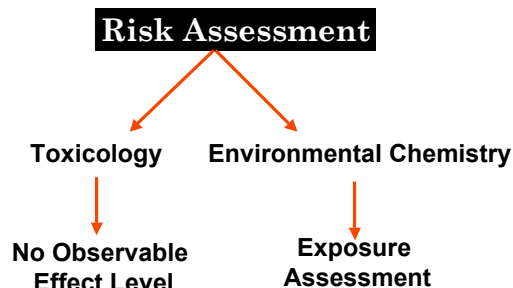


ES/RP 531  
Fundamentals of Environmental Toxicology

Lecture 20  
Environmental Chemodynamics  
Physicochemical Properties  
Phase Transfers

What Is Needed to  
Estimate (Guess) The Risk?

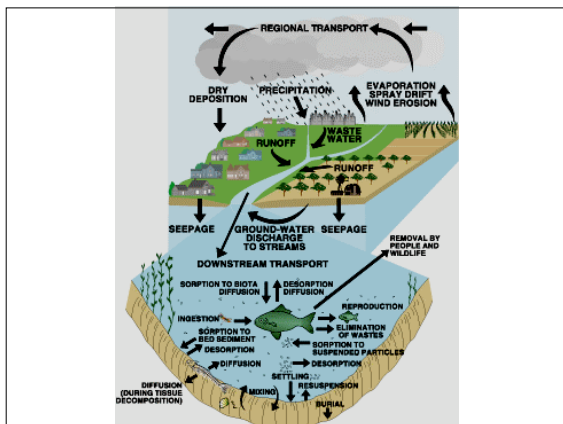
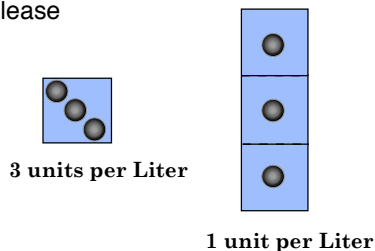


Residue Definition

- Residue
  - > The parent chemical or any toxic transformation product residing in soil, water, air, or biotic components of the environment following application or release to the environment
- Expressed as a concentration
  - > mass per unit area
  - > mass per unit volume
  - > mass per unit body weight

Dilution Is the Solution to Pollution

- Exposure results from the distribution of residues in the environment following release

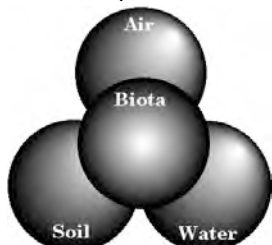


Can We Predict Residue Distribution  
(& Thus Exposure)?

- Environmental Chemodynamics
  - > Interdisciplinary study of the relationship between physicochemical properties and environmental behavior
- Focus Areas
  - > Physicochemical properties
  - > Partitioning (Phase transfers)
  - > Transport (Mass Transfer)
  - > Attenuation
  - > Modeling

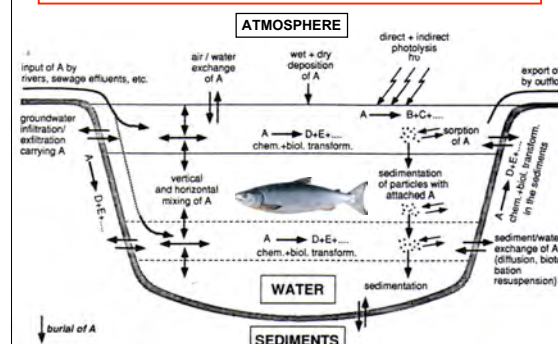
## Holistic Perspective

- Environment is perceived as interfacing compartments or phases



## Theoretical Framework

- Biosphere is composed of compartments with interfaces



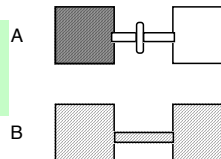
## Fundamentals of Chemical Behavior

- All molecules are governed by
  - Thermodynamics** (energy relationships in a system)
    - Molecules naturally arrange themselves so that the total energy in a system is at the lowest possible level
  - Kinetics** (reactivity of system components)
    - How fast are chemical reactions?
    - What kinds of reactions are possible?

## Thermodynamic Perspective of Chemical Behavior

Thermodynamic theory predicts which direction substances tend to diffuse to reach equilibrium. Tendency to maximize entropy (i.e., minimize free energy in the system)

System A has a defined chemical potential of substance  $i$



At equilibrium, the chemical potential in each system is equal

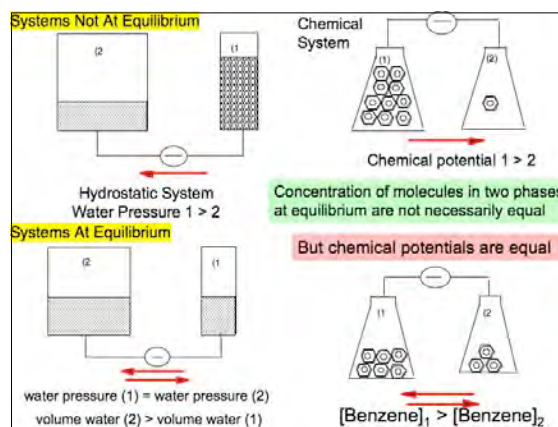
Systems tend to maximize entropy  
Entropy system A > Entropy system B

Chemical potential is the free energy added to a system with each added increment of a molecule

## Chemical Potential ( $\mu$ )

- Defined as the free energy added to a system with each added increment of component  $i$
- Chemical potential changes as a function of the abundance of components
- Chemical equilibrium is characterized by equal chemical potentials for all constituents in two phases (or systems).

$$G \text{ (Total Free Energy)} = \sum_i n_i \mu_i$$



### Fugacity (Escaping Tendency)

- Molecules of **pure substances** escape (disperse) from one another and recondense with each other until equilibrium is reached
- At equilibrium there is no net movement & energy of system is at lowest level.
- A unifying concept (parameter) for aiding predictions of environmental concentration in each environmental phase (including organisms)
- Expressed as pressure units
- Equilibrium occurs when fugacity of a chemical in two phases are equal

### Bottom Line

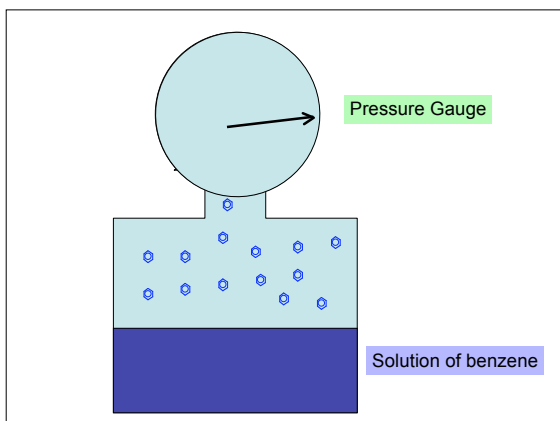
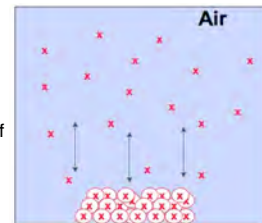
Interested in final composition of a system when no net changes occur. At this point the system has attained a minimum energy state (maximum entropy), and the system is in equilibrium.

### Physicochemical Properties

- Intrinsic directly or indirectly measurable characteristics of molecules that vary with the environment they are measured in
  - Magnitude of properties results from the specific chemical structure (i.e., the 2-D & 3-D arrangement of the atoms)
  - These unique characteristics are the driving forces for distribution in the environment, allowing us to make predictions of behavior

### Vapor Pressure

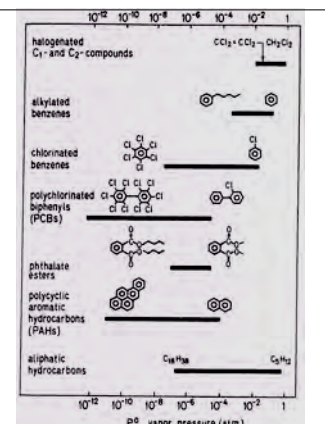
- The pressure of the vapor of a compound at equilibrium with its pure state
  - Think of VP as the escaping tendency of the molecules of a pure substance from itself
- Compound to compound variations arise as a result of intermolecular forces



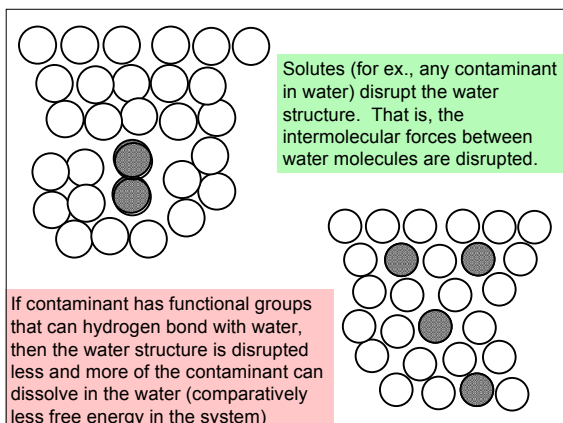
### Vapor Pressure Ranges for Several Groups of Contaminants

Smaller molecules in homologous series tend to have higher VPs

Schwarzenbach et al. 1993

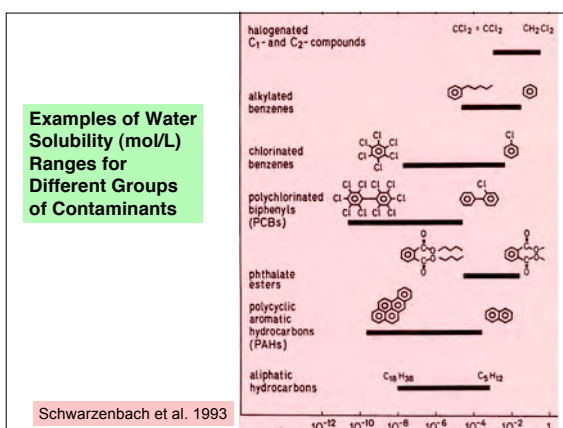






### Facilitation & Limitations of Water Solubility

- If a dissolving molecule has functional groups that allow hydrogen bonding, then the regularity of the water structure is disrupted less than if the molecule lacked the capability of hydrogen bonding
- If no polar functional groups, than more energy must be expended to disrupt the water structure
  - Thus, entropy would necessarily be higher, and consequently, WS would be less



### Water Solubility is Influenced by Temperature

Compound	Molar Volume (mL)	Log WS (ppb)		
		15°C	20°C	25°C
Toluene	109	5.61	5.61	5.62
Acenaphthene (PAH)	150	2.33	2.74	3.26
Pyrene (PAH)	172	1.75	1.85	1.95

Rossi & Thomas, Environ. Sci. Technol. (1981), p. 715

### Water Solubility is Influence by Other Solutes

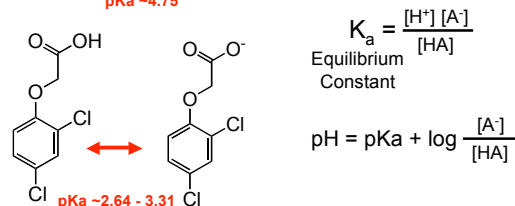
Compound	WS (ppm)	
	Solubility (Distilled H2O)	Solubility (Seawater)
Toluene	507	419
Acenaphthene	2.42	1.84
Pyrene	0.13	0.09

Rossi & Thomas, Environ. Sci. Technol. (1981), p. 715

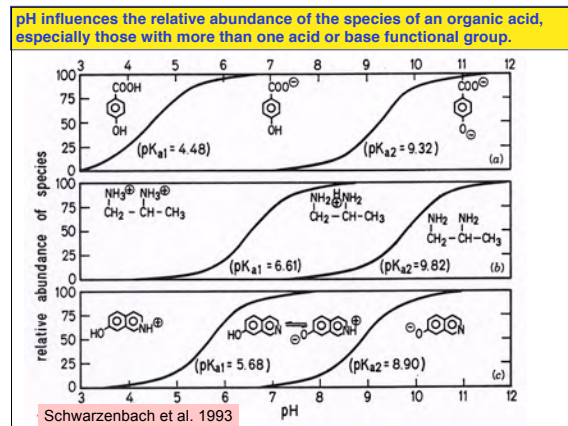
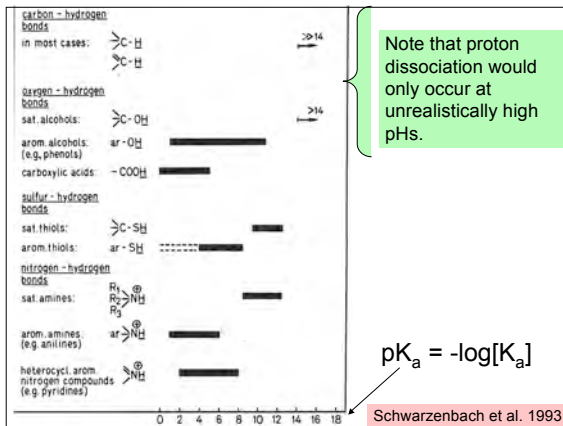
Organic solvents dissolved in water can increase the water solubility of a contaminant

### Acids & Bases

pKa (and pKb) can be thought of as the tendency of an acid to dissociate or a base to accept a proton ( $H^+$ ).



When  $pH = pKa$ , the concentration of  $A^-$  (the salt form) and  $HA$  are equal. Thus, at  $pH = pKa$ , half the molecules will be neutral and half will be ionized.

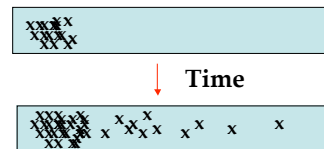


## Physicochemical Properties & Fugacity

- Water Solubility (WS) and Vapor Pressure (VP) can be thought of as the escaping tendency of molecules from the pure liquid or solid state
- Fugacities of pure substances are related to the partial vapor pressure of the substance modified by an activity coefficient,  $\gamma$ , when there are intermolecular interactions

## Diffusion

- Tendency of molecules to move within a medium (phase) from high concentration to low concentration

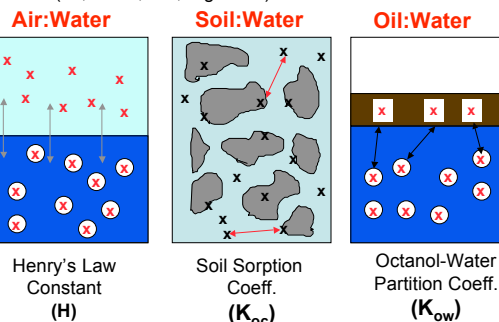


## Phase Transfer Processes

- Reversible partitionings of dilute concentrations of a compound between two phases
- Expressed by the partition coefficient
  - Ratio of the concentration of the chemical in one phase (air, soil, biological tissue, organic solvent) relative to the concentration in water

## Phase Transfer (Partitioning)

- Tendency of molecules to escape from one medium (air, water, soil, organism) into another medium





### Air-Water Partitioning Henry's Law Coefficient

- Designated as  $K_H$ 
  - Defines the escaping tendency of a compound existing as a vapor as opposed to the fugacity of being dissolved in water
  - 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., these compound will tend to partition from water to air more easily than from air to water

### Air-Water Partitioning Henry's Law Coefficient

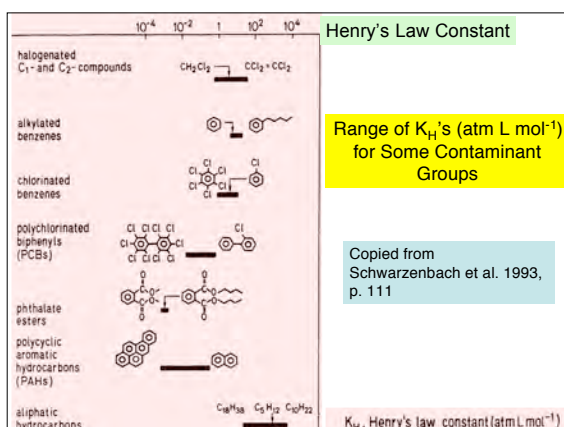
- Molecules with low activity coefficients in water and high fugacity in air will tend to have lower  $K_H$ 
  - Low activity coefficient (low fugacity) indicates molecules will tend to remain dissolved
  - High fugacity in air indicates a tendency to condense (as pure substance or back into the water phase)

### What Do You Think?

- Which will have a higher  $K_H$ ?
  - Molecule with a carbonyl group, or a molecule with a butyl group?
- What other information could help you make your decision?

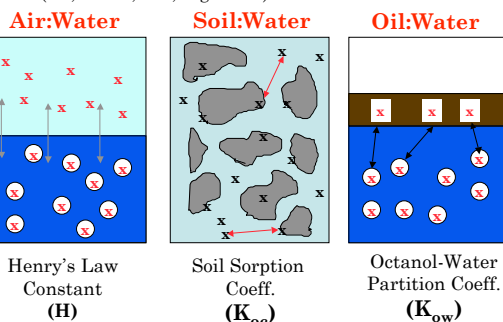
### Approximation of $K_H$

- Henry's Law Constant is directly proportional to both the activity coefficient of the compound in water and the vapor pressure of the pure organic liquid, thus,
  - Can approximate  $K_H$  by taking the ratio of VP to  $C_w$  (at saturation)
- Units of  $K_H = \text{atm L/mol}^{-1}$



### Phase Transfer (Partitioning)

- Tendency of molecules to escape from one medium (air, water, soil, organism) into another medium



## Organic Solvent-Water Partitioning

- Octanol-Water Partition Coefficient
  - Partitioning behavior is between two immiscible liquids
  - Main difference with  $K_H$  is that the compound is moving into a phase with nonideal behavior (interactions with solvent).
- Octanol used as the partitioning solvent against water
  - Surrogate for an organism's membranes
- $K_{ow} = C_g/C_w$ , where  $C_g$  is the abundance in the organic solvent phase &  $C_w$  in the water

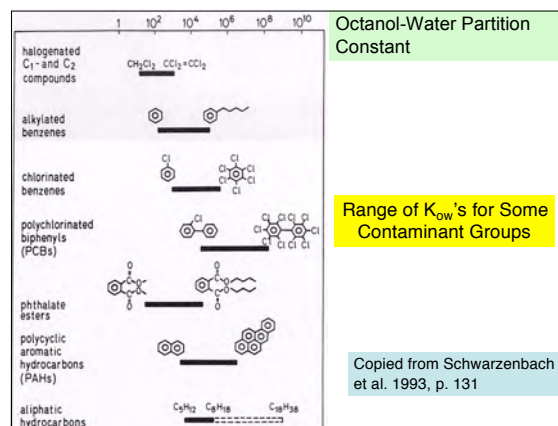
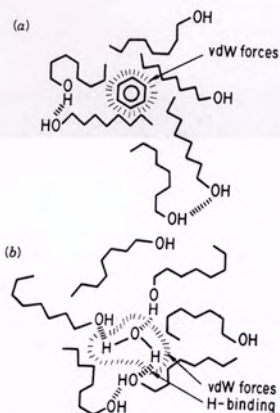
## Kow

- If place an organic compound in water, and then add octanol, the compound will move from water into octanol until fugacities are equal, i.e., until the system is at equilibrium
  - Theoretically, you could measure the partial pressure in the headspace above each phase

In the octanol phase, benzene can interact via van der Waals forces with the alkyl chain.

Water can hydrogen bond with the hydroxyl of octanol; thus, some water will move into the octanol phase

Copied from Schwarzenbach et al. 1993, p. 130



## What Would You Predict & Why?

- Kow (comparatively high or low)
  - Dodecane
  - Dodecanal
  - Dodecanoic acid

## Kow & WS ( $C_w$ ) are correlated

$$\log Kow = -a (\log C_w) + b$$

Analogous Compounds	# Tested	R2	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
Benzenes (polar substituents)	32	0.86	0.72	1.18
Phthalates (plasticizers)	5	1.00	1.06	-0.22
PCBs	14	0.92	0.85	0.78
Alcohols	41	0.94	0.90	0.83
Miscellaneous pesticides	14	0.81	0.84	0.12

Table data copied from Schwarzenbach (1993)



## Soil-Water Partitioning

- Nature of soil
  - Clays
  - Organic polymers
- Distribution Coefficient ( $K_d$ )
- Freundlich Coefficient
- $K_{oc}$
- Aging Effect

## Soil Structural Properties

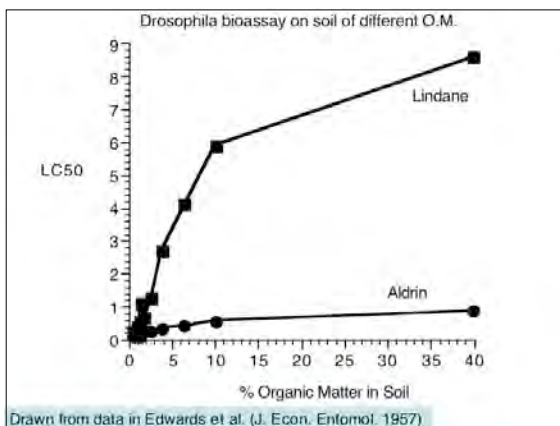
- 3 phases
  - Air; Water; Solids
- Solids
  - Inorganic polymers
    - ✓ Clays (phyllosilicates)
    - ✓ Layered sheets of tetrahedral and octahedral monomers sharing an oxygen atom at helices
      - In center of tetrahedron and octahedron is a Si, Al, Mg, or Fe atom
      - a.k.a. aluminosilicate units

## Organic Polymers

- Nonhumified
  - Constituent biochemicals (proteins, carbohydrates, lipids, etc)
- Humified
  - Amorphous, colloidal polydispersed
  - End products of decomposition
  - Humic and fulvic acids
  - Large molecular weight
- Complexation with metals
- Hydrogen bonding
- Large hydrophobic component

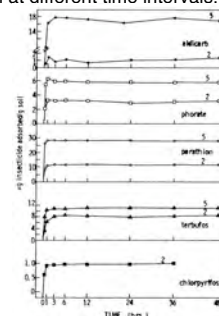
## Sorption

- Phase transfer from solution or vapor phase to the solid phase
  - Occurs in water, air, and soil
  - Sorbate: chemical that is partitioning
  - Sorbent: solid phase
- Key factor affecting fate of chemicals in environment
  - Rate limiting
  - Limiting mass transfer
  - Limiting bioavailability



## Rate of Sorption Equilibrium

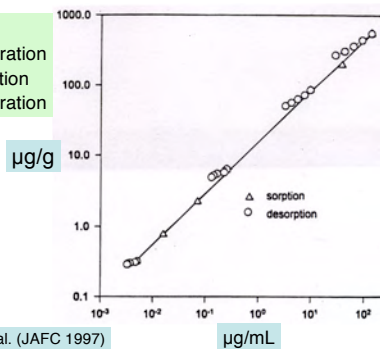
Measured by shaking saturated solution of contaminant with known weight of soil. Determine solution phase concentration at different time intervals.



Copied from  
Felsot & Dahm  
(JAFS 1979)

## Sorption Isotherm

- Plot of sorbed phase concentration relative to solution phase concentration



Copied from Cox et al. (JAFC 1997)

## Sorption Coefficient

### Distribution Coefficient

$$C_s = K_d C_w$$

$$K_d = C_s / C_w$$

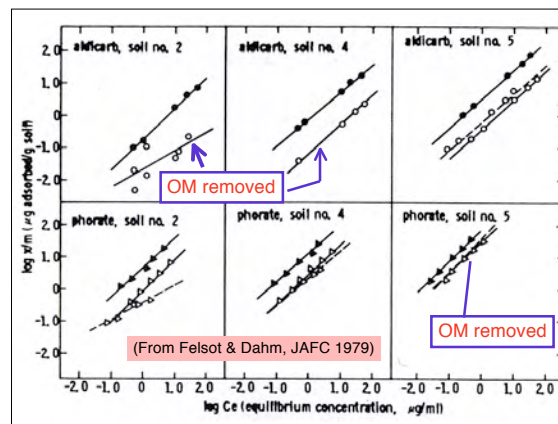
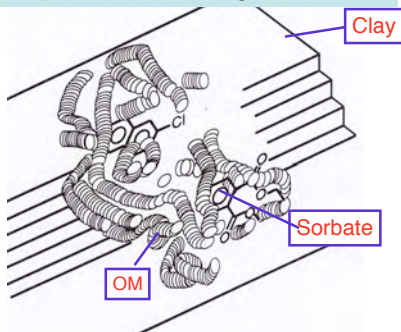
### Freundlich Isotherm

$$C_s = K C_w^n$$

$$\log C_s = n \log C_w + \log K_f$$

$$K_f \sim K_d$$

Soil OM is the most influential factor on sorption of neutral organics

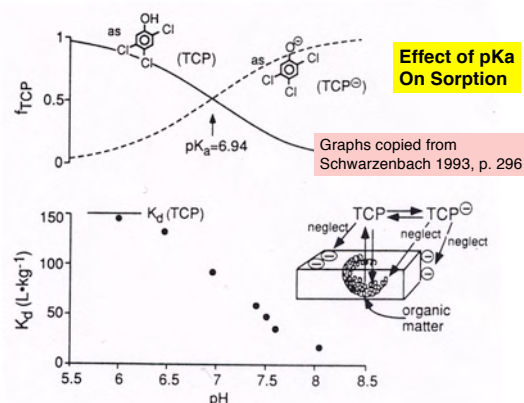


Normalize  $K_d$  or  $K_f$  to  $K_{oc}$  or  $K_{om}$  by dividing by fraction of organic carbon or organic matter, respectively

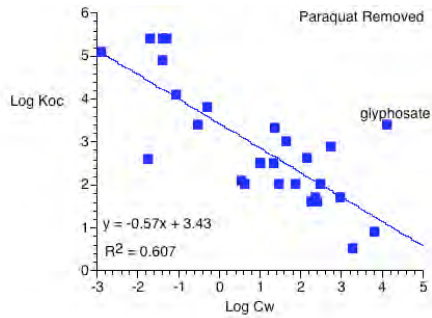
Soil	Organic Matter (%)	$K_f$	$K_{om}$
1	0.88	2.32	264
2	1.84	5.48	298
3	4.56	4.56	211
4	6.55	6.55	246
5	31.65	31.65	233

(From Felsot & Dahm, JAFC 1979)

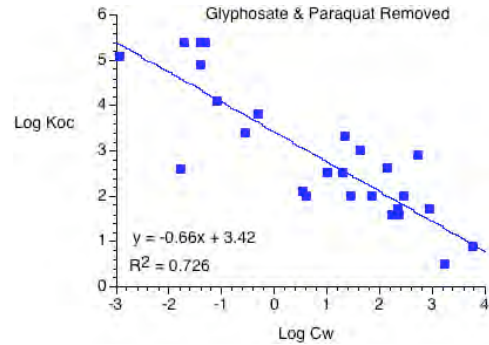
## Effect of pKa On Sorption



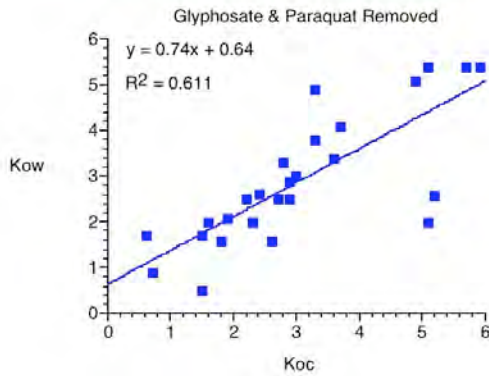
For neutral organics, good correlation between  $K_{oc}$  &  $K_{ow}$



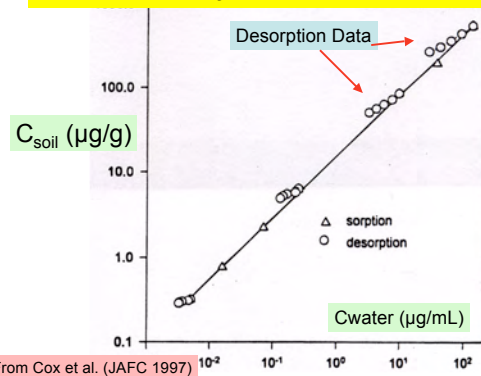
For neutral organics, good correlation between  $K_{oc}$  &  $K_{ow}$



Positive Correlation Between  $K_{ow}$  and  $K_{oc}$



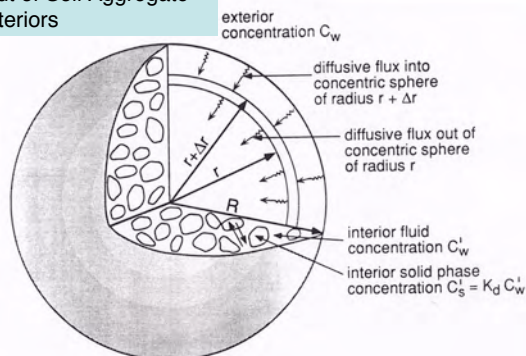
**Hysteresis**



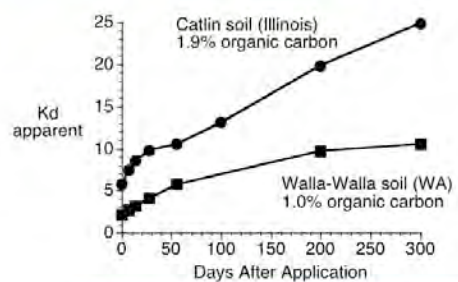
From Cox et al. (JAF 1997)

Slow Diffusion Into and Out of Soil Aggregate Interiors

From Schwarzenbach et al. 1993



Effect of Residue Aging on Sorption Potential



Note that sorption tends to increase with time

McCall & Agin, ETAC 1985