Adsorption isotherms

- Assume equilibrium
  - Which, as we know, does not always occur in soils
- Usually two stages
  - Initial: rapid and reversible
    - Easily accessible sites
  - Secondary: slow and irreversible
    - Diffusion into micropores, interlayers
    - Formation of inner-sphere complexes

Kinetics

- A study of the rate of change will inform one about the reversibility of the sorption
  - e.g. Figure 7.27
- The K_d for the reaction should stay constant over time
- Slow change suggests slow, irreversible reactions

Hysteresis

- If the sorption is truly reversible, the same results should be obtained when either adding or removing the substance from the solution.
  - e.g. Fig 7.28
- Desorption is often more sluggish than sorption—this is termed hysteresis.
- May be caused by slow desorption kinetics or by irreversible reactions (or experimental artifact).

Adsorption Models

- Surface Complexation
  - similar to Gouy-Chapman
    - deal with diffuse double layer
  - model effect of bound ions on surface charge
  - Have been used to describe:
    - proton dissociation
    - ion adsorption on oxides, clays, and soils
    - organic ligand adsorption on oxides
    - competitive adsorption reactions on oxides

Adsorption Models

- Surface Complexation
  - Information obtained:
    - material balance
    - information for describing electrokinetic phenomena
  - Several models
    - Inner sphere
    - Outer sphere

Adsorption Models

- Surface Complexation

Constant Capacitance	Inner Sphere only
Generalized two-layer	Inner Sphere only
Triple-layer	Inner Sphere: H^+, OH^- Outer Sphere: metal ions, ligands, cations, anions
Modified Triple-layer	Allows metals and ions to be adsorbed as inner sphere
Stern (four-layer)	Inner Sphere: H^+, OH^-, oxyanions, metals Outer Sphere: cations, anions
One-pK Stern	Inner Sphere: H^+, OH^- Outer Sphere: metal ions, ligands, cations, anions

Adsorption Models

- Surface Complexation
  - Problems
    - Do not consider surface precipitation
    - More than one model can fit experimental data well
    - Results provide limited information about adsorption mechanisms

Trace Metals

- Important for plant nutrition, toxicity, ecotoxicity
  - Low natural abundance, limited solubility
  - High degree of complexation, chelation, ion pair formation
  - Sensitive to redox transformations

Sorption of Metal Cations

- Electronegativity

  Cu >Ni > Co > Pb > Cd > Zn > Mg > Sr

- Charge-to-radius ratio

  Ni > Mg > Cu > Co > Zn > Cd > Sr > Pb

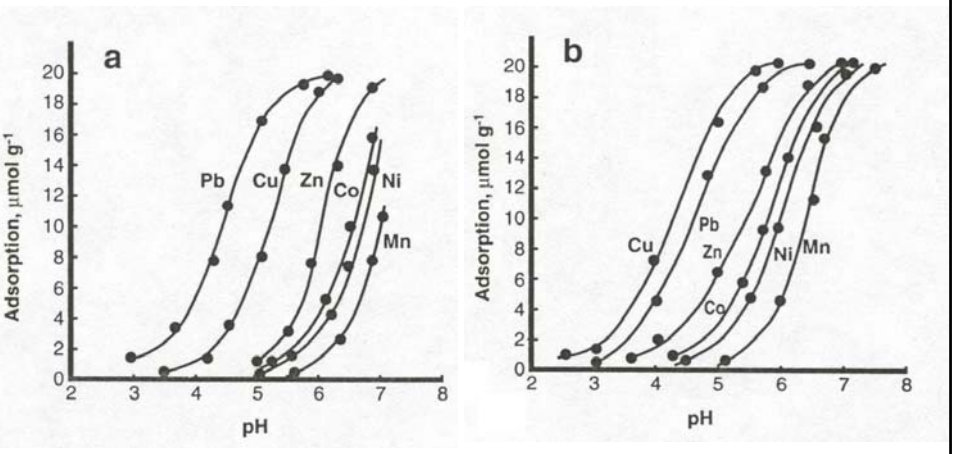
- Ease of hydrolysis

  Pb > Cu

Sorption of Metal Cations

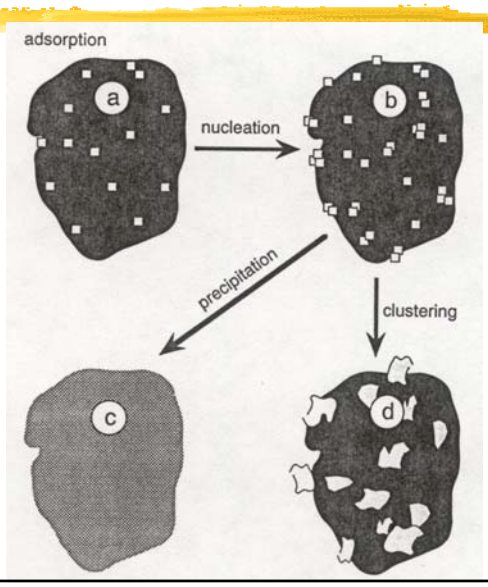
- Mn oxides
  - High selectivity for Cu^{2+}, Ni^{2+}, Co^{2+} and Pb^{2+}
  - Implies important contribution of covalent bonding to adsorption
- Fe oxides
  - Pb^{2+}, Cu^{2+} adsorbed more strongly than other divalent cations

Sorption of Metal Cations



Hematite Goethite

Surface Precipitation



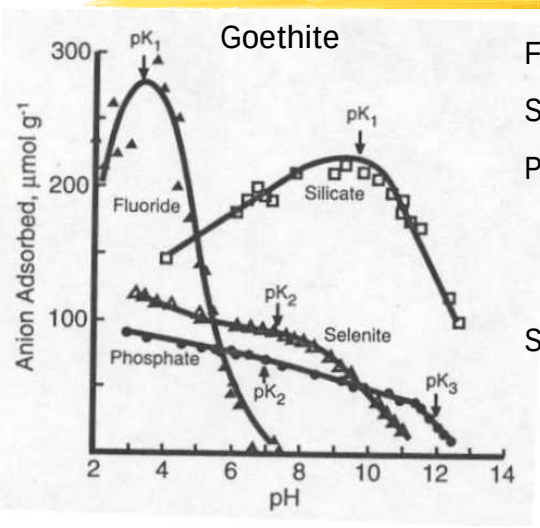
Ion Sorption to OM

- Little or no anion sorption
- High degree of selectivity for some metals
- Both inner sphere and outer sphere complexes

Anion Sorption

- Most anions adsorb very little in humus
- Anion bonding at mineral surfaces
  - Tends to be specific adsorption
    - high anion specificity
    - independent of surface charge
    - tendency toward irreversibility
  - Weak acids - sorption at moderate to high pH
  - Strong acids - sorption at low pH
  - Max. adsorption at pH = pKa
  - High soil pH, competition with OH^-, CO_3^{2-}

Anion Sorption



Fluoride	$pK_1 = 3.25$
Silicate	$pK_1 = 9.7$
Phosphate	$pK_1 = 2.2$
	$pK_2 = 7.1$
	$pK_3 = 12.3$
Selenite	$pK_1 = 2.6$
	$pK_2 = 7.3$

Anion Sorption

			pK_1	pK_2	pK_3
Inner Sphere	Borate	H_2BO_4			
	Silicate	H_4SiO_4			
	Phosphate	H_3PO_4	2.2	7.1	12
	Arsenate	H_3AsO_4	2.3	7.0	13
	Selenite	H_2SeO_3	2.6	8.3	
	Carbonate	H_2CO_3	3.6	10.3	
	Molybdate	H_2MoO_4			
	Chromate	H_2CrO_4			
	Sulfate	H_2SO_4	< 0	1.9	
Outer Sphere	Selenate	H_2SeO_4	< 0	2.0	
	Nitrate	HNO_3			

Sorption of Organics

- Classification of Organics
  - Functional groups
  - Acidity or basicity of functional groups
  - Size and shape of molecule
  - Polarity and charge of molecule
  - Polarizability of molecule

Classification of Organics