Chapter 5. Partitioning, Sorption, and Exchange at Surfaces

◎ Partitioning;

a) a general phenomenon describing the tendency of a contaminant to exist at equilibrium between two phases

b) a general term describing the distribution of a contaminant among phases including air, water, and soil (and NAPL)
  - between air and water (i.e., surface water, groundwater)
  - between water and solid (i.e., soil, aquifer, living organisms...)
  - between air and solids (i.e., particles in the air)
  (- between NAPL and air/water/solid)

c) sometimes used to describe one mechanism of sorption

◎ Sorption (desorption);

a) a specific partitioning and exchange phenomena in which contaminants accumulate at the solid surface from the surrounding solution

b) one of the most important mechanisms controlling the rate at which contaminants move in soil and subsurface systems

c) affects a number of other pathways such as volatilization, hydrolysis, oxidation, biodegradation, and so on

d) may (or may not) reduce the effectiveness of remediation processes

◎ Exchange;

- the displacement of charged species (mainly metal ions) by another species on the solid surface

◎ Fugacity;

① a molecule's tendency to escape the system it is in
(e.g., inflated balloon and slack balloon connected each other)
- for an ideal gas, fugacity is the pressure
- for nonideal gases, fugacity is the "effective pressure"
  -> roughly considered as "partial pressure" ($f = P$)

② "When equilibrium partitioning among phases (air, water, soild...) is attained, the chemical potentials in all phases are equal and the fugacities become equal"

$$f_{air} = f_{water} = f_{biota} = f_{sorb} \text{ (at equilibrium)}$$

③ at low chemical concentrations (usu. found in the env),

$$C \propto f \;\; \rightarrow C = Zf$$

Z; fugacity capacity constant (mol/atm.m^3)

④ Z is the key to calculating the distribution of a chemical in the env.

$$C_{air}/C_{water} = Z_{air}f/Z_{water}f = Z_{air}/Z_{water}$$

similarly, $C_{biota}/C_{water} = Z_{biota}/Z_{water}$ and so on....

⑤ deriving Z values

- in air phase,

$PV = nRT \rightarrow P=n/V*(RT) \rightarrow P = C_{air}*RT \rightarrow \underline{C_{air} = P/RT}$

since $f=P$ and $C=Zf$,

$C_{air} = Z_{air}*f = f/RT \quad \rightarrow \quad \underline{Z_{air} = 1/RT}$

indicating that at a given temperature, Z_{air} is the same for any gas

for example, at 25C, $Z_{air} = 4.04 \times 10^{-4}$ mol/m^{3}Pa

- in water phase,

$P = HC_{water}$ (H; Henry's law contant in Pa*m^3/mole)

since $f=P$ and $C=Zf$,

$f = HC_{water} = H*fZ_{water} \quad \rightarrow \quad \underline{Z_{water} = 1/H}$

- in soild phase,

$C_{sorb} = K_d*C_{water}$

since at equilibrium $C_{sorb} = fZ_{sorb}$ and $C_{water}=fZ_{water}$,

$fZ_{sorb} = K_d*fZ_{water} \rightarrow \underline{Z_{sorb} = K_d/H} \rightarrow \underline{Z_{sorb} = \rho*K_d/H}$

- in biota,

$C_{biota} = K_B*C_{water}$

similarly to the solid phase, $\underline{Z_{biota} = K_B/H} \rightarrow \underline{Z_{biota} = \rho*K_B/H}$

⑥ chemical distribution

- once Z value for each phase is calculated, mass of a chemical in each phase can be calculated as follows

$M = CV = fZ*V$ (M; moles of chemical in a phase)

$\underline{M_{total} = \Sigma M_i = \Sigma(fZ_iV_i) = f\Sigma(Z_iV_i)}$

(e.g.) $M_{air} = fZ_{air}*V_{air}$

$M_{water} = fZ_{water}*V_{water}$ and so on...

$M_{total} = M_{air} + M_{water} + \ldots\ldots = fZ_{air}*V_{air} + fZ_{water}*V_{water} + \ldots$

$= f(Z_{air}*V_{air} + Z_{water}*V_{water} + \ldots)$

- assumes an closed system without chemical/biological decomposition

1. Sorption (p. 255)

1) General concept

a) sorption; an equilibrium phenomenon in which hydrophobic compounds partition onto surfaces in a two-phase system (e.g., water-soil)

b) in most cases, a physical process involving weak and reversible bonds between the contaminant and the soild

c) repeated sorption and desorption in the environment

d) terminology;

- adsorption/absorption, desorption
- sorbent, sorbate (solute), solvent

e) when $\Delta G = (-)$ from $\Delta G = \Delta H - T\Delta S$

-> sorption occurs

- f) mechanisms; electrostatic, physical and chemical processes
  - electrostatic mechanism; from charged attractive forces between sorbent and sorbate (e.g., heavy metal sorption onto a negatively charged surface)
  - physical mechanism; weak bonding processes by attractions of intermolecular forces (i.e, van der Waals forces, hydrogen bonding, dipole-dipole interaction,...)
  - chemical sorption (chemisorption); a stronger and permanent bond (i.e,. covalent bond) and has a high heat of sorption
  - Fig. 5.1 **(all are enthalpy-driven)**
- g) another important sorption mechanism; **hydrophobic sorption**
  - **entrophy-driven**
  - a main mechanism for most nonionic hydrophobic organic contaminants
  - occurs when sorbates are not stabilized in solvent (e.g., PAH-water)
  - sorbate-solvent interaction ≪ sorbate-sorbent interaction

2) Advanced concept

- a) "As sorption proceeds sorbed contaminants move into another place inside the sorbent, generating more strongly and irreversibly bound fractions"
- b) biphasic sorption/desorption;
  - first stage; fast, reversible fraction
  - second stage; slow, irreversible fraction
- c) sorbed contaminants; reversible and irreversible fractions
- d) irreversible fractions;
  - resistant to desorption, availability (biological, chemical), remediation,...
  - mechanisms not clear, but....
    - i) association with soil organic matter (physical or chemical binding)
    - ii) enter into micropores in sorbent
    - iii) combination of the two
- e) formation of persistent fractions
  - nonextractable residues
  - aged (sequestered) compounds
  - bound residues (primarily for pesticides by IUPAC, 1972)

2. The Governing variables: Sorbent Characteristics, Contaminant Hydrophobicity, and the Solvent (p. 258)

1) Sorbent characteristics that influence sorption
- hydrophobicity; soil organic matter (SOM), granular activated carbon (GAC)
- specific surface area; colloidal particles (clay minerals, SOM)
- porosity, tortuosity

2) Sorbate properties
- water solubility

- hydrophobicity; octanol-water partition coefficient (K_{OW})

3) Solvent
  - in most cases, water
  - organic solvents such as NAPLs

◎ Another two phase system

sorption of volatile organic carbons (VOCs) onto solid particles (e.g., soils, GAC) from the air

3. Properties of Soils and Other Sorbents (p. 258)

- highyl variable physical structure and chemical composition; heterogeneity
- important properties; texture, mineralogy, bulk density, porosity, OC content
- four major components (Fig. 5.2);
    soil solid; inorganic fraction (clay minerals & metal oxides), organic matter
    pore space; air, water

1) Particle size distribution
  a) USDA system most widely used; clay, silt, sand, gravel (Table 5.1)
  b) classification of soil texture based on particle sixe distribution (Fig. 5.3)

2) Soil minerals (inorganic colloids)
  a) primary minerals
    - small pieces of parent material (i.e., rocks)
    - strong Si-O covalent bonds; resistant to weathering
    - e.g.) quartz, feldspar,...
  b) secondary minerals
    - formed through chemical trnasformations (wegthering)
    - clay minerals and metal oxides (Table 5.2 & Table 5.3)
  c) clay minerals
    - a great influence on the interation of contaminants with soils (depending on the situations such as moisture content, organic matter content,...)
    - high surface area (due to micrometer scale sizes)
    - negative surface charges (due to permanent and pH-dependent charges)
    - linked to SOM (humic materials), metal (Fe-, Mn-) oxides
      -> generates pores, aggregates, structures among soil particles
      -> provides more sorption sites (both chemically & physically)
      -> influences on the transport and fate (sorption, retardation, trnasformation...) of contaminants
  d) metal oxides occurs in soils as
    - coatings on soil particles often mixed with clays
    - fillings in voids
    - concrete nodules

3) Cation exchange capacity (CEC)
  a) a measure of surface density of exchange sites (of positive ions) on a soil ; "total positive charges per mass of soil that can be exchanged"
  b) unit; meq/100 g soil -> cmol/kg soil
  c) greatly influenced by clay and SOM contents (e.g., sand < silt < clay)
  d) CEC calculation; understand "equivalent charge concept" (Example 5.2)
4) Bulk density (kg/m^3)
  a) the density of soil while in place (i.e, not compacted or disturbed)
  b) SOM < clay, silt < sand (Table 5.3)
5) Porosity
  a) total porosity; the percent content of a soil occupied by the pore space
  b) greatly influences on transport, retardation, mass transfer,....
  c) generally 30 - 50% (Table 5.5)
  d) effective porosity
    - excludes dead-end porosity from total porosity
    - used to calculate pore water velocity (refer to Darcy's law)
6) Volumetric water content
  a) the fraction of soil pores filled with water (i.e., 100% when saturated)
  b) used to calculate pore water velocity of unsaturated zone
7) Soil organic matter
  a) the most important soil property affecting transport and fate of contaminants
  b) SOM = 1.724 x SOC (but not absolutely correct!!!)
  c) SOM = nonhumic materials + humic substances
  d) an exponential decrease in SOM with depth (Fig. 5.6)
  e) works as a primary sorbent for (hydrophobic) organic contaminants over 1% of SOM (more exactly over 0.1%?)
  f) Nonhumic materials
    - unaltered known chemicals such as amino acids, carbohydrates, lipids,...
    - not effective in sorption
  g) Humic substances (humus)
    - definition still operational
    - yellow to dark brown polymer-like completely decomposed materials formed by microbially mediated reactions
    - originates from plants, animals, and microorganisms
    - very diverse composition depending on the origins
    - containes (hydro)quinones, cornifeyl alcohols, and polymerized phenols with many kinds of side chains (functional groups) such as carboxylic, carbonyl, ester, and methoxy groups
    - approximately 44-53% of C, 40-47% of O, 3.6-5.4% of H, 1.8-3.6% of N
    - greatly involved in the sorption of contaminants (often primary sorbent)
    - classical, generalized structure (Fig. 5.5)

◎ Recent concept on SOM as a primary sorbent

- three dimensional structure
- flexible with many microvoids (that serve as adsorption sites)
- hydrophilic and hydrophobic; amphiphilic
- adsorption domain as well as partitioning medium

◎ Role of SOM

- nutrient sources
- water-holding capacity
- buffering capacity; base neutralization
- CEC; deprotonation with an increase of pH
- binding to clay surface; polyvalent cations or H-bonding
- stable chelation; trace elements and heavy metals
- adsorption (binding) of pesticides through H-bonding;
- anion exchange capacity; present in acidic soils but little in neutral/alkaline soils

h) Fractionation of humic substances

- humin; insoluble in alkali solution (strongly bound to clay minerals)
- humic acid; insoluble in acid and soluble in alkali solution ($C_{187}H_{186}O_{89}N_9S$)
- fulvic acid; soluble both in acid and alkali solutions ($C_{135}H_{182}O_{95}N_5S_2$)

4. Sorption Isotherms (p. 267)

- isotherm; a plot of the extent to which sorption occurs at successively higher concentrations of sorbate at constant temperature
- a graphical representation of chemicals sorbed (mass of sorbate/mass of sorbent) as a function of the equilibrium concentration of sorbate

1) Langmuir isotherm

a) assumption;

- a single monolayer accumulation at a solid surface
- each sorption site has the same property (for binding chemicals)
- number of sorption sites limited (i.e, fixed)

b) sorption sites saturated at higher concentrations (Fig. 5.7)

c) represents "ADSORPTION"

d) Langmuir relationship;

$$C_s = \frac{x}{m} = \frac{abC_e}{1 + bC_e}$$

C_s; contaminant concentration sorbed on the solid (dimensionless)

C_e; conc. of contaminant remaining in solution at equilibrium (g/m^3)

a: empirical constant / b; saturation coefficient (m^3/g)

x; mass of contaminant sorbed onto the solid phase (g)

m; mass of sorbate (g)

e) linear expression;

$$\frac{C_e}{C_s} = \frac{1}{ab} + \frac{C_e}{a}$$

2) Freundlich isotherm

a) continuous sorption as the sorbate conc. in solution increases (Fig. 5.8)

- **At Low Concentration,** mass of contaminant sorbed ∝ conc. in solution
- at high conc, sorption to a diminishing degree, but never saturated

b) multiple layer sorption possible

c) Freundlich relationship;

$$C_s = \frac{x}{m} = K_F C_e^n$$

K_F; Freundlich sorption coefficient

n; empirical coefficient (a measure of linearity)

d) linear expression;

$$\ln C_s = \ln K_F + n \cdot \ln C_e$$

e) establishing sorption isotherms; Example 5.3

3) Types of isotherm graphs

a) L-type; Langmuir isotherm (high affinity between sorbate and sorbent)

b) C-type; partitioning (constant affinity); Freundlich relationship with n = 1

c) S-type; cooperative adsorption (sorbate-sorbate interaction≫sorbate-sorbent)

d) H-type; chemisorption (very strong sorbate-sorbent interaction/covalent bond)

5. The Octanol-Water Partition Coefficient (p. 271)

a) K_{ow};

- a good indication of hydrophobicity of a chemical
- inversely related to water solubility (Fig. 5.9)
- the most important prediction parameter for the behavior of contaminants

b) determined by shake-flask method

$$K_{ow} = \frac{chemical\ \ conc.\ \ in\ water - saturated\ \ octanol\ (mg/L)}{chemical\ \ conc.\ in\ octanol - saturated\ \ water\ (mg/L)}$$

c) ranges from 0.001 to over 10^8 -> expressed as Log K_{ow}

d) Log K_{ow} values for hazardous compounds (Table 5.7, Appendix G)

e) estimation method available (Appendix H)

6. The Soil Adsorption Coefficient and the Soil Distribution Coefficient (p. 272)

1) Soil distribution coefficient (K_d)

a) most accurate measure of sorption capacity of a soil **(As a Whole)**

b) K_d (mL/g) = $\frac{mass\ of\ contaminant\ sorbed\ (mg/g)}{mass\ of\ contaminant\ dissolved\ in\ the\ aqueous\ phase\ (mg/mL)}$

c) experimentally determined when sorption equilibrium is attained

d) used to calculate retardation factor

e) biological inhibitor used (e.g., NaN_3, $HgCl_2$) to insure no chemical loss from biodegradation

f) can be estimated from the Freundlich isotherm;

from $C_s = \frac{x}{m} = K_F C_e^n$,

replace K_F with K_d and assume a linear isotherm (meaning n=1),

-> $K_d = \frac{C_s}{C_e}$

(assumptions) - low contaminant concentration
- at equilibrium

g) positively related to SOM (SOC) content (mainly for nonpolar contaminants)

◎ Inorganic soil fraction as a primary sorbent

- in soils with low SOM content
- usually less than 0.1% of organic carbon (i.e., $f_{OC} < 0.001$), but depends on the soil and contaminant properties
- empirical estimation of f_{OC}^*

$$f_{OC}^* = \frac{S_a}{200\,(K_{OW})^{0.84}}$$

f_{OC}^*; the minimum SOC content in which SOM serves as a primary sorbent (g/g)

S_a; surface area of the soil (m^2/g)

K_{OW}; K_{OW} of the contaminant to be sorbed

- "f_{OC}^* increases as a function of S_a and decreases with higher K_{OW}"

2) Soil adsorption coefficient (K_{OC})

a) assumes that soil organic carbon is the primary sorbent

$$K_{OC}\ (mL/g) = \frac{mass\ of\ contaminant\ sorbed\ to\ the\ soil\ organic\ carbon\ (mg/g)}{mass\ of\ contaminant\ in\ the\ aqueous\ phase\ (mg/mL)}$$

b) organic carbon-normalized K_d
- can be comparable among soils with different SOM contents
- but no consideration on the nature and diversity of SOM
- K_{OC} for a chemical is the same (i.e., constant); Table 5.8

c) Koc can be derived from K_{OW} from empirical correlation equations (Table 5.9)

d) Kd = $K_{OC} \cdot f_{OC}$ (Example 5.5)

7. The Retardation Factor (p. 280)

a) describes relative contaminant velocity

b) retardation occurs by repeated sorption/desorption during the movement

c) other phenomena such as dispersion, transformation not included

d) for non-ionizable chemicals, related directly to contaminant hydrophobicity through correlations with K_d, K_{OC}, and K_{OW}

e) for ionizable chemicals (i.e., weak acids), normalized to unionized fraction (α) (ionized forms are miscible in water -> no retardation)

f) retardation factor $R = \frac{groundwater\ velocity}{contaminant\ velocity}$

$$= \frac{dissolved\ conc\ + sorbed\ conc}{dissolved\ (mobile)\ conc} = 1 + \frac{sorbed\ conc}{dissolved\ conc}$$

$$= 1 + \frac{\rho_B}{n} \cdot K_d$$

ρ_B; soil bulk density (g/m^3)

n; porosity (n_e; effective porosity)

K_d; soil distribution coefficient

g) determination of R; Example 5.6

8. Reactions of Metals in Soils and Solids (p. 282)

- physical sorption; van der Waals forces
- chemical sorption; ion exchange (CEC, AEC)
- in most cases, surface interactions; adsorption
- fixation; incorporation of metals within the inner structure of minerals, resulting in more permanent immobilization
- mobility in soil very limited (esp. in oxic soils at neutral pH ranges)
- extremely wide range of K_d (Table 5.11) due to complex governing variables (Fig. 5. 10)

a) oxidation-reduction
  - redox potential (i.e, difference of electron activity in aqueous phase) affects the mobility of metals
  - expressed as pE, E_h ; positive value- oxidation condition
    negative value- reduction condition
  - in general, reduced forms are more soluble and thus mobile (e.g., Cd^+, Cu^+ vs. Cd^{2+}, Cu^{2+})
  - exceptions; Cr^{6+}, Se^{6+} vs. Cr^{3+}, Se^{4+}

b) pH
  - metal solubility and mobility high at low pH (i.e, pH 2-5)
  - metal dissolution high in acidic, reduced soil
  - pH-E_h diagram showing metal speciation (Fig. 5.11)

c) ion exchange
  - sorbate; mostly heavy metals - positively charged
  - sorbent; clay minerals, SOM - negatively charged (in the natural env.)
  - charges need to be balanced to maintain electroneutrality
  - adsorbed cations can be displaced by another species with a higher affinity for the surface

- displacement ability; $Me^{3+} > Me^{2+} > Me^{+}$
- but the law of mass action is applicable, meaning that "a high conc. of a less exchangeable species displaces a more exchangeable ion"
- occurs in both SOM and inorganic colloids (clays, metal oxides)
- CEC; clay > silt > sand

◎ <u>pH dependency of CEC</u>

- SOM; mostly pH-dependent (due to lots of functional groups)
- clay minerals; mostly permanent CEC (due to isomorphous substitution) and small pH-dependent CEC (from -OH groups at crystal edges)

d) selectivity
  - sorbent-specific
  - in general, Pb, Cu are strongly bound while Cd, Ni, Hg are easily mobile
  - <u>Lewis hard-soft acid-base (HSAB) principle</u>

e) complexation
  - metal-ligand reaction
  - M_i (metal ion; Lewis acid) + L_j (ligand; Lewis base) $\leftrightarrows$ M_iL_j
    (L_j; hydroxide, carbonate, sulfate, salts of organic acids,...)
  - M_iL_j may be more soluble or sorbed more than the free metal

f) precipitation
  - due to the extremely low solubility products of metals with carbonates, hydroxides,...

9. Synopsis of the Partitioning Behavior of Important Hazardous Metals (p. 287)

a) Arsenic
  - found as anionic species
  - As^{5+} ; found in oxic env., mobile
  - As^{3+} ; found in reducing conditions
  - microbially transformed (methylation reaction like Hg), but organoarsenic compounds are less toxic than inorganic arsenics

b) Cadmium
  - relatively mobile in the env.
  - Cd^{2+} predominates in soil

c) Chromium
  - found as anionic species
  - Cr^{3+}; less mobile and toxic
  - Cr^{6+}; more mobile and toxic (dichromate, $Cr_2O_7^{2-}$)

d) Lead
  - relatively immobile and toxic

e) Mercury

- three major species; Hg^0, Hg^{1+}, Hg^{2+}
- microbial methylation; CH_3Hg^+ - bioaccumulated
  $(CH_3)_2Hg$ - volatile, global circulation

f) Nickel

10. Estimation of Partitioning and Potential Mobility of Metals (p. 289)

- "Partitioning or attenuation of metals is highly variable depending on the environmental conditions"
- "An empirical equation estimating relative metal mobility based on soil properties is available"
- major soil properties; organic carbon content, iron oxide content, clay content
- Example 5.7