November 2, 2005
Lecture 20: Environmental Chemodynamics (Physicochemical Properties; Phase Transfers)

I. **Exposure Assessment—A Theoretical Basis**
    A. Thus far, we have reviewed the first two processes of the risk assessment paradigm, hazard identification and assessment, and dose-response relationships.
        1. Although we have discussed toxicological endpoints and the NOAEL, we have not put this in context to what exposures are likely to be.
    B. From an ecotoxicological perspective, exposure will depend on the magnitude of residues in the environment.
        1. In an ideal world, we would measure everything, using an army of environmental analytical chemists.
        2. Of course, the resources don't exist to carry out the ideal so we would like to predict exposure and ultimately predict effects.
    C. Prediction of exposure requires a theoretical framework that explains exposure from release of a contaminant (i.e., from its source) to uptake or absorption by an organism.
        1. Such prediction depends on a model that incorporates the complexity of the environment and all possible interactions within its abiotic compartments and between the abiotic and biotic compartments.
        2. The complexity is aptly illustrated in Figure 1 and shows just for an aquatic environment, the processes are quite numerous.
    D. The task, however, has been made somewhat more approachable by a realization of how thermodynamics and kinetics controls chemical fate; thus, a new theoretical paradigm has evolved to help us understand environmental behavior of chemicals.
        1. With the new paradigm, we can dispel the myth of a difference between natural and synthetic, for all chemicals behave in accordance with the "laws" of thermodynamics (direction and extent of change or reaction); changes in a system or reactions, however, could be fast or slow (kinetics).
    E. Environmental Chemodynamics has developed as an interdisciplinary study of the relationship between physicochemical properties and environmental behavior, and has brought us one step closer to adequate predictions of chemical behavior and biological exposure.
        1. A holistic perspective
            a. Viewing the biosphere as compartments with interfaces between all compartments
                a. Exception: note in Figure 1 that sediment at the bottom of an aquatic system does not interface directly with the atmosphere.
                    1. However, if the sediment is perturbed, and smaller particles become suspended in the water, then equilibrium processes will cause diffusion of a contaminant back in to the water column, and eventually increase its potential for diffusion into the atmosphere.
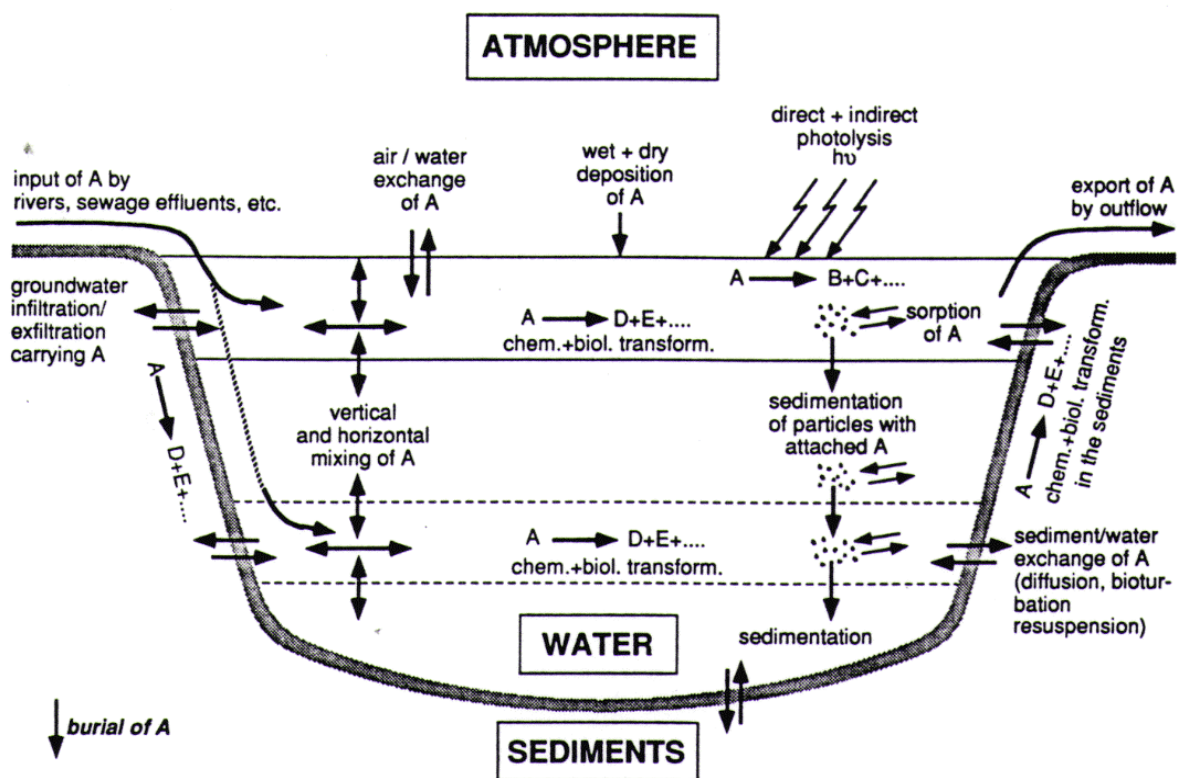
Figure 1. Possible interactions of contaminant A in an aquatic habitat. Note that the
water is "connected" to the sediments and the air. Also, the water is an open
system, receiving contaminants from the terrestrial compartments via runoff or
influent from rivers, but also from atmospheric deposition. Similarly,
contaminants can be exported from this aquatic habitat to downstream areas or
to the atmosphere. (From Schwarzenbach et a. 1993.

   b. The compartments are thought of as phases; knowing the magnitude of
       each phase would allow a "back-of-the-envelope" calculation of
       concentrations of contaminants if one knew their total emissions (from
       Haque and Freed 1974)
       1. air (atmosphere) [5.3 x 10^{18} kg]
       2. water (lithosphere) [1.3 x 10^{21} kg]
       3. soil (lithosphere) [to 6 inches = 1.1 x 10^{17} kg]
       4. biota
       5. plants [1.1 x 10^{15} kg]
       6. animals [2 x 10^{13} kg]
   2. Focus areas of Environmental Chemodynamics
       a. Physicochemical properties
           1. vapor pressure
           2. water solubility
       b. Partitioning (phase transfer)

         1. air:water
         2. soil:water
         3. organic solvent:water
         4. organism:environmental phase
    c. Attenuation (reactions: degradation, transformation)
         1. abiotic degradation/transformation
         2. biotic degradation/transformation
    d. Transport (mass transfer)
         1. volatilization
         2. leaching
         3. runoff
    e. Modeling
         1. deterministic (based on empiricism; i.e., observations)
         2. stochastic (inductive; based on mechanistic understanding and probability)

II. The Thermodynamic Perspective of Chemical Behavior

    A. When we want to predict chemical behavior in the environment, we are essentially focusing on the final chemical composition of a given system when no more net changes occur; at this point the system has attained minimum energy, and the system is said to be in equilibrium.

    B. Thermodynamics is concerned with direction and extent of a reaction (i.e., chemical equilibria), but we are also interested in pathways and time course of processes, which is described by chemical kinetics (the speed of a reaction).

    C. To illustrate the difference between thermodynamic considerations and kinetics consider two environmental processes:

        1. Movement of a molecule from a dilute solution of water into the air immediately above the water

           a. The tendency to move from one phase or another is controlled by the expected equilibrium of the molecules between the air and water; in this case the movement or phase transfer is reversible, but the overall direction of movement depends on how far the system is from equilibrium (thermodynamics)

        2. Biotransformation of a highly toxic molecule to a less toxic compound that can be excreted by cells

           a. In this situation we would be interested in how quickly this process occurred (kinetics)

    D. Thus, when two phases (or compartments) are not in equilibrium, thermodynamics tells which direction substances tend to diffuse to reach equilibrium.

        1. Note that within a phase, a mass of substance moves or diffuses directionally because of concentration differences in different parts of the phase;

        2. Substances move across interfaces between phases (i.e., they partition) because of tendency of systems to maximize entropy

           a. Entropy is the randomness or disorder of a system and it is comparable to the degrees of freedom that a molecule has to move

    1. For example, in Figure 2, situation A shows contaminant molecules confined to the box on the left and is prevented from moving to the box on the right by a closed valve.
        a. In situation B, the valve is opened and the contaminant is free to move from the box on the left to the one on the right.
        b. The entropy is greatest in situation B, because the contaminant molecules have more room to move about than in situation A.
            1. Equilibrium is reached when the entropy is maximized.
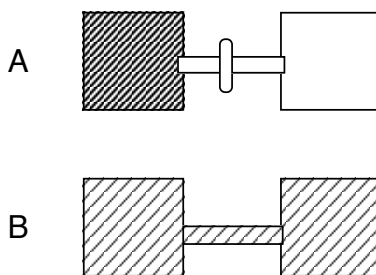
Entropy of substance in B greater than in A

Figure 2. Model illustrating entropy as related to the concentration of molecules in a compartment
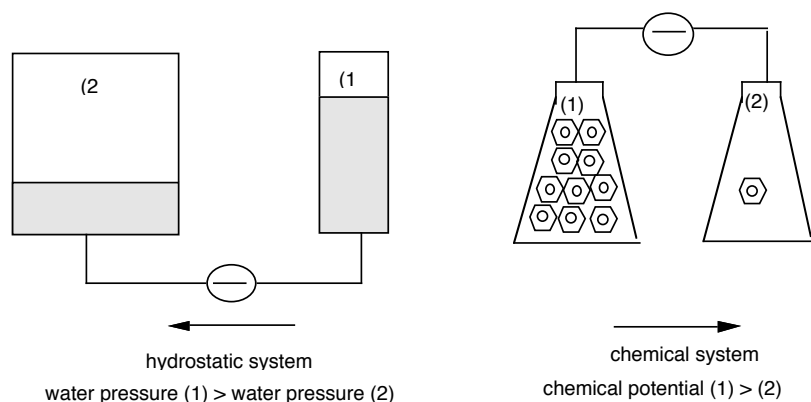
E. Use of Chemical Potential to Assess Tendency of Transfer between Systems or Transformation within a System
    1. Do not mistake an equilibrium condition as two phases (for example, air and water) having the same concentration of contaminant or substance. In other words, the concentration of a substance in each of two phases in equilibrium is not equal in each phase.
        a. For example, oxygen in equilibrium between air and water has a concentration of about 0.3 mol/m^3 (10 mg/L) in water and 8.0 mol/m^3 in the air.
        b. This partitioning result at equilibrium corresponds to a maximum of entropy
    2. The partitioning of chemicals across compartments or within a defined, closed compartment can be expressed by the chemical potential, which is related to the free energy in any system.
        a. Note for purposes of illustration, we are going to consider each environmental compartment as being a definable, closed system, but as you know, the compartments are interfaced and are not definite in size nor structure (i.e., the compartments are open systems).
    3. The average energy status of a group of i molecules is the total free energy
        a. Each molecule has an internal energy resulting from its chemical bonds (i.e., bond vibrations, flexations, and rotations)
        b. Each molecule has an external energy resulting from whole-molecule translations, orientation, and especially interactions of the molecules with the surroundings (which can include other like and/or different molecules)

   c. The total free energy is expressed as the sum of the contributions from all of the different components in a system; the total free energy of a system can also be expressed as the sum of chemical potentials of all the components in the system, as shown below

4. At a constant temperature (T), pressure (P), and composition, the free energy added to the system with each added increment of *i* is referred to as the chemical potential (μ_i) of component *i*.

   a. $$G \ (\ \text{Total Free Energy}\ ) \ = \ \sum_i n_i \ \mu_i \quad \text{where } n_i \text{ is the}$$

molar concentration of component *i* in the system.

   b. Thus, chemical potential changes as a function of the abundance of components.

   c. Chemical equilibrium is characterized by equal chemical potentials for all constituents in two phases (or systems).

5. Chemical potential can be illustrated by an analogy with hydrostatic water pressure and tendency to move between two vessels as controlled by height of water in a given volume (hydrostatic pressure) (Figure 3)

Systems Not At Equilibrium

hydrostatic system
water pressure (1) > water pressure (2)

chemical system
chemical potential (1) > (2)

Systems At Equilibrium

water pressure (1) = water pressure (2)
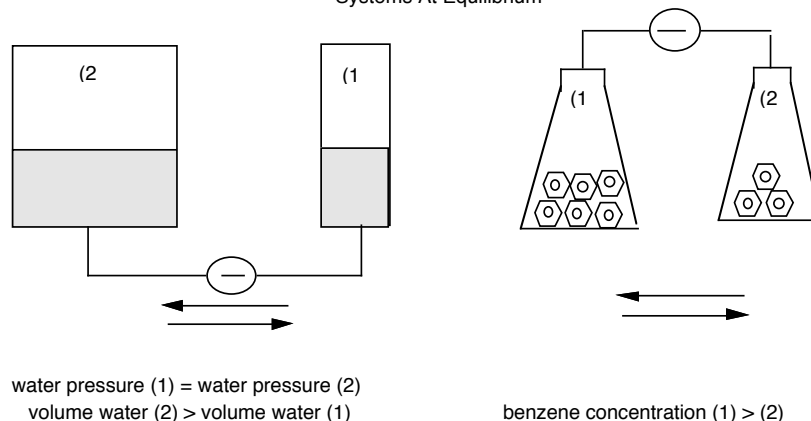volume water (2) > volume water (1)

benzene concentration (1) > (2)

Figure 3. Model for chemical potential at equilibrium

  a. In the above analogy (model), at time 0, the two systems, (1) and (2) are connected by a valve which has just been opened. In the water (or hydrostatic) system and the chemical (benzene liquid) system, a measurable pressure (head pressure and vapor pressure, respectively) exists in each container.

  b. When the valves are open, water and benzene move into the containers of lower relative pressure (i.e., system 2). Think of pressure in this model as a surrogate measure for the chemical potential. The movement is caused not by the number of molecules but by the chemical potential. In other words the chemical potential of benzene in the liquid state is higher than in the vapor state.

  c. Movement stops when equilibrium is reached. Equilibrium occurs in the water system when the head pressures (a.k.a. head potential or hydrostatic potential) are equal. In the chemical system, equilibrium occurs when the pressure in (2) is equal to the pressure in (1). This is equivalent to saying that the chemical potential of x in (1) and (2) are equal.

  d. However, when the potentials are equalized after the valves are opened, the volumes are not equal; thus, in the water system, there is more water in system (2) at equilibrium, but the head potentials are now equal.

   1. In the chemical system, after the valve is opened, the pressure (as a surrogate for chemical potential) in the gas phase becomes equalized, but the amount of x in each system is unequal (and the volume of x would be different).

   2. Thus, the amount of chemical present in two systems at equilibrium can be unequal. This model will aid an understanding of phase transfers, but the direction of transfer and the resulting equilibrium depends largely on the physicochemical properties of water solubility and vapor pressure.

F. Fugacity

 1. Chemical potentials cannot be directly observed; therefore, the concept of fugacity (as a surrogate for chemical potential) was used to describe the "urge" of a molecule to want to "flee" a system; i.e.., the escaping tendency.

  a. Thus in the above systems, when the valves are closed, the material x in vessel (1) of the chemical system and vessel (1) of the water system are said to have higher fugacities than in the opposite vessels.

  b. When the valves are open, the fugacities in the two systems become equalized; thus at equilibrium, the fugacity of the molecules in vessels (1) and (2) are the same.

  c. Note that at equilibrium, the chemical potential of components in flask 1 and 2 are equal, but the concentration of components and thus, the free energy is greater in flask 1 than in flask 2.

 2. Rather than attempt to quantify the chemical potential energies of all components in a system, it is more practical to assess the tendency or "urge" to escape or flee that system; thus fugacity (from the Latin fugere, to flee) is the escaping tendency

a. Relative tendencies to flee various environments is indicative of the relative chemical potentials in those environments;

b. By measuring parameters that lead to a calculation of fugacity and thus coincidentally relative chemical potentials, the direction and extent of transfer and transformation could be quantified

3. A compound with a high fugacity in a phase has a strong tendency to want to leave that phase to a phase where its fugacity is lower [i.e., partition from high fugacity to low fugacity, or in other words, direction of a process is from higher (μ_I) to lower (μ_i)].

4. All concentrations of chemicals in any environmental compartment or phase can be expressed as pressure units (for ex., atmospheres or Pascals)

a. If convert concentrations in a phase to common units like pressure can compare concentrations between phases;

1. Thus can predict the potential to transfer (or the direction of transfer) from one phase to another.

2. Remember, the tendency to move from phase to another is influenced by concentration; molecules tend to move from higher concentrations to lower concentrations.

5. At equilibrium, fugacities of a substance in different phases are identical (if concentrations are expressed in pressure units)

a. Fugacity is linearly proportional to concentration when dealing with the comparatively low concentrations characteristic of environmental contamination

6. Natural systems do not really come to equilibrium; thus one must consider the effects of inputs, outputs, and degradation or transformations within the system; thus kinetic considerations in addition to thermodynamic considerations are important.

7. Practical utilization of fugacity conceptualization

a. One use of the fugacity concept is a rough prediction of the likely environmental fate of a compound that is being marketed for the first time.

III. Physicochemical Properties

A. The key to understanding movement of chemicals toward an equilibrium state (and therefore, predicting concentrations as equilibrium is approached) first starts with a knowledge of the innate physicochemical properties.

1. Physicochemical properties are dependent on the specific molecular composition and three-dimensional structure of a compound, but they are not static. Rather they are dynamic properties that vary depending on the environmental conditions under which they are measured.

2. Physicochemical properties influence all partitioning of chemicals from one environmental compartment to another.

3. Physicochemical properties can be thought of as a measure of chemical to "escape" from itself in the pure state.

4. The two most important physicochemical properties that are predictive of distribution of chemicals in the environment are vapor pressure and water solubility.

B. Vapor Pressure
  1. Defined as the pressure (P^0)of the vapor of a compound at equilibrium with its pure condensed phase, solid or liquid. [Note that journal give the units of pressure in units of pascals; 1 Pa is equal to 7.5 x 10^{-3} mm Hg)
      a. The boiling point is the temperature at which the P^0 is equal to 1 atmosphere or 101,325 Pa or 760 mm Hg).
      b. Compound to compound variations in V.P. arise because of intermolecular interactions.
      c. Over the ambient temperature range, V.P. of a compound may change by an order of magnitude
  2. Vapor pressure determines to a large extent the tendency of a chemical to transfer to and from gaseous environmental phases (for. ex., the atmosphere, the gas bubble brewing in the Hanford tanks, marsh gas bubbles, etc.); it describes the ideal tendency in the absence of intermolecular interactions or the influence of the aqueous phase.
  3. V.P. arises because at a given temperature, a certain number of molecules thermally jostling about in the condensed phase will continuously acquire sufficient energy to overcome intermolecular attractive forces and escape to the gas phase.
      a. Meanwhile in the gas phase, there will be a continuous collision of gas phase molecules with the surface of the condensed phase; causes dissipation of energy and combining with the condensed phase.
      b. At a given temperature, the opposing processes of escape and condensation reach an equilibrium that is controlled by molecule-molecule attractions in the condensed phase and is characterized by the abundance of molecules in the vapor above the condensed phase.
      c. Comparatively more polar compounds and larger molecules tend to have comparatively lower vapor pressures as a result of attractive forces caused by hydrogen bonding and van der Waals interactions (recall that van der Waals interactions are weak intermolecular attractions caused by very transient changes in electron density about an atom).
          1. High surface tension of water owing to hydrogen bonding
          2. The bigger the molecule the greater the van der Waals attractions.
      d. Examples for compounds in three different states:
          1. Solid: DDT ~ 0.00015 Pa (1.125 x 10^{-6} mm Hg)
          2. Liquid: alachlor ~ 0.0048 Pa (3.6 x 10^{-5} mm Hg)
          3. Gas: methyl bromide 243,200 Pa (1824 mm Hg)
      e. Figures 4, 5, and 6 illustrate the relative magnitude of vapor pressures among different chemical structures and the influence of chemical structure and environmental conditions (namely, temperature) (All figures were copied from Schwarzenbach et al. 1993)
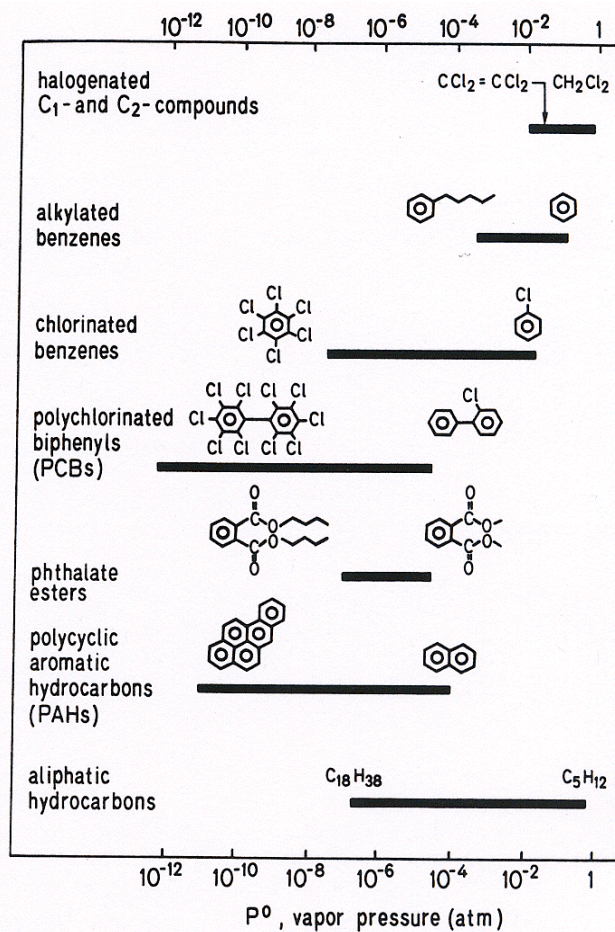
Figure 4. Range of saturation v.p. (P°) for different classes of potential organic contaminants

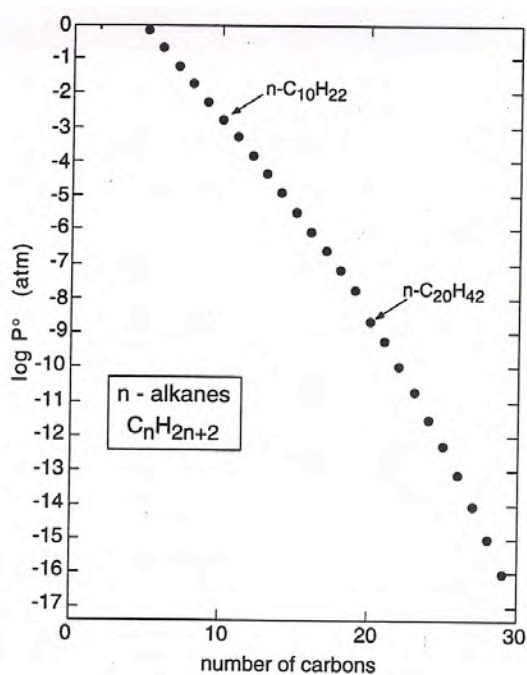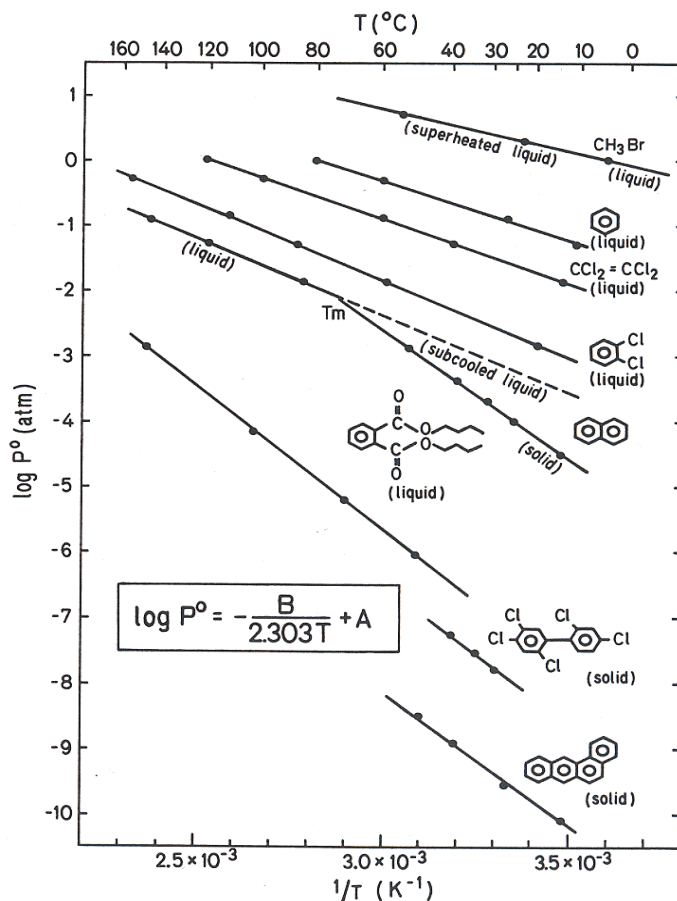Figure 5. Inverse relationship between no. of carbons and v.p. (P°).

Figure 6. The inverse relationship between vapor pressure and temperature.

C. Water Solubility
1. Water solubility (WS) can be defined as the amount of a substance that dissolves in a given quantity of water at a given temperature to form a saturated solution.
   a. Note that water solubility is temperature dependent; thus the WS measured at 15°C will be different than that measured at 25°C
2. Why is WS limited; in other words what limits the total dissolution of a given weight of a substance in a given volume of water?
   a. Water molecules form a highly ordered structure as a result of hydrogen bonding; this property also gives water a very high surface tension (i.e., the intermolecular, cohesive attractions between like molecules of a liquid that cause it to minimize its surface area) as well as its higher than predicted boiling point and lower density as ice than as a liquid.
   b. Hydrogen bonding is a type of intermolecular attraction that exists between hydrogen atom in a polar bond (particularly an H-F, H-O, or H-N bond) and an unshared electron pair on a nearby electronegative ion or atom (usually an F, O, or N atom)
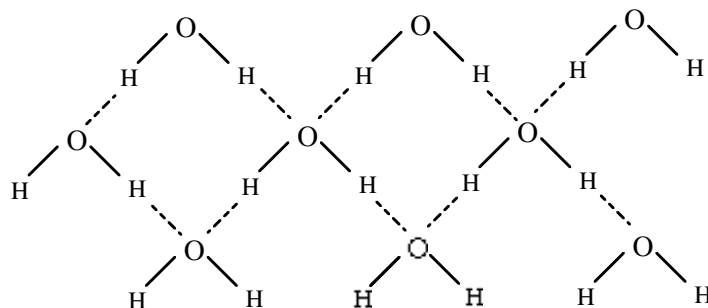
Figure 7. Hydrogen bonding and regular structure of water molecules. Solid lines
represent covalent bonds between H and O of same water molecule; dashed
lines represent hydrogen bonds between H and O of different water molecules.

c. Now if we represent each H_2O molecule by a circle, and the hydrogen
    bonding (i.e., intermolecular forces by arrows), then we see an imbalance
    of forces at the surface (or edge) of the liquid, where the forces are tending
    to draw the water into the interior, thereby reducing the surface area.
    (Figure 8)
    1. (Note that the molecules in the interior are attracted equally in all
        directions). The inward force at the edges of the liquid also makes the
        molecules at the surface pack closely together, causing the liquid to
        behave almost as if it had a skin. A measure of the inward forces that
        must be overcome to expand the surface area of the liquid is given by
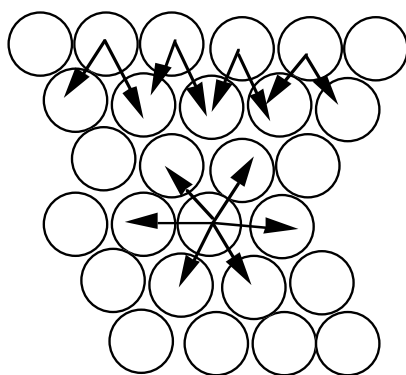   its surface tension.

Figure 8. Model for surface tension of water

d. Now consider what happens if molecules (e.g., a liquid or solid pesticide)
    other than H_2O are placed in the water. The pesticide molecules
    essentially disrupt the water structure. It's analogous to punching a hole
    in the structure.
    1. There are several intermolecular forces at work: the solvent:-solvent
        attractions; solute-solute attractions; and solvent-solute attractions;
        maximum solubility occurs when the solvent-solute interactions are

stronger than the sum of the solute-solute and solvent-solvent interactions (or energy required to separate like molecules)

2. If the pesticide molecules have functional groups that can hydrogen bond, then the water structure is disrupted less (by analogy, the hole is not as big) and more of the molecule can dissolve in water (i.e., the greater the tendency for pesticide molecules to disperse or escape from one another and become surrounded by water molecules)
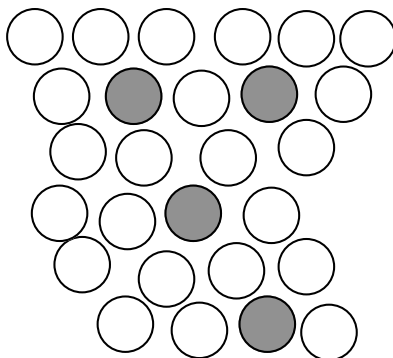
Figure 9. Dissolution of a hydrophilic solute in water

e. If the pesticide molecules lack the ability to hydrogen bond and/or is very hydrophobic ("water fearing"), then the "hole" that is punched is necessarily very large (i.e., larger disruption of the water structure) and comparatively less of the pesticide molecule can be accommodated in the water volume (or in other words fewer pesticide molecules will escape or disperse from one another and become easily surrounded by water molecules); by the same reasoning, fewer water molecules will separate from one another (i.e., the solvent-solvent interactions are much stronger than the solvent-solute interactions).
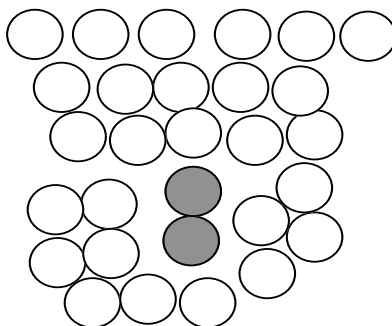
Figure 10. Dissolution of a hydrophobic solute in water

3. Thus the energy costs in overcoming solvent-solvent and solute-solute interactions when mixing a nonpolar or hydrophobic contaminants with water are too great to be compensated by the gain in energy from solute-solvent interactions.

a. Rule of thumb "likes dissolve likes"
4. In another view of the rearrangement of water molecules upon addition of substance, we can assess the associated enthalpy (heat content, which is energy) "costs" associated with breaking and forming bonding interactions of the organic molecules with water (Figure 11).
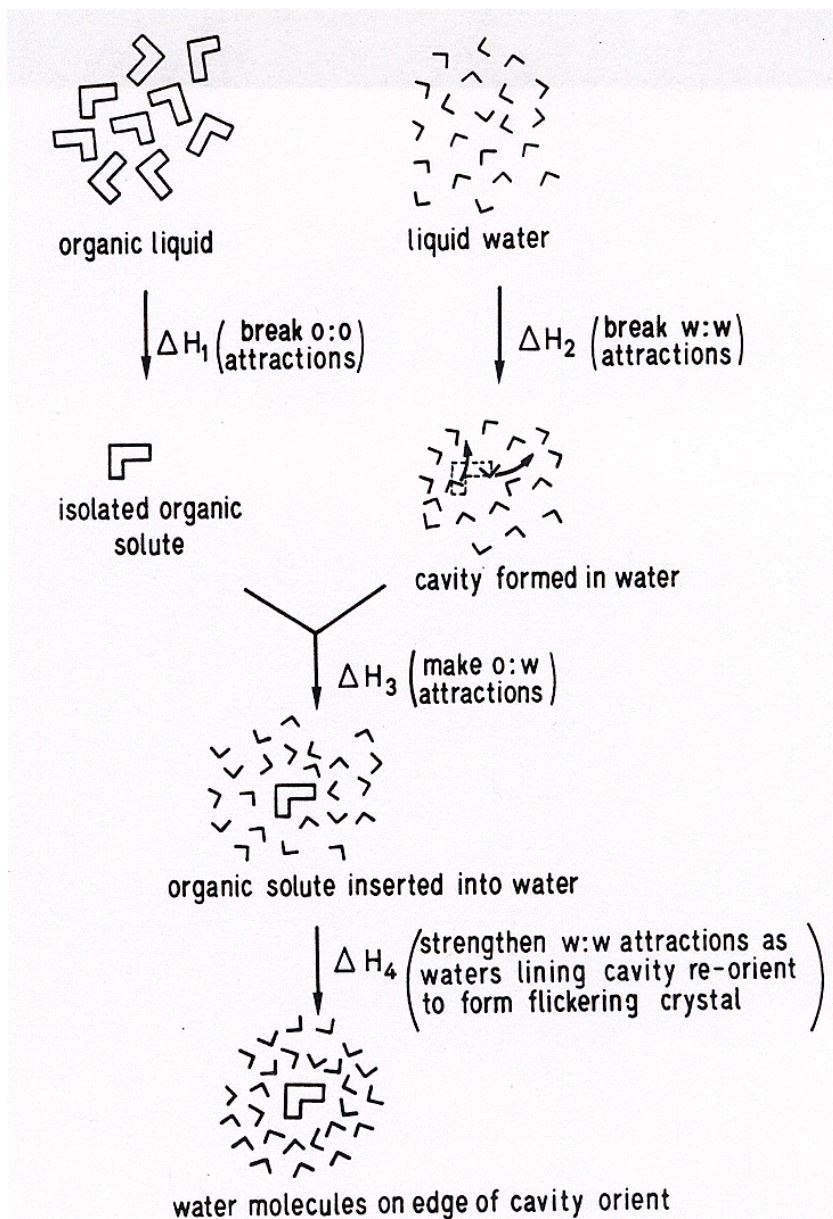

Figure 11. Model showing that each bonding interaction (in this case we are referring to breaking and forming hydrogen bonds) costs energy, which can be measure as heat content or ΔH (o = organic compound; w = water; H is the heat content of the reaction). (Copied from Schwarzenbach 1993)

5. Figure 12 shows the range of water solubilities of some classes of environmental organic contaminants
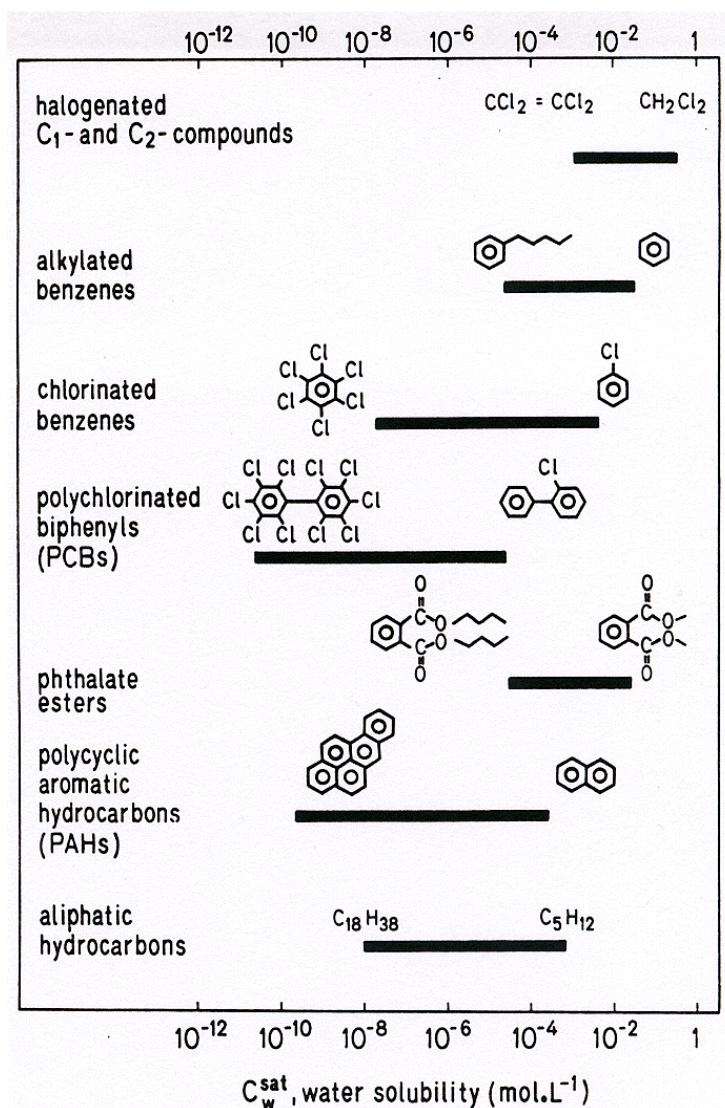
Figure 12. Structure and range of water solubilities of representative classes of environmental organic contaminants.

6. Water solubility, like vapor pressure, is affected by temperature. It is also affected by salt concentration in the water.

Table 1. Effect of temperature on solubility of several aromatic compounds. Note that molar volume is a measure of the "size" of the compound (defined literally the volume occupied by one mole of an ideal gas). You can think of it as the size of the hole the compound "punches" in the structured molecular matrix of water. (from Rossi and Thomas 1981)

Compound	Molar Volume (mL)	log solubility (ppb)		
		15°C	20°C	25°C
toluene	109	5.61	5.61	5.62
acenaphthene	150	2.33	2.74	3.26
pyrene	172	1.75	1.85	1.95

Table 2. Solubility of aromatic compounds in distilled water and in seawater (about 3% mineral salts) (from Rossi and Thomas 1981)

Compound	Solubility, distilled H_2O (ppm)	Solubility, seawater (ppm)
toluene	506.7± 6.1	418.5 ± 5.0
acenaphthene	2.42 ± 0.02	1.84 ± 0.04
pyrene	0.13 ± 0.01	0.09 ± 0.01

7. Other dissolved organic molecules or macromolecules can also increase the solubility of the contaminants of interest; the effect depends on the concentration (if >10% by volume, may act as a cosolvent; if <<10% may act as a co-solute); very dilute concentrations of other organic contaminants are not likely to have any effect on solubility.

D. Acidity and Basicity
1. Some environmental contaminants and pesticides can become acids and/or bases at environmental pH levels.
    a. The consequent ionization imparts a charge (negative if an acid; positive if a base) that can influence water solubility, vapor pressure, and movement across environmental compartments or within an environmental compartment.
2. The tendency of a compound to become an acid (or a base) is described by a measurement called the pKa.
    a. pK_a can be thought of as a measure of the tendency of an acid to dissociate (i.e., deprotonate); by the same analogy, pK_b is the tendency of a base to protonate
3. Theoretical considerations:
    a. Recall that solution pH is the negative logarithm of the hydrogen ion [H+] concentration.
        1. $H_2O \Longleftrightarrow H^+ + OH^-$
        2. $H^+ + H_2O \Longleftrightarrow H_3O^+$, and K = 1 at equilibrium;
        3. Kw = [H+] x [OH-] = 1 x 10^{-14} M (the ion product constant for water)
    b. For any acid (or base):
        1. $HA + H_2O \Longleftrightarrow H_3O^+ + A^-$

        2. $K_a = \dfrac{[H^+][A^-]}{[HA]}$ = acidity dissociation constant

        3. $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$

    c. The concentration of A- and HA is equal when the pH = pK_a

1. Note in Figure 13 an organic compound that can become both a base and an acid, depending on the pH of the solution it is dissolved in.
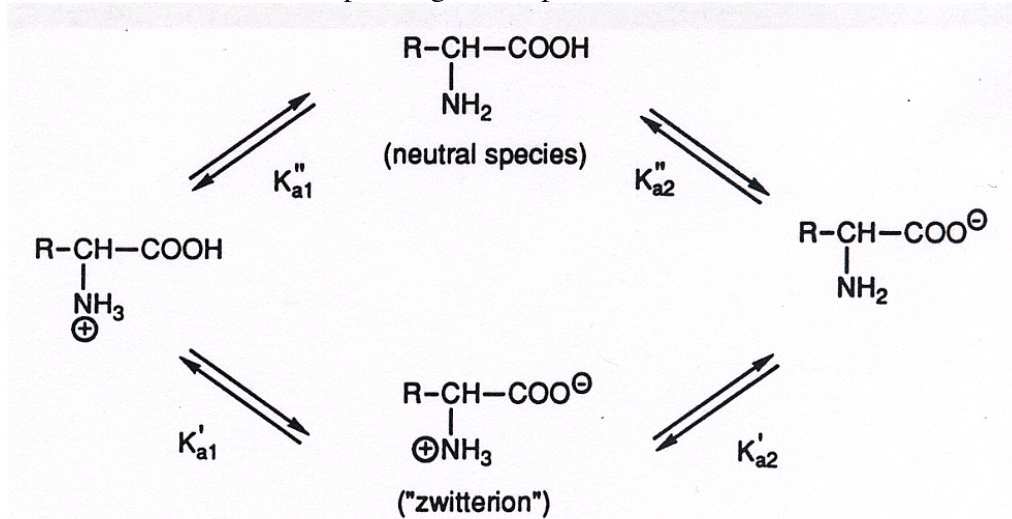

Figure 13. A compounds pKa and the solution pH will determine whether a compound is ionized or neutral. Ionized compounds will have a comparatively increased solubility, but the vapor pressure might correspondingly decrease.

4. The pH of a solution will influence the relative abundance of a "species" of an organic acid or base, especially those that have more than one acid or base functional group.
   a. Thus, the pH of a system in which an organic acid or base is dissolved can influence the environmental behavior of the compound by virtue of it's effect on water solubility and as you will see later, interactions with solid surfaces. (Figure 14)
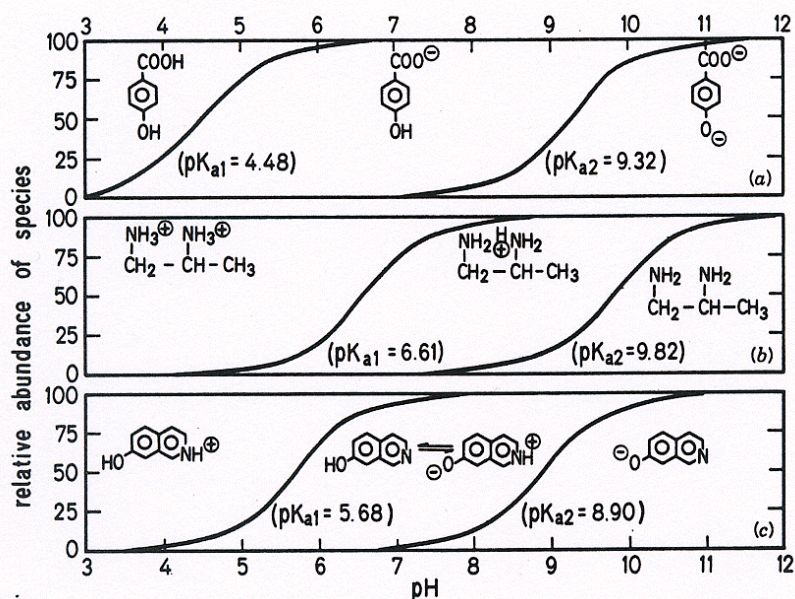

Figure 14. Influence of pH on speciation (ionized or neutral) of several organics. (copied from Schwarzenbach 1993)

IV. Phase Transfers (Partitioning)
   A. The physicochemical properties studied thus far, namely water solubility and vapor pressure, represent an escaping tendency of molecules from pure liquids or solids.
      1. Keep in mind that the energy required for vaporization or dissolution of a solid will have to involve energy of melting in addition to the energy cost associated with establishing equilibrium with the air or water phase
   B. Phase transfer processes can be described as **reversible** partitionings of dilute concentrations of a compound between water and air, soil, or an organic phase (lipid material, octanol or other organic solvent or natural organic matter) (i.e., across interfaces, or the boundary where two phases meet and interact with one another).
      1. The equilibrium distribution of a chemical between two phases can be used similarly to the traditional physicochemical properties of pure substances to predict environmental behavior;
         a. Partitioning can be defined as the subdivision of a population of molecules of a given compound between any two phases, for example gas and solution phases
         b. The ratio of the concentration of the chemical in the phase of interest (air, soil, organic) to the concentration in water is commonly called a partition coefficient
            1. Such a ratio actually describes the extent of partitioning among the environmental compartments at an ideal equilibrium
      2. Thermodynamic conceptualization of phase transfers:
         a. The partitioning:
            1. Compound A (phase 1)<-----------> Compound A (phase 2)
         b. The net flow of compound is from the phase where A has a higher chemical potential to the phase where A has a lower chemical potential; flow occurs until A's chemical potential in each phase is equal
      3. For purposes of predicting exposure once a chemical is released in to the environment, we would like to know the extent of partitioning from the water into the air (and vice versa), partitioning from soil into water (and vice versa), and partitioning from water, soil, and air into an organism (the biotic compartment or phase).
   C. Air-Water Partitioning (Henry's Law Coefficient)
      1. Movement of molecules dissolved in water into the gas phase.
      2. The tendency to "escape" from water is described by the ratio of the compound's abundance in the gas phase to that in the aqueous phase at equilibrium.
         a. The ratio is called Henry's Law Coefficient (K_H)
            1. It defines the fugacity (escaping tendency) of a compound existing as vapor molecules as opposed to the fugacity of being dissolved in water
         b. K_H of a compound can be reasonably estimated as the ratio of vapor pressure to water solubility
            1. Molecules with high activity coefficient in water (high fugacity or tendency to want to escape from water) and low fugacity in air (i.e.,

high vapor pressures) will have a relatively higher K_H (i.e., should partition appreciably from water into air)

2. Molecules with low activity coefficients in water (tendency to want to remain dissolved) and high fugacity in air (tendency to want to condense), have low K_H.

   a. Implications: for polar molecules, K_H is very low because of low vapor pressure and high water solubility, but scavenging in rain is very important; i.e., these compounds will tend to be displaced from atmosphere during precipitation

   b. However, for nonpolar, high boiling point compounds like PCBs or PAHs, K_H can be very high, but scavenging by rain is also high because these compounds have high fugacities in both air and water phases. (see Figure 15 for ranges of K_H and note comparison with previous Figures 4 and 12).
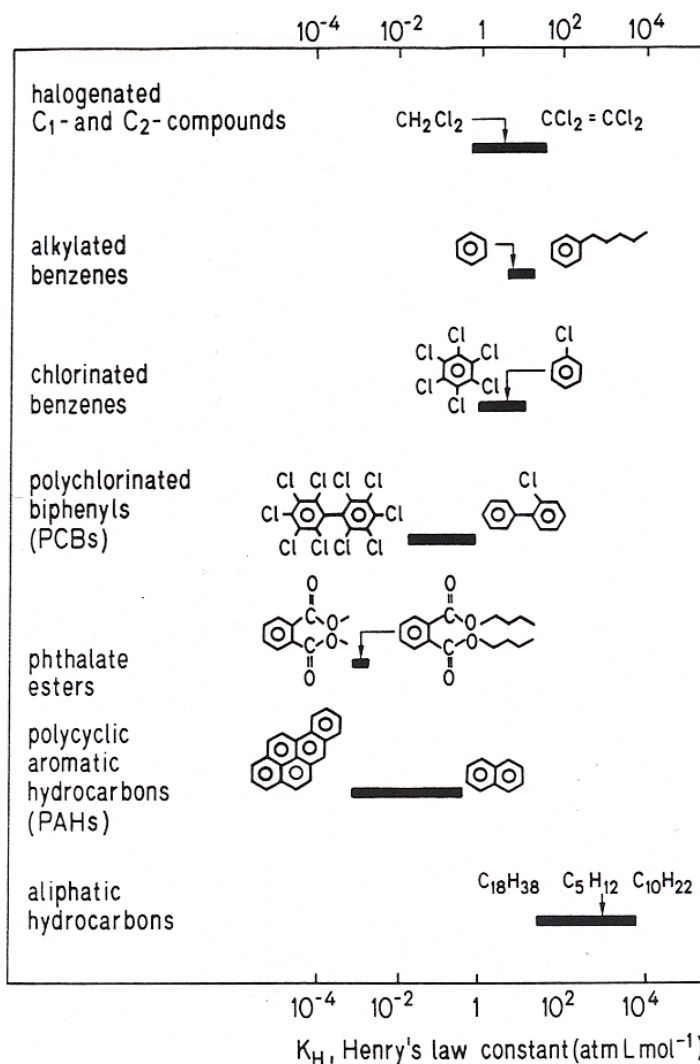

Figure 15. Ranges of K_H values for selected environmental organic contaminants.

D. Organic Solvent-Water Partitioning (The Octanol-Water Partition Constant)
1. Partitioning behavior of organic compounds between two immiscible liquids;
    a. Main difference with K_H is that partitioning is **not** into a medium where compound shows ideal behavior (i.e., no interaction with other compounds, "pure" substance only), but instead exhibits nonideal behavior (not pure system; interacts with organic solvent molecules)
    b. Historically, octanol was used for the water-immiscible liquid as a surrogate for an organism; uptake of nonpolar drugs by organisms was found to be proportional to partitioning into octanol
    c. Expression of partitioning constant:
        1. K_{SW} or $K_{OW} = C_S/C_W$ (i.e., ratio of relative fugacity in each phase), where C_s = concentration of compound in organic solvent and C_w = concentration of compound in water
        2. In pharmacology textbooks, Kow is also called P.
        3. Expression of Kow or P is often in the logarithmic form because of the large numbers involved in expressing the ratio (in other words, the concentration in the organic solvent is many orders of magnitude larger than in the water phase.
2. If place an organic compound in water in a container with octanol, organic compound will move from water into octanol until fugacities are equal, or in other words, until the system is in equilibrium. At this point, one could actually measure the partial pressure of the compound in the headspace above each phase;
    a. Note that some water will move into the octanol phase and vice versa (octanol moves into the water phase),
    b. Compounds with low water solubilities (i.e., high escaping tendency or fugacity) will tend to have comparatively higher log Kow than compounds with relatively greater water solubility (i.e., lower escaping tendency or fugacity). See Figure 16 for ranges of Kow and compare this with Figure 12 on water solubility).
E. When Kow information about a compound is not available, it can be estimated by referring to published empirical regression equations that have related known K_{OW}'s with C_W's (water solubilities).
1. For example, given the regression equation, **log Kow = - *a* log Cw + b**, where Cw is saturated water solubility, and *a* & *b* are coefficients (slope and intercept, respectively), experiments with compounds in the following groups yield the values for *a* & *b*. (Table 3)

Table 3. Use of linear regression to predict log Kow from water solubility (from Schwarzenbach et al. 1993)

Set of Compounds	n, number empirically tested	R^2, correlation coefficient	*a*	*b*
alkanes	16	0.91	0.81	-0.20
PAHs	8	0.99	0.87	0.68
benzenes				

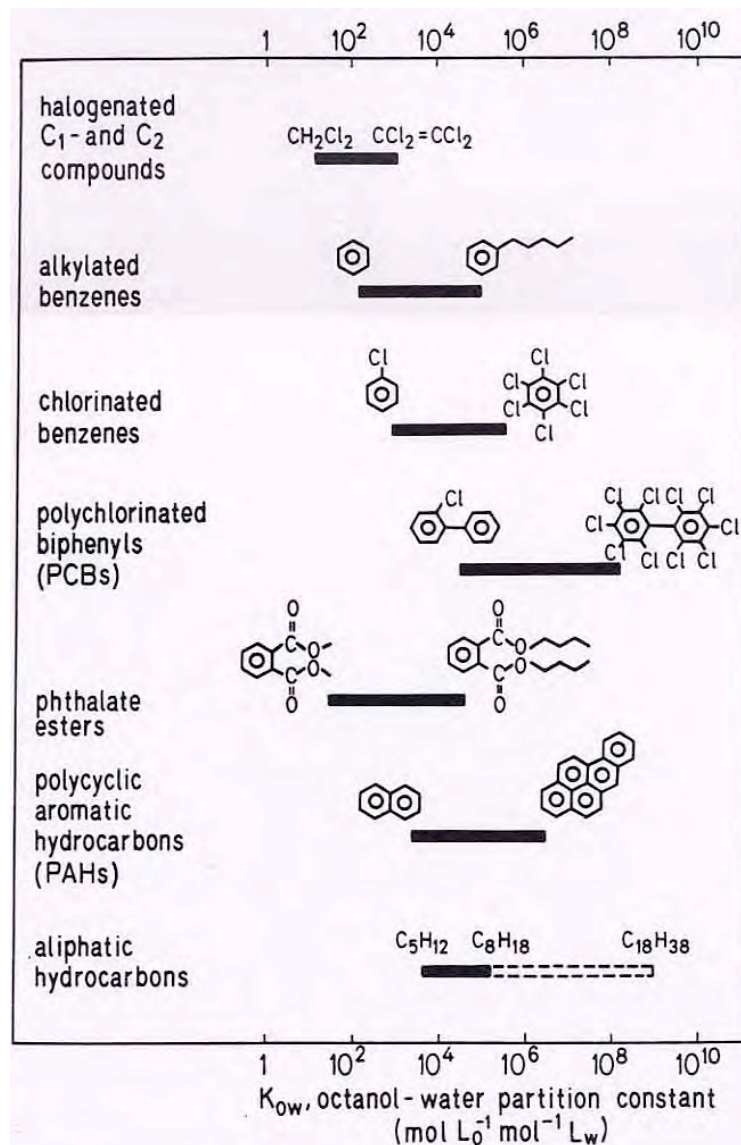|				
nonpolar substituents	23	0.98	0.86	0.75
polar substituents	32	0.86	0.72	1.18
phthalates	5	1.00	1.06	-0.22
PCBs	14	0.92	0.85	0.78
alcohols	41	0.94	0.90	0.83
misc. pesticides	14	0.81	0.84	0.12

Figure 16. Ranges of Kow for selected environmental organic contaminants (copied from Schwarzenbach et al. 1993).

F. Soil-Water Partitioning (Soil Sorption Coefficient)
    1. Definitions

a. <u>Sorption</u>--the phase transfer from the solution or vapor phase to the solid phase, whether in soil, air, or water. There is an unfavorable free energy relationship in the existing water phase, thus the chemical "escapes" to the solid phase.
  1. However, the equilibrium is reversible, so that some of the sorbed contaminant will move into the water phase (called desorption).
      a. Remember that at equilibrium, concentrations are not necessarily equal.
      b. Adsorption is often the term used to describe the diffusion from water to the soil; sorption is often substituted for this term, but I personally use it to describe the whole process of adsorption and desorption.
      c. Some researchers use the term adsorption when speaking about diffusion and interaction with clay surfaces. They use the term partitioning when talking about diffusion into the soil organic matter. Whatever term is used, however, it refers to sorption in general.
b. <u>Sorbate</u>==chemical that is partitioning, i.e., undergoing the phase transfer
c. <u>Sorbent</u>==the solid phase
d. <u>Sorption isotherm</u>: the relationship of total sorbate concentration associated with the sorbent, C_S (μg/g or mol kg^{-1}), relative to the total chemical concentration in solution, C_W (μg/mL or mol L^{-1}), measured at a constant temperature
  1. Thus, sorption can be described as a coefficient over a range of concentrations.
  2. This description is fit to a model called the Freundlich equation

$$C_s = K \cdot C_w{}^n$$

      a. K is the Freundlich constant sometimes denoted K_f
      b. n=a measure of the nonlinearity of sorption
      c. The isotherm can be determined by plotting the logarithmic form of the Freundlich equation, which then linearizes the curve and allows log K to be determined at unit concentration
        1. $\log C_s = n \log C_w + \log K_f$
        2. Note that n is the slope
      d. The larger K_f, the greater the tendency of a contaminant to move from water onto the soil solids.
e. The <u>soil distribution coefficient</u>, $K_d = C_S/C_W$, is used to described the extent of partitioning or adsorption for one concentration of contaminant only.
  1. K_d is a lumped parameter, i.e., it reflects the contributions from many chemical species, i.e., concentration of neutral sorbate in natural organic matter, on mineral surfaces, in water solution and ionized sorbate in water and on reversible exchange sites.
      a. K_d is empirically determined.
2. Factors influencing the extent of sorption

    a. Soil properties
        1. Organic matter content
           a. For neutral organic compounds, organic matter has been found to be the one soil property that is most predictive of the magnitude of K_f or K_d. (Table 4)

Table 4. Sorption of phorate by five soils (Felsot & Dahm, 1979)

Soil	Organic Matter	K_f	K_{om}
1	0.88	2.32	264
2	1.84	5.48	298
3	4.56	9.62	211
4	6.55	16.14	246
5	31.65	73.79	233

           b. Note that K_{om} is K_f (or K_d) normalized by the fraction of organic matter (similarly, the Koc is the Kf or Kd normalized by the fraction of organic carbon)
               1. Note that organic matter includes all organic compounds while organic carbon includes only the carbon content of organic matter

  b. Physicochemical factors
        1. Water solubility
           a. Tendency for low water solubility compounds to be more strongly adsorbed.
           b. There is a strong inverse correlation between K_{om} (or K_{oc}) and C_W
               1. However, this correlation has many exceptions; it probably only applies to groups of closely related compounds (i.e., homologous series) and also to neutral organics; ionized compounds or compounds that exist as cations will also defy the correlation.
                   a. Note below that the correlation for a group of 28 pesticides has an R^2 of only ~0.22 (the regression coefficient, R^2, accounts for the percentage of variability in the dependent variable accounted for by the independent variable); (Figure 17)
                   b. However, if two compounds that are ionized at normal soil pHs (glyphosate and paraquat) are removed from the correlation, then ~70% of the variations in sorption can be accounted for by the variations in water solubility. (Figure 18)
           c. Note that dissolved organic matter can increase the apparent water solubility of compounds due to their sorption into this phase.
               1. Thus, the Kd of very low water soluble compounds might be lower than we would predict on the basis of water solubility along.
        2. pKa and the ambient pH will influence sorption because by virtue of their influence on the proportion of neutral and ionized species in solution.

a. Note, however, that clay surfaces are usually negatively charged, so any bases at low pH (as well as cationic compounds) can be highly adsorbed (owing to the positive charge).

3. In general, any factor that affects water solubility will affect sorption potential (for example: temperature, salts, solvents present in the solution)
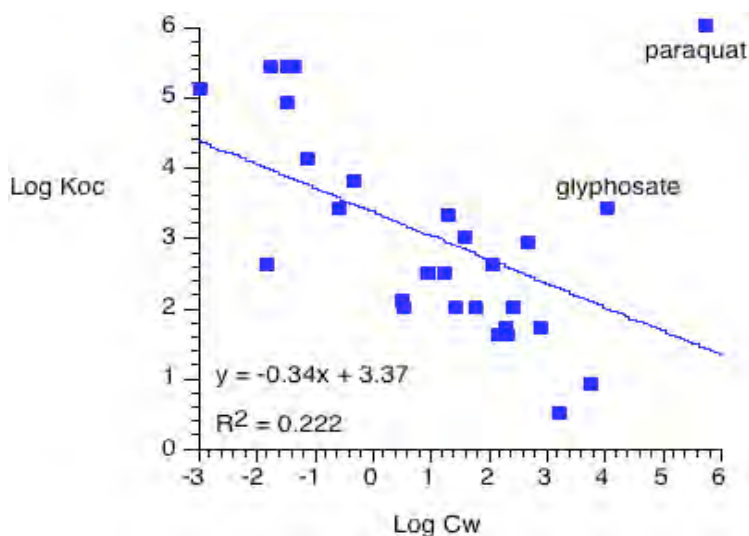

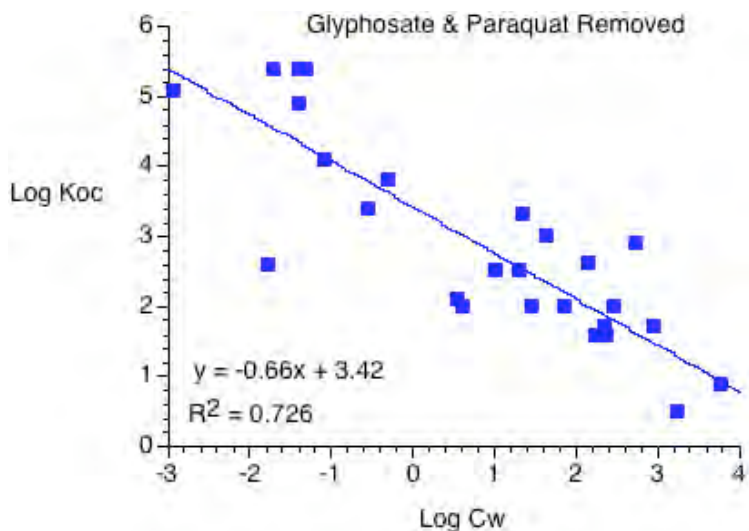Figure 17. Linear regression of log Koc on log Cw with two ionizable compounds in the database of 28 pesticides.

Figure 18. Linear regression of log Koc on log Cw with two ionizable compounds removed from the database of 28 pesticides

3. Reversibility
    a. Sorption mechanisms generally involve relatively weak interactions or bonding

1. For example, much of the bonding is due to van der Waals forces and/or hydrogen bonding at surfaces of organic matter and/or clay
2. Some researchers have postulated a partitioning into the matrix of organic matter, somewhat like being "dissolved" in the organic matter, but the process is still under thermodynamic control
3. Being an equilibrium process, one would expect full desorption (movement back into the water phase) of a chemical when "clean" water passes over the solid matrix

b. However, hysteresis has been observed
   1. Consider that the sorption partition is exothermic, but the desorption process is endothermic requiring a small activation energy;
   2. Thus, there is nonsingularity of the sorption isotherms; the desorption isotherm tends to be displaced to the left on the graph.
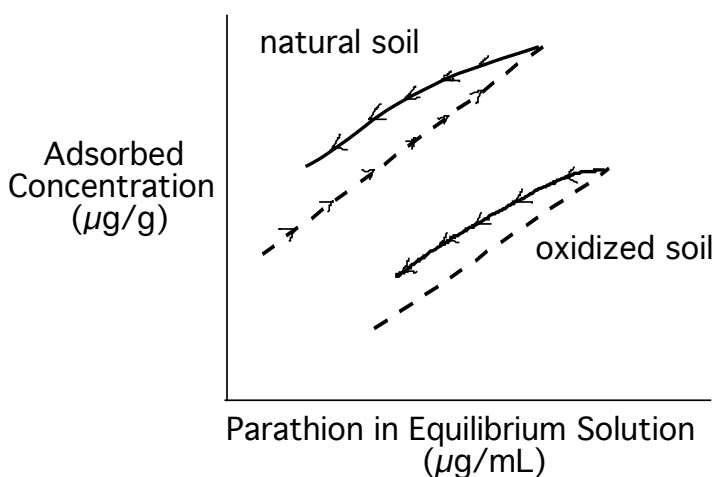
(adapted & redrawn from Saltzman et al.)

Figure 19. Hysteresis in the parathion sorption isotherm. Note that the dashed lines represent adsorption or partitioning in the soil and the solid lines represent desorption back into solution. At any given solution concentration, the adsorbed concentration is higher going in the direction of desorption than in the direction of adsorption. This difference is called hysteresis and arises because the magnitude of the forces pushing the system in one direction are different than in the reverse direction. Note also that removing organic matter by oxidizing the soil decreases the extent of adsorption. (Adapted and redrawn from Saltzman et al.)

4. Biological Importance of Sorption: affects every fate process of a chemical
   a. The importance of sorption in environmental chemistry of pesticides was probably first recognized for DDT and the chlorinated cyclodienes--its was observed that bioactivity varied with soil type (Hadaway and Barlow 1951; Edwards et al. 1957) and with moisture content of the soil (Barlow and Hadaway 1956).
      1. Probably the first publication on sorption of pesticides by soil was by Hadaway and Barlow (1951)

a. Bottom line: "....it has been found that the residual toxicity of particles of any one size is influenced considerably by the type of material to which they are applied."
2. Paper by Edwards et al., J. Econ. Entomol. 50:622-626 (1957), "Bioassay of aldrin and lindane in soil"; notice how toxicity (as measured by the LC50, or lethal concentration of chemical to 50% of the test population) is reduced as organic matter (OM) in soil increases (see section F below for effects of OM on sorption).
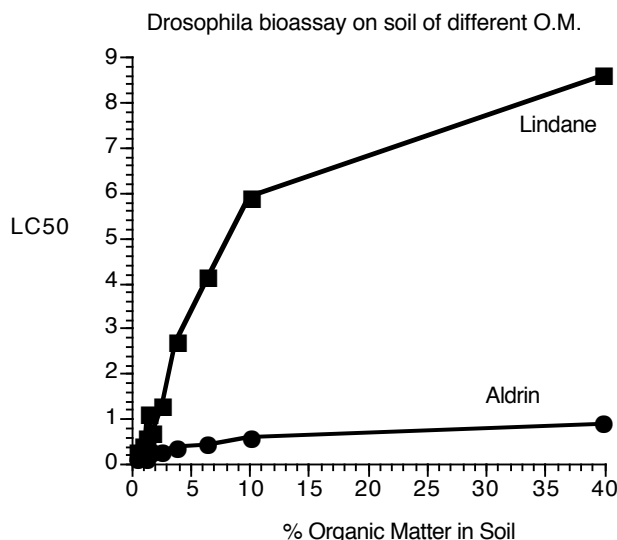

Figure 17. Importance of sorption in influencing bioactivity in soil. Presumably, more pesticide is adsorbed and unavailable to the test insect (*Drosophila melanogaster*, a.k.a. vinegar flies) as it walks on the surface of the soil.

5. Aging Phenomena
   a. Apparent Kd increases with time
      1. Results from continued diffusion of sorbate into organic molecular matrix, and the consequent slow diffusion back into the aqueous phase
      2. The phenomenon is somewhat related to the nonsingularity of isotherms in the desorption direction, but the time scales involved in the aging phenomenon are longer then the experiments showing hysteresis in the isotherm.
   b. An experiment by Pignatello & Huang (1991, J. Environ. Qual. 20:222-228) resulted in support of the hypothesis that sorption increases with time. (Figure 18)
      1. Soil that had been treated with the herbicides atrazine and metolachlor was removed from the field after many months of incubation;
      2. The concentration of pesticides was determined; the soil was extracted with water to remove water-extractable (i.e., desorbable) pesticide; an apparent distribution coefficient (i.e., a sorption coefficient determined at a singular concentration) was calculated based on the amount recovered and the total solvent extractable amount in the soil.

   a. This measurement is the apparent or aged Kd.
   3. To the same batch of soil as above, radiolabelled pesticide was freshly
       added and its sorption coefficient determined; this is the "fresh" Kd.
   4. When the ratio of the "aged" pesticide Kd to the "fresh" pesticide Kd
       was plotted relative to number of months after field application of the
       pesticides, a positive relationship was obtained, which suggests that
       the longer a residue is present in the soil (i.e., it hasn't degraded yet)
       then the greater the opportunity for movement into the interior of soil
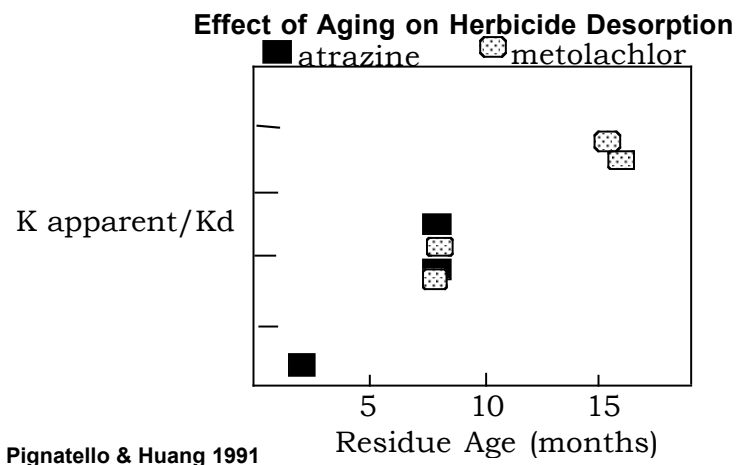   particles, thus increasing the apparent sorption coefficient

Effect of Aging on Herbicide Desorption

Figure 18. The ratio of the apparent Kd and the Kd for two herbicides in soil
            increased with age of the residues in the soil. In other words, with
            time, it looks like the Kd is much higher than if just freshly added
            the herbicide to soil.

   c. An experiment by McCall and Agin (1985, ETAC 4:37), shows that with
       prolonged incubation time the apparent Kd (calculated by adjusting for the
       amount of picloram left after degradation) for the desorption process
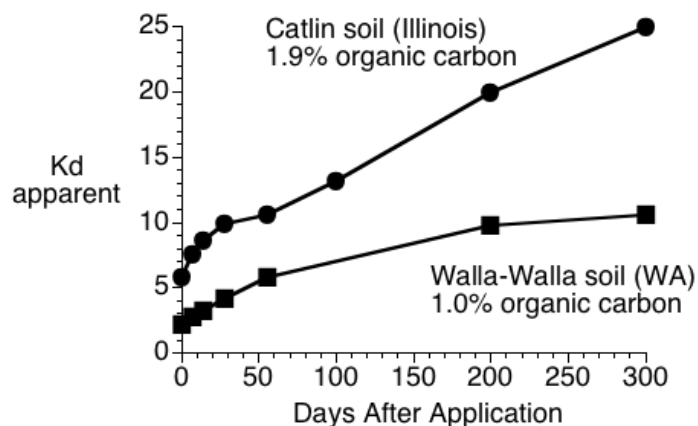   increases with time. (Figure 19)

Figure 19. Aging of intact picloram residues in two soils over time.

1. In this experiment, you can see both the effect of soil organic carbon content (note the separation between the lines indicating greater sorption in the Catlin soil than in the Walla Walla soil) and the aging phenomena (Kd apparent increases with time).
   2. McCall and Agin hypothesized (which has been the prevailing hypothesis to this day) that there are two types of sorption sites: external sites, to which sorption (and desorption) occurs relatively fast, and internal sites, which are less accessible and therefore slow to equilibrate.
6. Implications of the aging phenomenon
   a. Compounds should become less bioavailable or uptake by organisms over time.
   b. Compounds should be less likely to leach from the soil environment over time.
   c. Compounds could become less biodegradable over time.

References

Felsot, A. and P. A. Dahm. 1979. Sorption of organophosphorus and carbamate insecticides by soil. J. Agric. Food Chem. 27:557-563.

Edwards, C. A., S. D. Beck, and E. P. E. P. Lichtenstein. 1957. Bioassay of aldrin and lindane in soil. Journal of Economic Entomology. 50:622-626.

Barlow, F. and A. B. Hadaway. 1956. Effect of changes in humidity on the toxicity and distribution of insecticides sorbed by some dried soils. Nature 178:1299-1300.

Hadaway, A. B., and F. Barlow. 1951. Sorption of solid insecticides by dried mud. Nature 167:854

McCall, P. J. and G. L. Agin. 1985. Desorption kinetics of picloram as affected by residence time in the soil. Environmental Toxicology & Chemistry 4(1):37-44.

Pignatello, J. J. and L. Q. Huang. 1991. Sorptive reversibility of atrazine and metolachlor residues in field soil samples. J. Environ. Qual. 20:222-228.

Rossi, S. and W. H. Thomas. 1981. Solubility behavior of three aromatic hydrocarbons in distilled water and natural seawater. Environ. Sci. Technol. 715-716.

Schwarzenbach, R. P., P. M. Gschwend, D. M. Imboden. 1993, *Environmental Organic Chemistry*. Wiley Interscience, Hoboken, NJ.