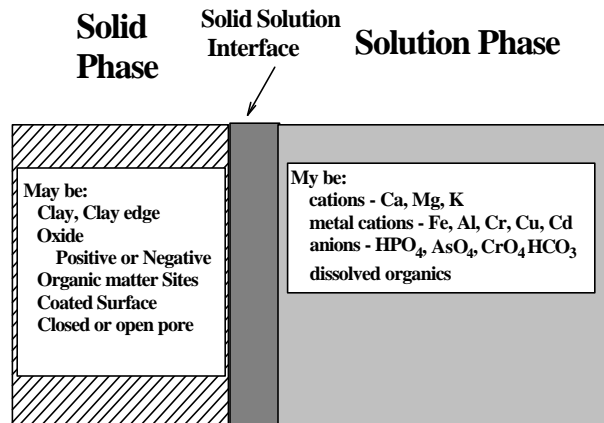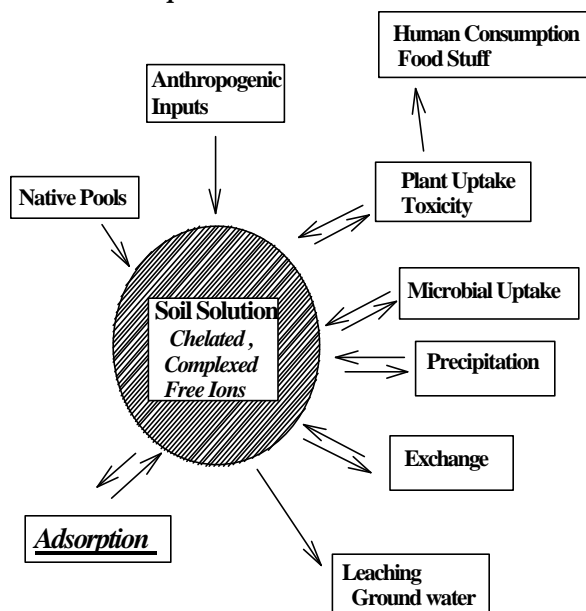## ADSORPTION

General Overview- The question of whether ions or compounds are associated with the soil solid phase (potential particulates) or the soil solution influences its behavior and environmental fate. Generally ions

and solution phases depending on the soil and material properties. The concept is illustrated in Figure 7-1. The solution phase is the reactive soil and provides ions and compounds for plant and microbial uptake, leaching and other process illustrated in Figure 7-2. Adsorption reactions are the main control on solution composition for cations other than the alkaline earth and alkali metals, for anions other than chloride and nitrate, and for organic compounds.

Adsorption is a general term that refers to the disappearance of solutes from solution with the presumption of adsorption on a solid phase. Adsorption is the accumulation at the solid-solution interface, and may result from either physical or chemical interaction with the surface. Physical adsorption is a relatively weak bonding to the surface while chemical (chemisorption) is a stronger interaction which involves ionic or covalent bonding in addition to van der Waal's and dispersion forces operative in physical adsorption. **Adsorption** refers to attraction and bonding onto a surface, while **absorption** is a process in which the solute is taken up into

7.1. Schematic of the solid solution interface.

7.2. The relation of solution phase to sources and sinks for ions and compounds.

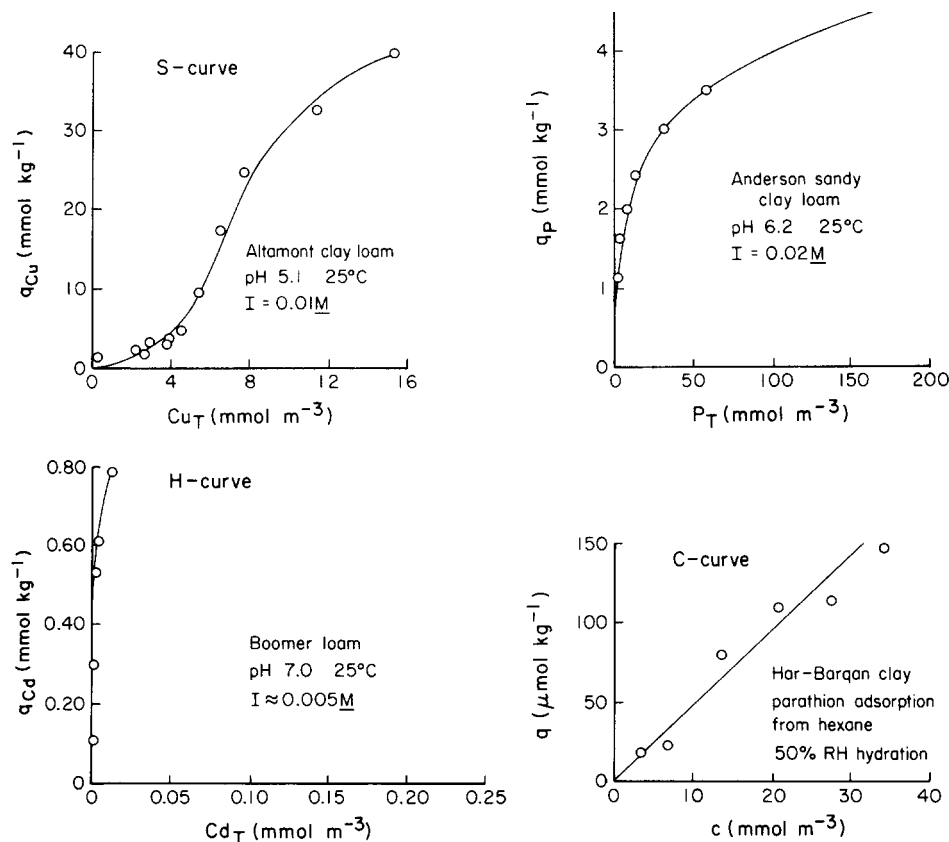*Figure 7.3 Examples of different isotherms, taken From Sposito 1984.*

Figure 4.1. General classes of adsorption isotherms. *S curve*, data courtesy of C. S. LeVesque; *L curve*, data from I.C.R. Holford *et al.*[8]; *H curve*, data from J. García-Mirayagaya and A. L. Page, Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition *Water, Air, and Soil Pollution* 9:289 (1978); *C curve*, data from B. Yaron and S. Saltzman, Influence of water and temperature on adsorption of parathion by soils *Soil Sci. Soc. Am. J.* **36**:583 (1972).

a structure or across a membrane. In some cases the distinction is difficult and the generic term **sorption** has been used. Nothing about the mechanism of this disappearance from solution is implied by the term sorption. Bulk precipitation would be excluded, but surface mediated precipitation is difficult to distinguish from sorption. Operationally, sorption is determined by the extent of solute removal from solution in either batch studies or in leaching studies with columns of adsorptive materials.

A typical technique is to supply a known concentration of **sorbate** to a known mass of **adsorbent**. After the solution and solid have come to equilibrium, (at a known constant temperature and known solid to solution ratio) solution concentration is then measured and the difference between the initial concentration and

final equilibrium concentration adjusted for the solution volume is assumed to be the amount of sorption per unit mass of sorbent. Algebraically this is:

$$Amount\ adsorbed\ =\ q\ =\ \frac{(c_f - c_i)\ v_{solution}}{m_{sorbant}}$$
(1)

Units for the sorption onto the solid phase depend on the units of concentration and mass, however mg kg^{-1} (ppm), mmol kg^{-1}, and : mol g^{-1} are commonly used units for q. Some times the adsorption is expressed in terms of surface area and the units are moles/meter squared. In order to determine the solution concentration, the solid and solute must be separated. Centrifugation, and filtration are the commonly used techniques.

Knowing the amount of sorbate per unit mass of sorbate, **(q)** a plot of equilibrium concentration (**C$_{eq}$**) vs **q** is constructed. This plot is called an adsorption sorption isotherm. The name refers to the constant temperature maintained during the sorption process. Figure 7.3 (*Sposito,* 1984) depicts four common isotherms types. The data contained in these isotherms are usually analyzed to ascertain whether they conform to specific isotherms types. Another way to consider these isotherms is to calculate a distribution coefficient, or the partitioning between the solution and solid phase. Distribution coefficients are simply the ratio of solid phase concentration to solution phase concentration. These coefficients increase as adsorption increases. Examination of the data presented in Figure 7. 3 indicates that the distribution coefficient is only a constant for the "C Curve" or linear isotherm. But at low and often environmentally reasonable concentrations many of the other isotherms are nearly linear. K$_d$ is commonly used for adsorption studies of organic compounds K$_d$ is defined by equation 2.

$$K_d = \frac{Concentration\ in\ the\ solid\ phase}{Concentration\ in\ the\ solution\ phase}$$
(2)

COMMON SORPTION ISOTHERMS TYPES (descriptors of partitioning)

Linear Isotherms - The simplest form is the linear relationship between q and c_{eq}. which is:

$$q = a + b(c_{eq}) \tag{3}$$

In this instance linear regression may be used to find the slope (b) and the intercept (a). Many sorbates exhibit linear isotherms at low concentrations.

Freundlich Isotherms - A second type of isotherm exhibits increasing adsorption with increasing concentration, but a decreasing positive slope as c_{eq} increases. Many organics and inorganic follow this type of sorption behavior. This isotherm is termed the "Freundlich Isotherm". It is described by:

$$q = K_F \ c_{eq}^{1/n} \tag{4}$$

Where K_F is the "Freundlich" equilibrium constant and 1/n is an arbitrary constant evaluated by linearizing the equation. If (1/n) approaches 1 the equation is linear. For non-linear isotherms the data can be plotted in linear form by taking the log of both sides of equation (3):

$$\log (q) = \log K_F + 1/n \log c_{eq} \tag{5}$$
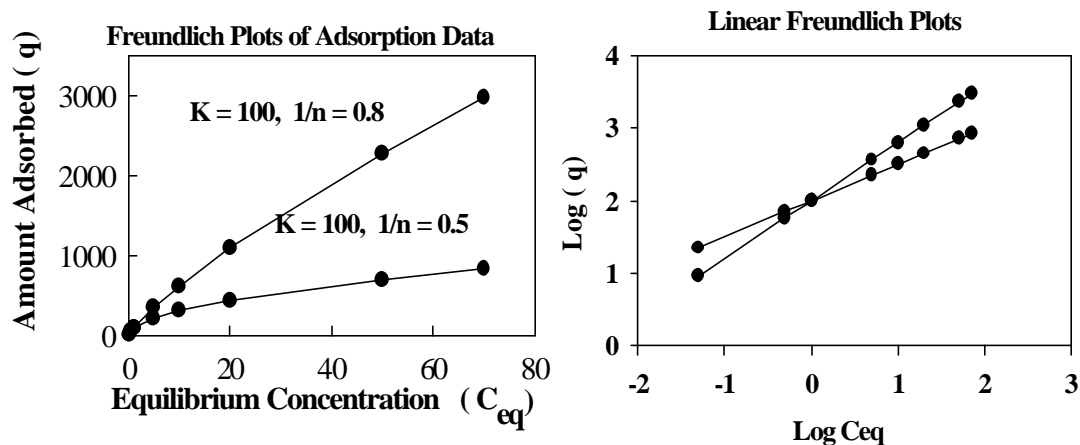

Figure 7.4   Examples of a Freundlich isotherm and the log-log plot of the data to give an linear representation.

Langmuir Isotherms - If sorption increases to a maximum value with C_{eq}, the data will often fit an equation of the form:

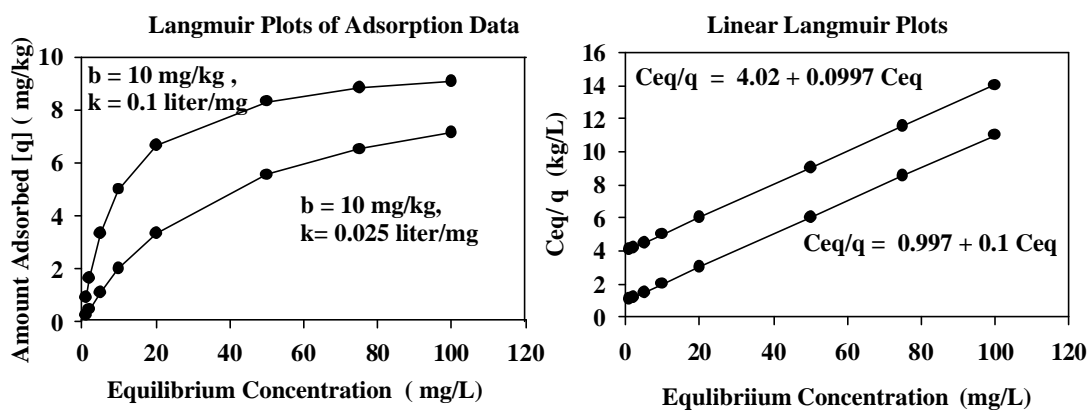$$q = \frac{b\,K_L\,c_{eq}}{1 + K_L c_{eq}} \qquad (6)$$

This formulation is called a Langmuir Equation. Note that if $K_L\,c_{eq} \ll 1$, the equation is linear. As mentioned, at low concentration a Langmuir isotherm may appear to be nearly linear. The non-linear form can be evaluated by transforming to the linear equation:

$$\frac{c_{eq}}{q} = \frac{1}{K_L} + \frac{n}{bK_L} \qquad (7)$$

Other linear forms are also used (for example):

$$\frac{q}{c_{eq}} = K_L b - K_L q \qquad (8)$$

Figure 7.5 Example of a Langmuir Isotherm and the linear form of the data.

Langmuir Plots of Adsorption Data

b = 10 mg/kg , k = 0.1 liter/mg

b = 10 mg/kg, k= 0.025 liter/mg

Amount Adsorbed [q] (mg/kg)

Equilibrium Concentration (mg/L)

Linear Langmuir Plots

Ceq/q = 4.02 + 0.0997 Ceq

Ceq/q = 0.997 + 0.1 Ceq

Ceq/ q (kg/L)

Equlibriium Concentration (mg/L)

Multisite Langmuir equation.

In cases where two or more distinct sites of sorption are present, a "Two-Site" or multi-site Langmuir equation can be used to describe the data. Competitive "Langmuir" equations have also been proposed.

BET Isotherms

Another important isotherm type describes multi-layer sorption and was developed by Brunauer, Emmett and Teller (1938). After its authors, the isotherm is called a BET equation and has the form:

$$q \;=\; \frac{B\,c_{eq}\,b}{(c_s - c_{eq})\left(1 + (B-1)\left(\dfrac{c_{eq}}{c_s}\right)\right)} \tag{9}$$
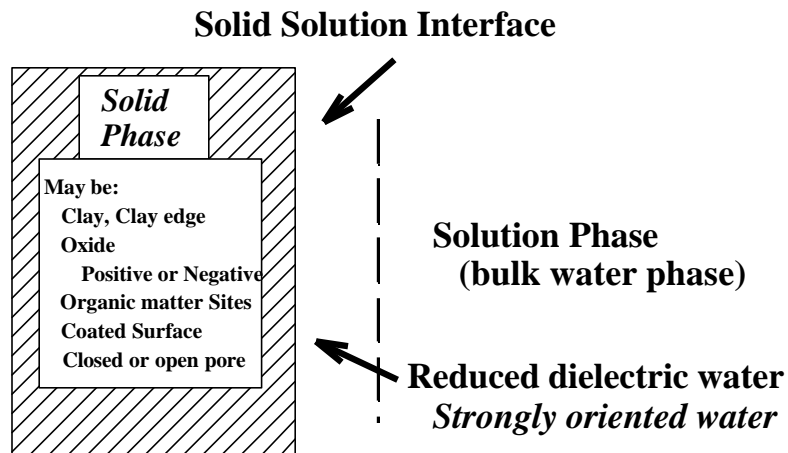
Like the other isotherms, the BET has a linear form:

$$\frac{c_{eq}}{(c_s - c_{eq})} \;=\; \frac{1}{Bb} + \left(\frac{(B-1)}{Bb}\right)\left(\frac{c_{eq}}{c_s}\right) \tag{10}$$

In the BET equations: B = a term for the energy of interaction with the surface; b = the monolayer capacity and; C_s = the concentration of the solute at saturation.

The BET equation is important because it is used to measure surface area. If the monolayer capacity can be determined, and the area of a monolayer can be found, then the surface area can be estimated. In practice, N_2 gas is adsorbed on the surface at liquid N temperature and each molecule covers $16.2\ \text{A}^2$. The equipment to perform this analysis requires high vacuum and is not available in every laboratory. McBride (pages 350 -353.) describes the use of the BET isotherm for gas adsorption and surface area measurements.

There are a number of other isotherms described in the literature, however this introduction to the "Classical" isotherms adequately develops the concept.

Figure 7.6. A schematic view of sorption in a soil water system.

Solid Solution Interface

Solid Phase

May be:
  Clay, Clay edge
  Oxide
    Positive or Negative
  Organic matter Sites
  Coated Surface
  Closed or open pore

Solution Phase (bulk water phase)

Reduced dielectric water
Strongly oriented water

It is important to note again that isotherms do not provide information about the mechanism of sorption and are best looked upon a mathematical descriptors of sorption data. Mechanistic details of sorption processes must be derived from other techniques. Surface spectroscopy has revealed a number of important details of the process, but or knowledge is incomplete. Details of adsorption on to soil organics where the structure is not know is particularly sketchy.

MECHANISMS OF REMOVAL FROM SOLUTION

The removal from solution implies that ions or compounds have been sorbed into the interfacial region between the soil solids and the solution phase. Interactions between compounds, ions an the surfaces in soils depend on the types of surfaces available and the compound or ion of interest. Inorganic surfaces in soils are mainly oxygen or hydroxyls. These surfaces are highly polar and normally they carry either a positive of negative charge. Organic surfaces can also be charged and have surfaces that range from strongly polar to nonpolar.

Sorption of Inorganic on Soil Surfaces. Inorganic compounds are adsorbed mostly by chemical interaction with soil surfaces. These interactions range from purely electrostatic (*e.g.* exchange) to strong covalent bonding. Exchangeable ions are considered to be fully hydrated and completely dissociated from the surface. The real picture of exchange is more complex and even the alkali metals may be adsorbed into a **Stern Layer** in which the ions are partially dehydrationed. Figure 7.7 depicts the interaction of Li, Na and K with a soil surface. Sodium and Li are strongly hydrated and too large to form specific bonds with the mineral surface.

However, K^+ can be strongly bound by many soil minerals. This specific binding is not considered in Figure 7.7.

Figure 7.7. A calculated distribution of cations near a clay mineral surface. Shainberg and Kemper, 1966.
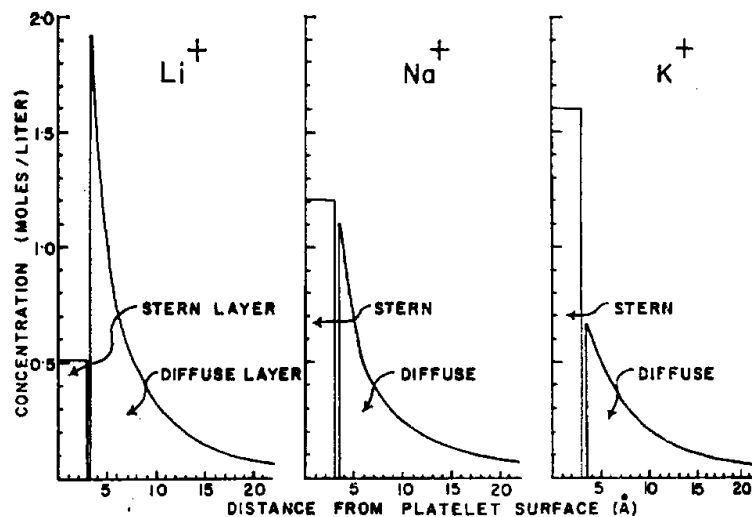

Fig. 2---Calculated cation distributions near a clay surface.

In contrast to the alkaline earth and alkali metals, that are easily replaced by other exchangeable cations, phosphorus is strongly adsorbed on soil surfaces. This sorption is believed to occur via displacement of surface hydroxyl groups and the formation of mono and bidentate surface complexes with covalent bonding character. Electrostatic exchange of alkali metals and covalent bonding of P are the end members of a continuous array of progressively stronger interactions with the colloidal surfaces. In this array of possibilities, the nature of the binding site on a particular sorbant may be different, the sorbant may change and the different sorbates can display a range of interactions.

A term has been coined which separates strong adsorption from weaker interactions. **Specific adsorption or sorption** is an operational term related to the electrophoretic mobility of the sorbant. Sorbates which can cause a charge reversal in the sorbant are said to be specifically adsorbed. Implicit in this definition is that the sorbates are entering a "Stern or Stern-like layer" at the interface. Also implicit in this is an interaction stronger than the electrostatic interaction ascribed to exchange. Figure 7.8 depicts the difference among cations in their ability to be adsorbed on colloidal MnO_2 in relation to pH. Those ions adsorbed below the point of zero charge are concentrated at the interface in opposition to electrostatic forces and are therefore considered to be specifically adsorbed.

Adsorption on MnO_2

PZC Co(II)

Cu(II)

K$^+$

Na$^+$

Adsorbed Metal (moles/gram)

Suspension pH
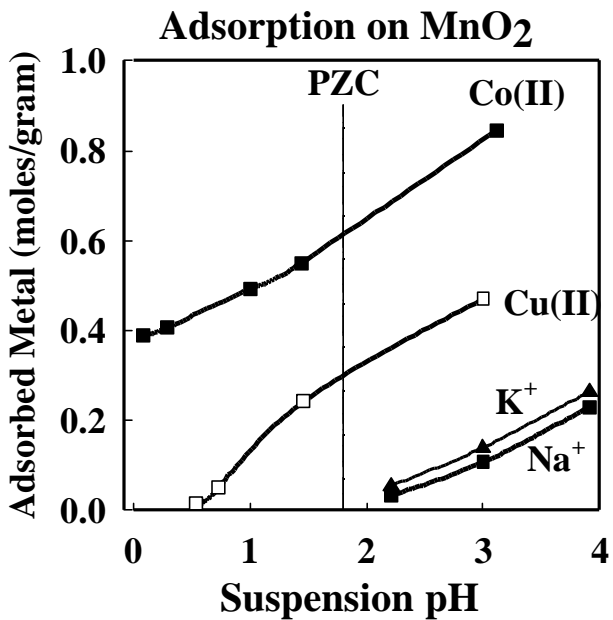
After **Murry et al. 1968**

Figure 7.8. Adsorption of trace metals and alkali metals on colloidal manganese dioxide

Ions adsorbed into the interfacial region by specific adsorption have the capability to change the potential at the interface between the solid and the solution and thereby change the electrophoretic mobility of the particle. If the particle undergoes a charge reversal, by definition, the ions causing this charge reversal are considered to be specifically adsorbed. Figure 7.9 and 7.10 depict the effects of Al on the electrophoretic mobility of SiO_2. At high pH where the surface is covered with Al, the Si surface appears to behave like aluminum oxide. If ions are specifically adsorbed in the surface they may be bonded by covalent linkages and will be dehydrated. Ions with strong ionic interactions with the surface may also be partially dehydrated.

Another way of distinguishing the bonding between a surface site and an ion is to determine whether they form **inner sphere** or **outer sphere** complexes. Inner sphere complexes do not have waters of hydration between the ion and the surface, while the outer sphere complexes are
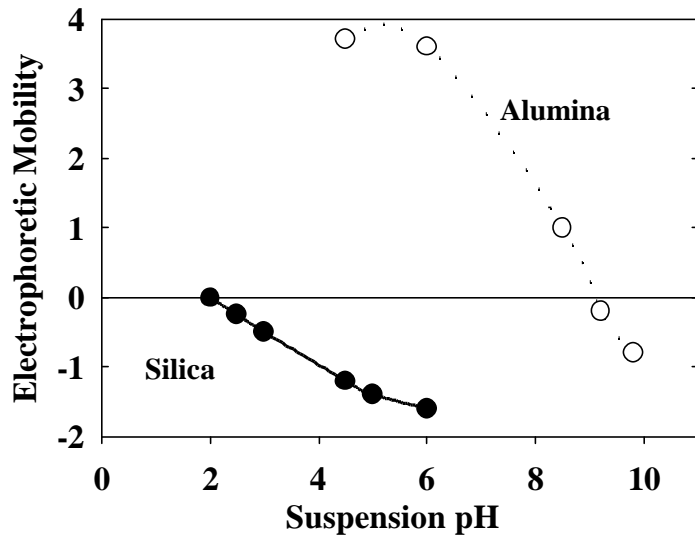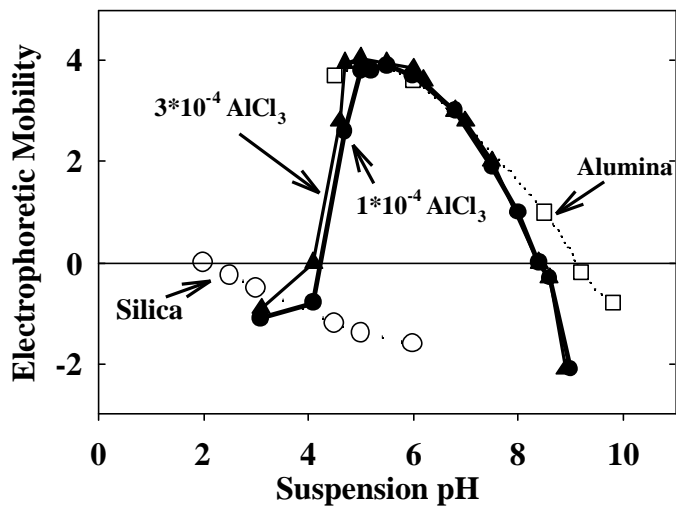hydrated. This is very similar to the distinction between an ion pair and a complex.

Figure 7.9. The electrophoretic mobility of colloidal aluminum hydroxide and colloidal silica in relation to pH. After Stiger, 1975.

Figure 7.10. The electrophoretic mobility of colloidal aluminum hydroxide and colloidal silica in relation to pH and added AlCl$_3$. After Stiger, 1975.
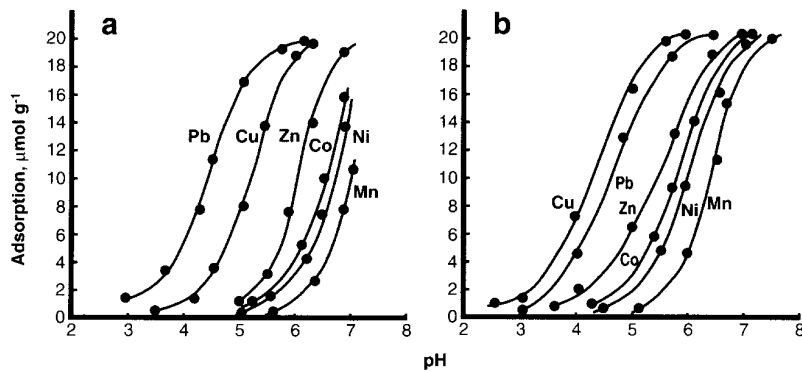
Figure 7.11.   The effects of pH on metal adsorption on (a) hematite and (b) goethite. **Data from McKenzie (1980) taken from Sparks (1995).**

When the level of solution ions increases, the amount adsorbed increases. At some point in the isotherm (depending on the ions and the surface), a so called **monolayer capacity** corresponding to complete surface coverage is reached. Any adsorption beyond this point is condensation of multi-layers or a clustering. Multi-layers are equivalent to surface precipitation (the development of a three dimensional phase). If the surface is not covered with a uniform layer and the precipitate occurs as islands of precipitate they are termed **surface clusters.**

Obviously, the adsorption of ions onto soil surfaces is a complex process that varies among the ions and surfaces that dominate the system. Therefore models have been used extensively to describe the processes that occur at the interface. Several recent soil chemistry text books do a very good job of describing the various models and it will not be repeated here. Because the models contain a number of adjustable parameters they can all normally be "manipulated" to fit the experimental data. Our modeling efforts have outstripped our ability to understand the surfaces that adsorb ions.

None-the-less there are a few generalities that describe cation and anion adsorption in soils.

1. Surface area and mineralogy are important factors affecting adsorption.

2. Metals are more soluble and less strongly adsorbed at low pH.

3. The identity of the metal affects absorption..

4. Anions (eg PO_4, AsO_4, AsO_3 MoO_4, SeO_4, $SeoO_3$) are more strongly adsorbed at low pH.

Adsorption of Organics on Soil Surfaces. The adsorption of organic materials to soils can occur via several different mechanisms depending on the characteristics of the adsorbing surface and the adsorbate. Because organic compounds can be either polar or nonpolar in all or part of the compound and because they may or may not be charged, the interactions of organics with soil surfaces can be quite different from those of inorganic ions. The differences in organic compounds is illustrated well by the Figure 7.12 from McBride (1994). As shown in this representation, differences in pH and polarity affect solubility.
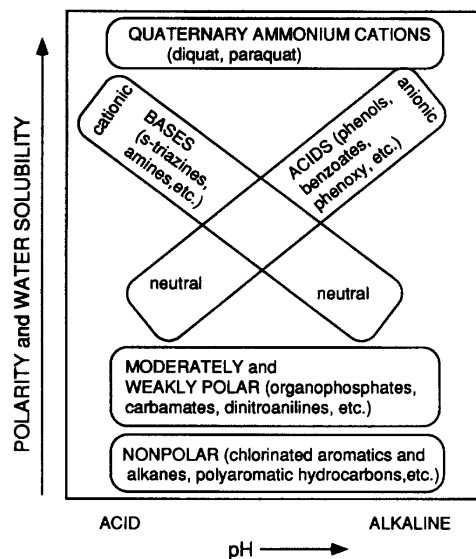

Figure 10.1. Classification of organic compounds on the basis of their polarity and charge.

Figure 7.12 Schematic representation of ranges in polarity and solubilities of organic compounds in relation to pH. From McBride 1994.

Table 1. (Sposito ,1984) lists several mechanisms of adsorption for organic compounds on mineral and organic surfaces. Given the large number of possible interactions and the large range in characteristics of soil organic compounds (Figure 7.12). The variations in adsorption for organic compounds by soils is large. The reversibility of adsorption is an important consideration. For many ions and compounds, the desorption does not follow the same isotherm as adsorption.

This difference occurs with inorganic ions, but the desorption of organic compounds is especially subject to **hysteresis**. Hysteresis is defined as a difference in partitioning during adsorption and desorption. Figure 7.13 illustrates an example of hysteresis for desorption of EDB. In this case, slow diffusion from small pores is a likely explanation for the differences observed over time.
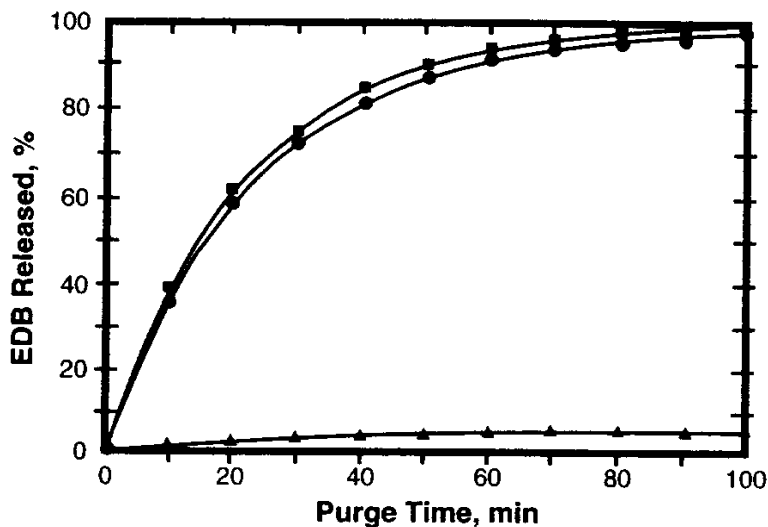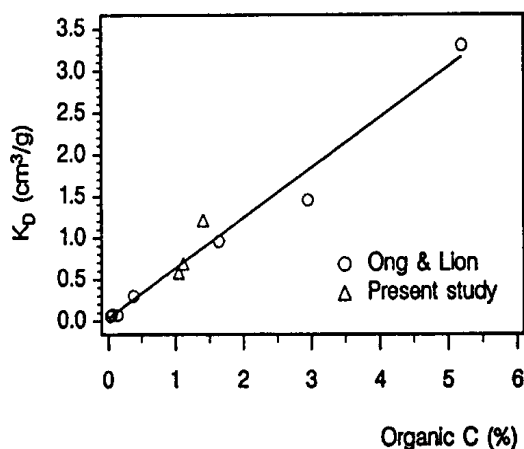
Figure 7.13 An example of hysteresis for EDB. From Steinberg et al. (1987)

Table 7.1. The mechanisms of organic matter interaction with solution ions.

Mechanism	Principal organic function groups involved.
Cation exchange	Amines, ring NH, heterocyclic N
Protonation	Amines, heterocyclic N, carbonyl, carboxylate
Anion exchange	Carboxylate
Water bridging	Amino, carboxylate, carbonyl, alcoholic OH
Cation bridging	Carbonylate, amines, carbonyl, alcoholic OH
Ligand exchange	Carboxylate
Hydrogen bonding	Amines, carbonyl, carboxyl, phenylhydroxyl
Van der Waals interactions	Uncharged, nonploar organic functional groups

In addition to the possibilities of organics being adsorbed to mineral surfaces, these compounds can be sorbed on soil organic matter. The distribution of organic compounds between solution and solid phase is often described in terms of the partition or distribution coefficient rather than an isotherm type (Equation 10), as shown earlier. Some organic surfaces are not as polar as mineral surfaces and provide sorption possibilities for less polar organics. For the nonpolar organics, water is a strong competitor for sites on minerals surfaces and the adsorption of organics decreases with increasing water content. For volatile organic compounds (VOC's) in dry soils, the distribution coefficient is can be much greater than in moist soils. Figure 7.14 shows that the log of K_d increases dramatically as soil moisture content decreases. This particular K_d is calculated for the partitioning between the vapor phase and the solid phase. Since organic compounds (particularly the less polar ones) are associated with organic materials, the distribution coefficient can be normalized for organic matter content. The resulting distribution coefficient often shows much less variability among soils.

Figure 7.14a. The relationship between Kd and %.
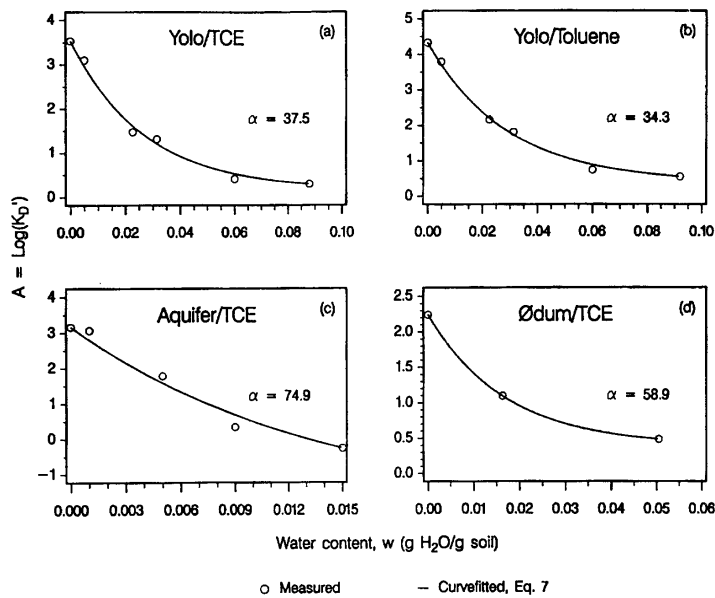
From Petersen et al. 1995.

Figure 7.14b. Effects of water on Kd for VOC's. From Petersen et al. 1995.

$$K_d = \frac{\text{Concentration in the solid phase}}{\text{Concentration in the solution phase}} = \frac{mg/kg}{mg/L} = \frac{L}{kg} \qquad (10)$$

Table 2 shows data for K_d and K_{oc} Koc is defined as:

$$K_{OC} = \frac{K_D}{\% \, OrganicCarbon} * 100 \qquad (11).$$

K_{oc} can be realted to the octanol water partition coefficient (K_{ow}). K_{ow} is defined as:

$$K_{OW} = \frac{\text{Concentration in octanol}}{\text{Concentration in water}} \qquad (12)$$

The empirical relationship is: Log K_d = a log K_{ow} + log foc + b.   (13).   Recognize that Log K_d - log foc = Log (K_{oc} /100), we can see that log K_d and log K_{ow} are related.

Figure 6.17. Illustrates the relationship between K_d (or in this case K_p) and K_{ow}. In this figure the organic compounds tested were mon, di, tri, and tetramethylbenzenes and chlorobenzenes. Water solubility has also been correlated with K_{ow}. As might be expected, compounds that are less soluble in water have higher K_{oc} values.
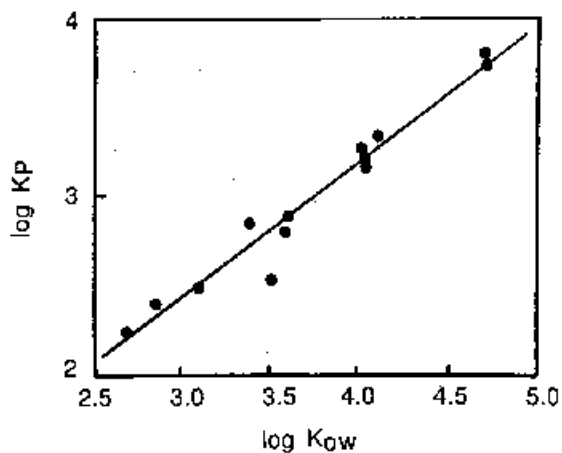
Figure 7.15. The relationship between Koc (Kp) and Kow. From Westall 1987.

The value of knowing the partitioning of chemical between the liquid and solid phase and to some extent the distribution between the solid and gaseous phase allow one to make some predictions about the environmental fate of chemicals in the environment. The question of whether the materials are likely to be associated with particulates is strongly related to the adsorption tendencies of the materials. Volatile chemicals can partition to the soil solids and this affects their volatility and transfer to the atmosphere.

Table 7.2. Partition coefficients for various soils adjusted for the organic carbon content of the soils.

SOIL	Organic Carbon %	K_D	Koc
1	0.08	0.40	491
2	0.62	3.2	514
3	0.86	5.4	627
4	0.97	4.4	457
5	1.45	9.1	627
6	3.80	15.9	417
7	5.67	44.0	764
8	21.7	132.4	611
mean		26.4	564
SD		44.9	114
CV		167 %	20 %

Review Questions

1. What is the distinction between adsorption and exchange?

2. What is an isotherm?

3. How does the distribution coefficient relate to an isotherm?

4. What are the distinctions between the Langmuir and Freundlich isotherms?

5. How would you distinguish adsorption from surface precipitation?

6. Why is the BET isotherm important?

7. What soil chemical factors affect metal adsorption?

8. Why does specific adsorption cause a charge reversal?

9. What is specific adsorption?

10. What is Koc and Kow?

11. What factors affect the adsorption of organic compounds in soils? Why?

12. How can the electrophoretic mobility of colloids be used to determine charge and charge reversal?

13. What is a Stern layer? How does this relate to specific adsorption and electrophoretic mobility?