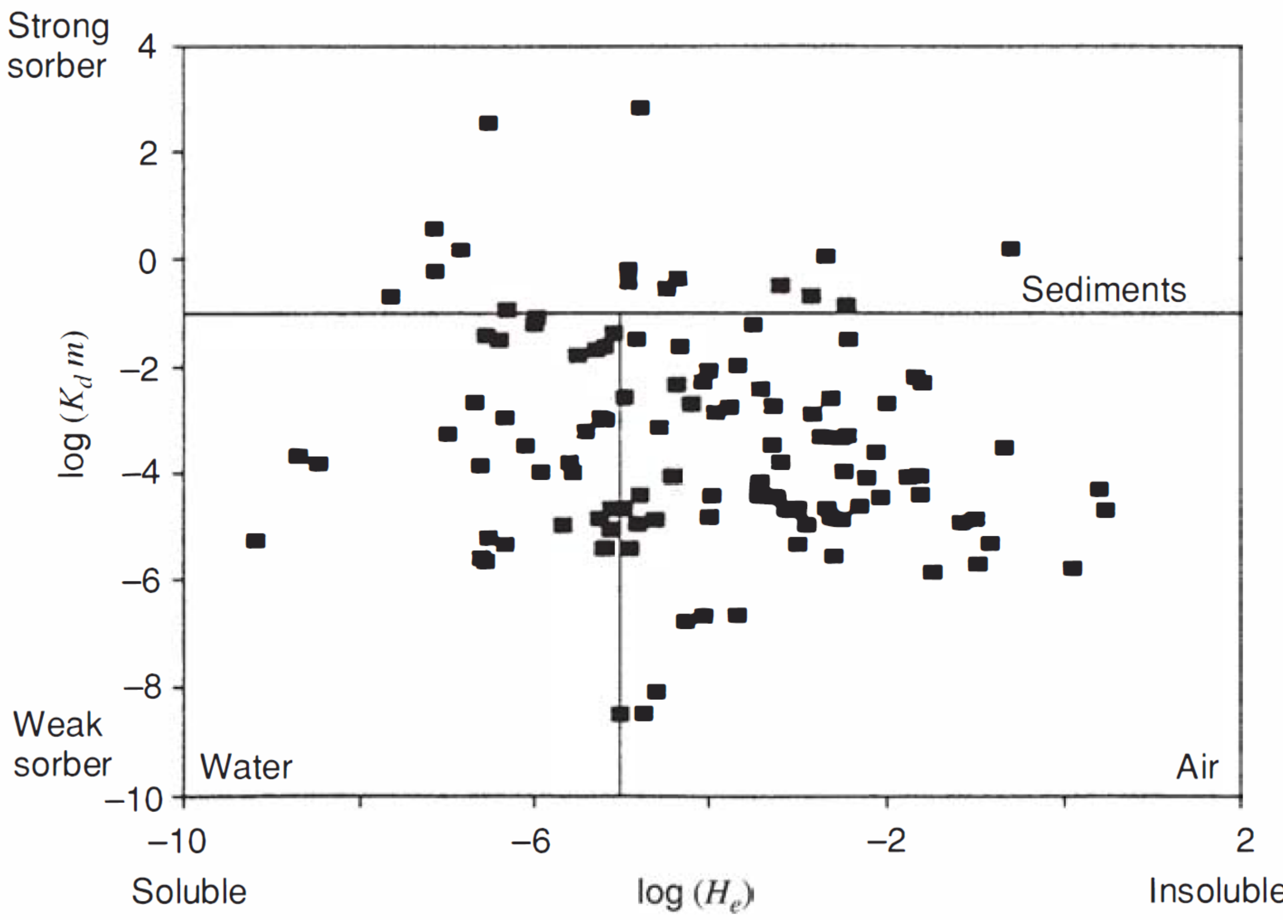


FIGURE 41.12
Mapping for organic priority pollutants on logarithmic space defined by sorption ($K_d m$) versus volatilization (H_e). A suspended solids concentration of 5 g m^{-3} was used to develop the plot.

Toxic-Loading Concept

Further, Chapra (1991) worked to arranged the pollutant categories across the sorption/volatilization space (Again using 5 g m^{-3}).

The first plot shows how the individual pesticides fall on the space.

These plots can demonstrate which chemicals among a large class of toxicants would have particular assimilation characteristics.

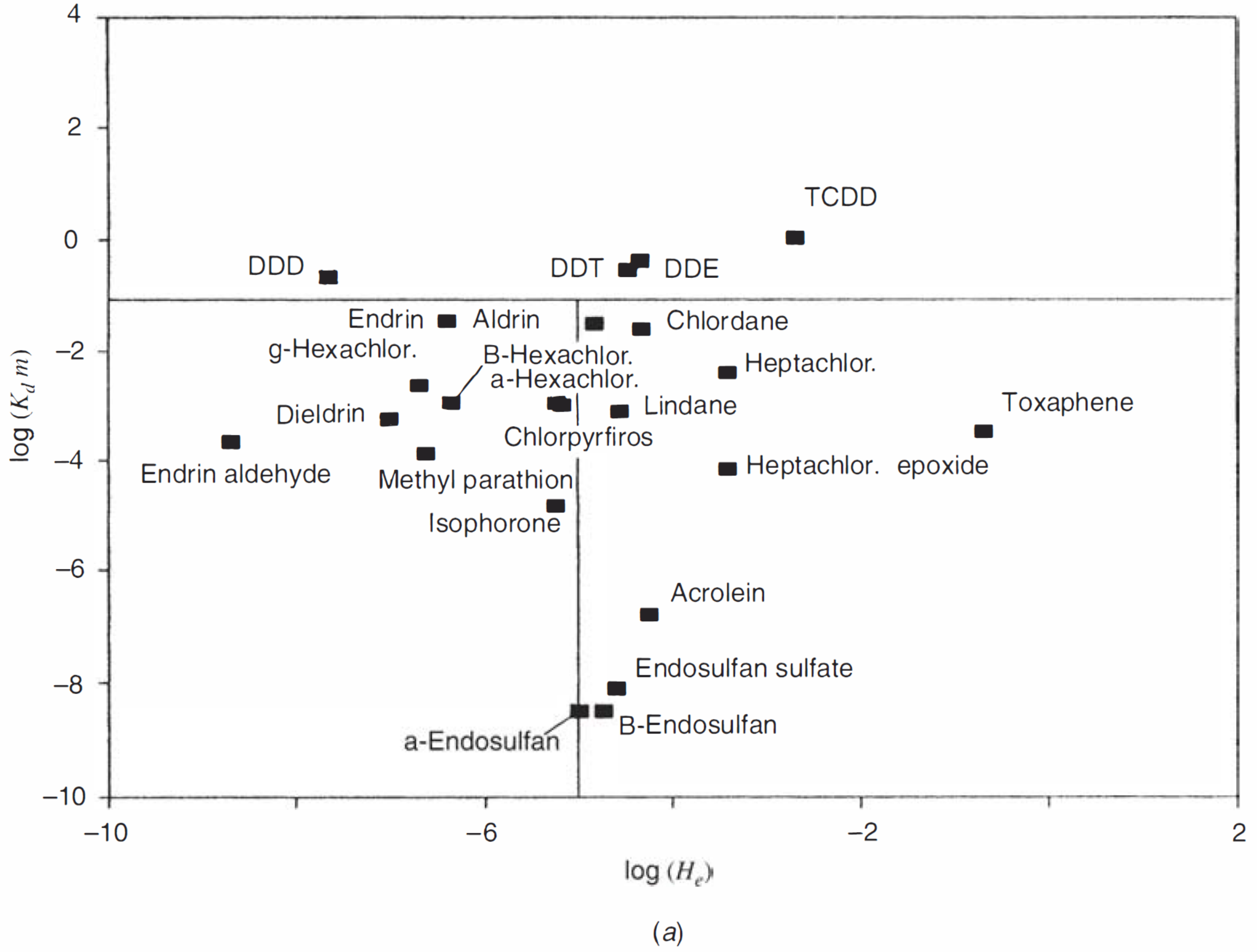
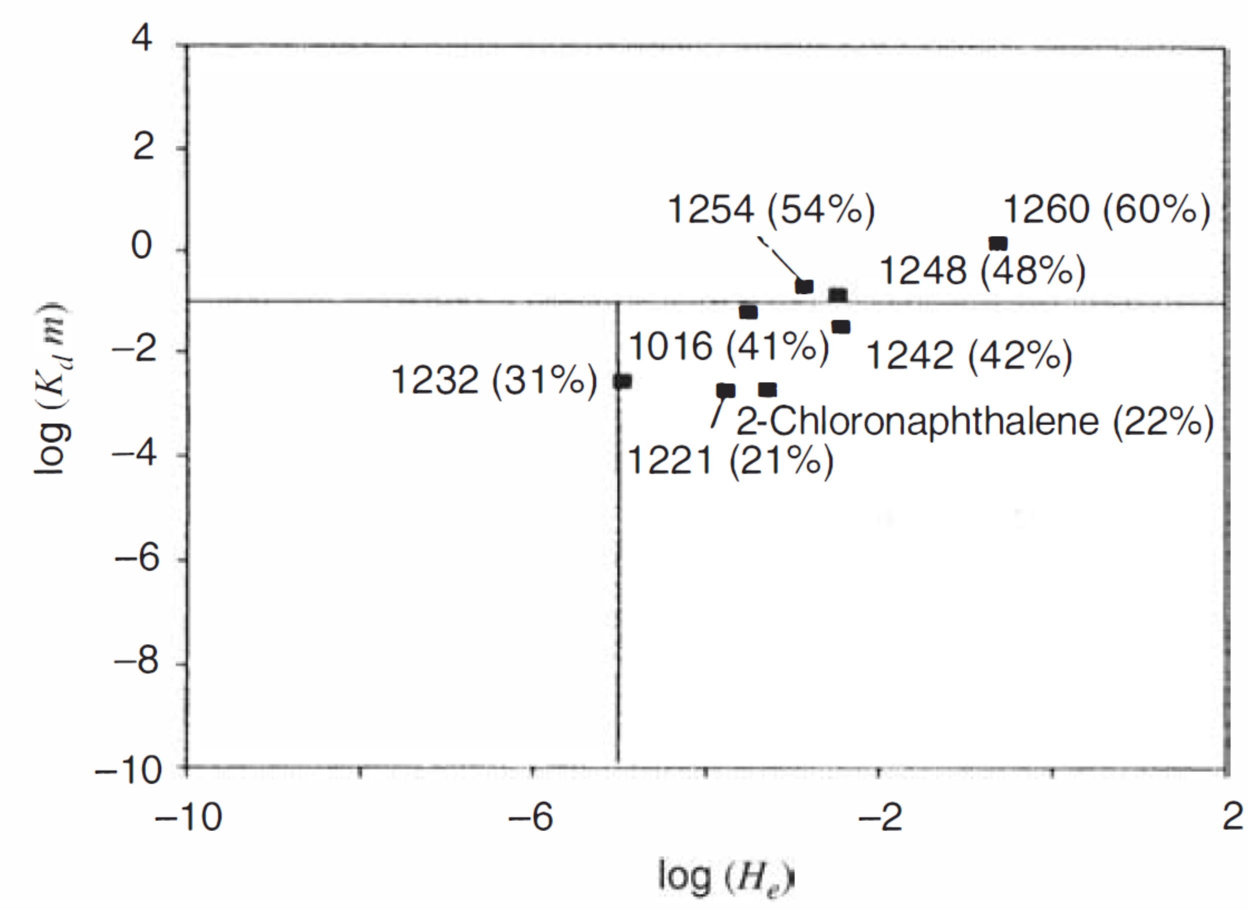


FIGURE 41.13
Mappings for (*a*) pesticides, (*b*) PCBs, and (*c*) PAHs.

Toxic-Loading Concept

This plot shows PCBs and attached more information to the plot. Here the numbers in the parentheses indicate the percent chlorine for each PCB Arochlor. This suggests a positive correlation between the sorption, volatilization, and percent chlorine.

While more chlorine indicates more volatilization, the increased association with particulate matter means retention.



Toxic-Loading Concept

This plot classifies the PAHs according to their number of aromatic rings. The trend here indicates that volatilization decreases as sorption increases.

As number of rings increases in lake with negligible resuspension, assimilation would occur through sedimentation, which would supplant volatilization.

These results are dependent however on simplifying assumptions, our choice of parameters (e.g. K_{ow}, H_e), etc. General patterns follow this visual framework.