

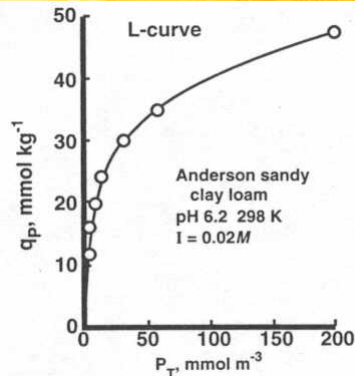
## Sorption Isotherms

- Formerly the most common method for studying sorption processes.
  - Equilibrate soil in solution of known composition.
  - See how element of interest partitions between solution and solid phase at different concentrations.
  - Plot final solution conc. (not what was added) vs. amount sorbed by soil.
- Indirect—does not elucidate mechanisms

$$C_{eq} = q / K_d \text{ or } K_d = q / C_{eq}$$

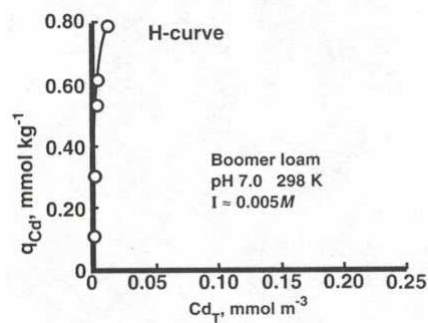
- $K_d$  = distribution coefficient with units of volume per mass.
- $q$  = equilibrium mass of adsorbed substance per unit mass of absorbent (kg of soil).
- $C_{eq}$  = equilibrium mass of substance in solution per unit volume of solution (L).

## Adsorption Isotherms



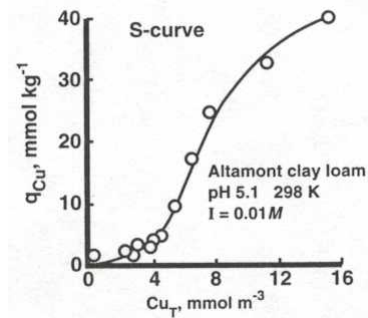
The surface has a high affinity for the adsorptive at low concentrations. Affinity decreases with increasing concentration.

## Adsorption Isotherms



The surface has a very high affinity for the adsorptive at low concentrations (formation of inner sphere complex). Affinity decreases with increasing concentration.

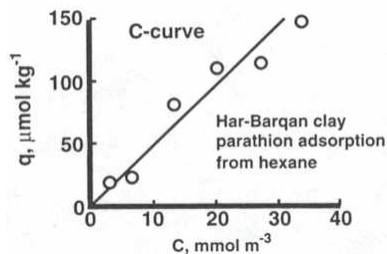
## Adsorption Isotherms



■ "cooperative adsorption"

- Adsorbate-adsorbate interaction stronger than adsorbate-adsorbent
- Favors clustering of adsorbate molecules at surface

## Adsorption Isotherms



- Constant relative affinity
- Partitioning mechanism
- Non-specific bonding
- e.g. Non-polar organics

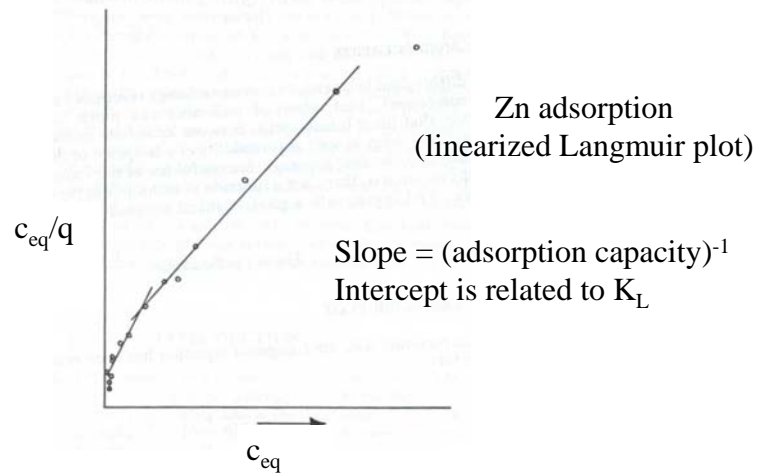
## Sorption Models

- Langmuir
  - Theoretically based but assumptions rarely met in soil systems
- Freundlich
  - Empirical and often successful, but not transferable
- Linear Partitioning
  - Applied to C-type curves, hydrophobic organics

$$\text{Langmuir } q = b K_L c_{\text{eq}} / (1 + K_L c_{\text{eq}})$$

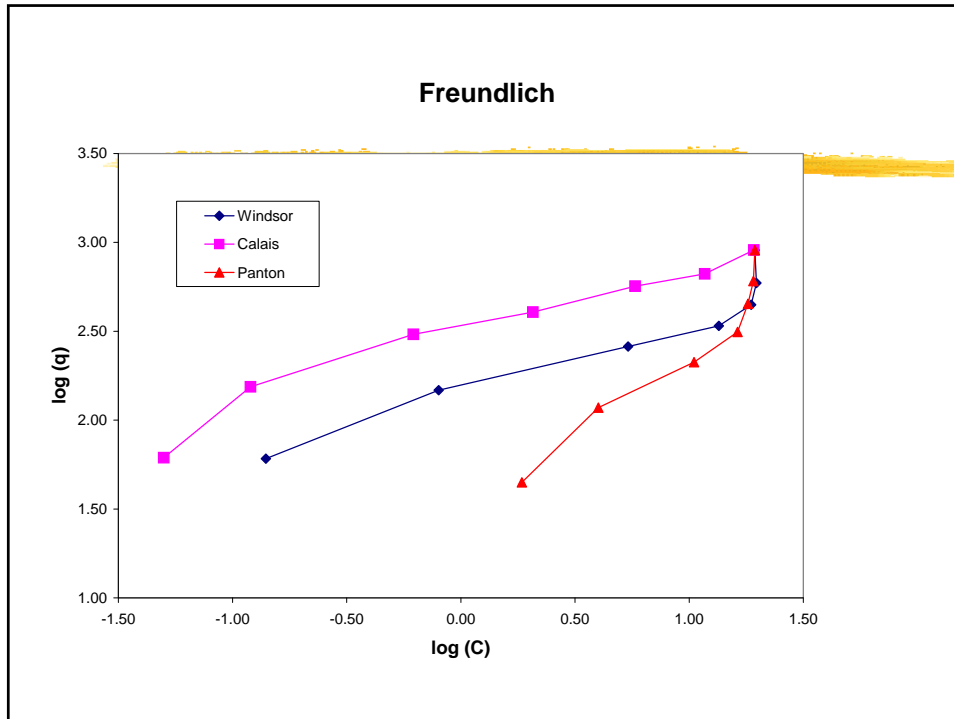
- Linear form:  $c_{\text{eq}}/q = 1 / b K_L + c_{\text{eq}}/ b$  (eq. 7.48)
- $K_L$  = constant related to the binding strength
- $b$  = adsorption maximum
- developed to describe gas adsorption on planar surfaces
- assumptions include:
  - planar surfaces with identical fixed sites
  - reversible
  - adsorption energy is similar for all sites and independent of surface coverage

## Adsorption Isotherms



## Freundlich (empirical)

- $q = K_F c_{eq}^N$
- $q$  = adsorbate per unit mass of adsorbent
  - mol kg<sup>-1</sup>
- $c_{eq}/q$  = "equilibrium" conc. of the adsorbate
  - mol L<sup>-1</sup>
- $K_F$  = distribution coefficient
- $N$  = correction factor, between 0 and 1
  - If close to 1, sites are homogeneous
  - If close to 0, sites are heterogeneous



## Linear Partition Theory

- C-type isotherm
- Sorption highly correlated to soil organic C
- Sorption is not influenced by temperature
- Sorption is not influenced by the presence of a second compound
- Organics with lower water solubility are more strongly sorbed
- Other soil properties (clay, pH, oxides) have little effect on the sorption of nonpolar cmpds

## Linear Partition Theory

$$K_d = \frac{\text{amount sorbed}}{\text{amount in solution}}$$

$$K_{OC} = \frac{K_d}{\% \text{ org. C in soil}}$$

- Constant for a particular compound.
- Applicable to different soils.
- Related to the solubility of the compound in water.  
(octanol-water partition coefficient)

## Relationship of $K_{ow}$ to $K_{oc}$

- $K_p = K_{oc} f_{oc}$  (eq. 7.61)
- $K_{ow} = C_{octanol} / C_{ag}$  (eq. 7.57)
- This relationship holds true for nonpolar, organic compounds:  
■  $\log K_{oc} = -0.223 + 1.004 \times \log K_{ow}$  (7.64)
- This relationship holds true for nonionic, polar pesticides:  
■  $\log K_{oc} = 1.188 + 0.532 \times \log K_{ow}$  (7.68)