Describing Soil Adsorption Processes
Equilibrium Based Adsorption Models
Adsorption Isotherms

\[ x = K_d C \]

- \( x \) = amount adsorbed per unit mass (mmol/kg soil)
- \( C \) = the equilibrium concentration
- \( K_d \) = the Distribution Coefficient

- \( K_d > 1 \): preference for soil over solution
- \( K_d = 1 \): no preference for soil or solution
- \( K_d < 1 \): preference for solution over soil

\[ K_d = \frac{\text{Chemical adsorbed to Soil}}{\text{Chemical in Soil Solution}} \]

Slope = \( K_d \)
**Surface Thermodynamics and Surface Loading**

Adsorbate molecules go on easy Favorable thermodynamics, $\Delta G < 0$

Harder to put adsorbate molecules on soil surface $\Delta G < 0$ but $\Delta G_{\text{time 1}} < \Delta G_{\text{time 2}}$

Harder to put adsorbate molecules on soil surface $\Delta G < 0$ but $\Delta G_{\text{time 2}} < \Delta G_{\text{time 3}}$

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**Surface Loading and $K_d$**

*Increasing Surface Loading*

- $x_{\text{max}}$
- $x$ in mmol/kg
- $K_d$ is a function of Surface Loading
  - $K_d$ decreases with Surface Loading

$C$ (in Molar)
Types of Adsorption Isotherms

C-Type – simple partitioning
“physical” not “chemical”
Adsorption of non-polar organic chemicals by SOM (soil)

L-Type – most common
Decrease in $K_d$ with surface loading

H-Type – high affinity for soil
Strong specific adsorption

S-Type – competing reactions
At soil surface and in solution

Cu ads
mmol/kg

Equilibrium (Cu)

Competition reactions

Dissolved SOM

Dissolved SOM saturated with Cu
Cu only can bind to soil
Looks like a L-isotherm

low loading
dissolved SOM-Cu
has preference
Adsorption Models

**Empirical adsorption models** –
description of chemical adsorption data without a “theoretical” basis
– without a detailed description of chemical adsorption processes

- Langmuir Adsorption Isotherm Model
- Freundlich Adsorption Isotherm Model
- Temkin Adsorption Isotherm Equation

**Chemical adsorption models**
description of chemical adsorption data with a theoretical basis
-- with a detailed description of chemical adsorption processes

- Constant Capacitance Model
- Triple Layer Model
- Stern variable surface charge-surface potential (VSC-VSP) model
- Cation Exchange equations

Adsorption Models

Allow you to predict partitioning of chemical between soil and solution

Provide information on the strength of adsorption between soil and chemical

Provide information on the maximum amount of chemical that the soil can adsorb
adsorption capacity or adsorption maxima.
Langmuir Adsorption Isotherm Model

Developed by Langmuir to describe adsorption of gas on metal surface
Assume adsorption sites are all same
Fixed number of adsorption sites
Monolayer coverage of surface
Adsorption is reversible

\[ x = \frac{bKC}{1 + KC} \]

- \( x \) = amount adsorbed/mass soil
- \( b \) = adsorption maxima
- \( K \) = bonding energy coefficient
- \( C \) = equil. conc. in solution

Linear transformation of Langmuir Equation
Reciprocal Langmuir plot

\[ \frac{C}{x} = \frac{1}{bK} + \frac{C}{b} \]

- \( \frac{1}{bK} \) = 0.50 cm
- \( C \) = equil. conc. in solution
- \( x \) = amount adsorbed/mass soil

slope = \( \frac{1}{b} \)

- \( b \) = adsorption maxima
- \( K \) = bonding energy coefficient
- large \( K \) means strong bonding
Generating a Langmuir Adsorption Isotherm
Phosphate adsorption to soil

Shake soil (know weight, 1 g) with solution containing known phosphate
Measure phosphate in solution at equilibrium

\[
\text{[Initial solution – final solution phosphate]} / \text{kg soil} = \text{adsorbed P/soil} = x
\]

\[
\text{mmol / L} \times \text{# L} \quad \text{mmol / kg}
\]

\[
C = [P]_{eq} \text{ in mmol/L}
\]

\[
x = [P]_{ads} \text{ in mmol/kg}
\]

Calculate \(C/x\) in kg/L

<table>
<thead>
<tr>
<th>C (mmol/L)</th>
<th>2.0</th>
<th>11.0</th>
<th>20.0</th>
<th>40.0</th>
<th>80.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>x (mmol/kg)</td>
<td>3.1</td>
<td>5.2</td>
<td>6.7</td>
<td>8.5</td>
<td>10.8</td>
</tr>
<tr>
<td>C/x (kg/L)</td>
<td>0.65</td>
<td>2.1</td>
<td>3.0</td>
<td>4.7</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Linear transformation of P Langmuir Equation

\[
y = 0.863 + 0.842 \\
\frac{C}{x} = \frac{1}{K_b} + \frac{C}{b}
\]

\[
\text{slope} = \frac{1}{b}
\]

\[
K = (y_{intercept} \times b)^{-1} = (0.863 \times 11.9)^{-1} = 0.0974 \text{ kg soil/mmol P}
\]

\[
b = (0.842)^{-1} = 11.9 \text{ mmol P/kg soil}
\]
What is the P adsorption max of this soil mean?

\[ b = \text{P ads max} = 11.9 \text{ mmol/kg} = 3.7 \times 10^{-4} \text{ kg P/kg soil} \]

\[ (2.24 \times 10^6 \text{ kg/ha soil}) \times (3.7 \times 10^{-4} \text{ kg P/kg soil}) = 829 \text{ kg P/ha} \]

kg/ha (0.893) = lbs/acre

so \ P ads max = 740 lbs/acre

Freundlich Adsorption Isotherm Model

Freundlich vs Langmuir
Freundlich assumes heterogeneous adsorption surfaces (not all same)
Freundlich does not have an adsorption maxima

\[ x = KC^{1/n} \]

K and n are empirical constants
Log transformation of Freundlich Equation

\[ \log x = \log K + \frac{1}{n} \log C \]

- **Slope** = \( \frac{1}{n} \)
- **K** = related to bonding strength

**Advantage:** experimental data usually fits log-log plot
**Disadvantage:** cannot predict adsorption maxima

Hydrophobic partitioning and the Freundlich equation

\[ x = KC^{1/n} \]

- **n** = 1.0 for very dilute solutions of C (ppm or less levels)
- **x** = **KC**

\[ x = KC^{1} = KC \]

- **Slope** = **K**
- **K** = **K_{oc}f_{oc}**

where \( f_{oc} \) = fraction OC in soil

\[ = (%OC/100\%) \]

- a single **K_{oc}** value for each organic chemical
- **K_{oc}** is independent of soil organic matter content
Adsorption of atrazine by soil

|          | atrazine adsorbed \(x\) in mg/kg soil | atrazine conc in solution, mg/L | \(K_d\) (mg/kg soil/mg/L) | SOM (%) | SOC (%) | K\(_{oc}\) (%)
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil 1</td>
<td>0.25</td>
<td>0.25</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>100</td>
</tr>
<tr>
<td>Soil 2</td>
<td>0.39</td>
<td>0.13</td>
<td>3.0</td>
<td>6.0</td>
<td>3.0</td>
<td>100</td>
</tr>
</tbody>
</table>

\(K_{oc}\) is independent of soil organic matter content
\(K_{oc}\) is an inherent property of the organic chemical

Large \(K_{oc}\) (>1000) – strong preference for SOM – little dissolved in water
Small \(K_{oc}\) (< 100) -- little preference for SOM – lots dissolved in water

Only need \(K_{oc}\) and Soil OC content \((f_{oc})\) to calculate dissolved chemical
commonly used in computer transport/fate models for organics/pesticides

Shortcomings of Soil Langmuir Adsorption Model

May be more than one type of adsorption site in soil

\[
x = \frac{b_1K_1C}{1 + K_1C} + \frac{b_2K_2C}{1 + K_2C}
\]
Reciprocal plot for linearized 2 surface
Langmuir Adsorption Isotherm

Binuclear P adsorption
\( b = (\text{slope})^{-1} \)
BEC = \( 1/K_b \)

Mononuclear P adsorption
\( b = (\text{slope})^{-1} \)
BEC = \( 1/K_b \)

Adsorption of Gases
Determination of Surface Area
using BET Equation

Brunauer, Emmett, and Teller -- BET Equation

Multilayer adsorption of gases

\[
\frac{P}{P_0} \cdot \frac{X}{X_m C} \cdot \left(1 - \frac{P}{P_0}\right) = \frac{1}{X_m C} + \frac{C - 1}{X_m C} \frac{P}{P_0}
\]

\( Y = y_{\text{intercept}} + \text{slope} \cdot x \)

\( \frac{P}{P_0} = \) partial pressure of gas
\( X = \) moles gas adsorbed
\( X_m = \) moles gas adsorbed
for monolayer
"Surface Area"
BET plot for adsorption of nitrogen gas on MnO$_2$ surface
0.314 g MnO$_2$
slope = 14760
$y_{\text{intercept}} = 272$
What is the surface area of the mineral?

\[
y_{\text{int}} = \frac{1}{X_mC} \quad \frac{1}{X_m} = y_{\text{int}} C
\]

\[
slope = \frac{C - 1}{X_mC} = \frac{14760}{272} = 54.26 = C - 1
\]

\[
C = 55.26
\]

\[
\frac{1}{X_m} = y_{\text{int}} C = (272)(55.26) = 15030
\]
\[ \frac{1}{X_m} = 15030 \quad X_m = 6.65 \times 10^{-5} \text{ moles N}_2 \]

MnO\textsubscript{2} surface area =
(6.65 x 10^{-5} moles N\textsubscript{2})(9.757 x 10^4 m\textsuperscript{2}/mole N\textsubscript{2}) = 6.73 m\textsuperscript{2}

MnO\textsubscript{2} specific surface area = \frac{6.73 \text{ m}^2}{3.14 \times 10^{-4} \text{ kg MnO}_2} = \frac{2.1 \times 10^4 \text{ m}^2}{\text{kg MnO}_2}

Total Surface Area = External Surface + Internal Surface

Only polar gas can measure internal sites

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Measuring Surface Area of Soil Minerals

Only External Sites – use N\textsubscript{2} gas (non-polar)

Internal + External Sites – use EGME (polar)

EGME – ethylene glycol monoethyl ether
polar organic liquid – evaporates easily and adsorbs

Internal area = Total (EGME) – External (N\textsubscript{2})
Chemical Adsorption Models
Chapter 5 - Sparks

Soil surface - collection of adsorption sites

Different adsorption mechanisms
Different models

Adsorption of cations by CEC
Ion-exchange models

Specific adsorption of anions / cations
Constant capacitance model, others

Must know the dominant adsorption mechanism of chemical species to select a chemical adsorption model

Chemical Adsorption Models
Ion Exchange Models
Diffuse Electric Double Layer (DDL) Model

Soil or Clay Particle

Diffuse Layer
+ > -

Bulk solution + = -
from Essington 2004

**DDL Model**

Electrical Potential $\psi$

$\psi_o$

Bulk solution

Diffuse Layer

Electrical potential – Potential of in an electrical field

$tanh \frac{Ze\psi}{4kT} = tanh \frac{Ze\psi_o}{4kT}e^{\kappa x}$
DDL Model Derivations

Soil or Clay Particle

\[ n_+ = \text{number of cations} \]
\[ n_- = \text{number of anions} \]

\[ n_i = n_{io} \left[ \frac{1 - \tanh(-Z e \psi_o / 4 k T) e^{-kx}}{1 + \tanh(-Z e \psi_o / 4 k T) e^{-kx}} \right] \]

Important consequences of DDL Model

DDL decreases with DDL cation charge

DDL decreases with soil solution ionic strength (I)
CEC Composition & Soil Structure

2 State of Clay Colloids

STABLE
- Dispersed in Solution
- Doesn’t Settle Out
- Few Aggregates – Poor Soil Structure

UNSTABLE
- Acts as one big structural unit
- Flocculated
- Settles Out of Solution
- Aggregates – Good Soil Structure

CEC Composition & Soil Structure

CEC Composition Determines Colloidal Stability

Van der Waals

Repulsive Force - DDL Cations (push clay apart)

Attractive Force - Van Der Waals (pull clay together)

- Only when Clay are Very Close

Repulsive > Attractive \(\rightarrow\) Dispersion
Attractive > Repulsive \(\rightarrow\) Flocculation
Hydrated Ion Size directs affects size of DDL

$Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Al^{3+}$

Repulsion

- $Na^+$
- $Clay 1$
- $Na^+$
- $Clay 2$
- Van Der Waals

Repulsion $>$ Attraction $=$ Dispersion

Too much Na on CEC --- Dispersed Soil – No Structure

Poor Drainage, Poor Aeration, High Erosion

Smaller ion hydrated radius, smaller DDL than $Na^+$

Less Repulsion, clays have closer approach

Attraction $>$ Repulsion

DDL thickness $Al^{3+} < Ca^{2+}, Mg^{2+} < K^+ < Na^+$

Attraction $>$ Repulsion $=$ Flocculated Soil

Good Structure, Good Drainage, Aeration, Low Erosion
Net surface charge of soil

\[ \sigma_p = \sigma_0 + \sigma_H + \sigma_{IS} + \sigma_{OS} \]

Particle charge  Permanent charge  Variable charge  Inner sphere charge  Outer sphere charge

Chemisorption of transition metal cations to hydrous oxide sorption sites

Chemisorbed Lead

Most metal cations except alkali and alkaline earth metals

Step 1 Metal Hydrolysis

\[ \text{Pb}^{2+} + \text{H}_2\text{O} \rightarrow \text{PbOH}^+ + \text{H}^+ \]

Pb hydroxocomplex

Step 2 Inner sphere adsorption of metal hydroxocomplex

\[ \text{PbOH}^+ + X = XPbOH^+ \]
Pb$^{2+}$ + $\text{H}_2\text{O}$ = PbOH$^+$ + H$^+$

Lead is a “weak acid”

$$K = \frac{(\text{PbOH}^+)(\text{H}^+)}{(\text{Pb}^{2+})}$$

$$\text{pH} - \text{pK} = \log \frac{(\text{PbOH}^+)}{(\text{Pb}^{2+})}$$

As pH increases
PbOH$^+$ increases
Specific adsorption of Pb increases

Strong soil pH dependence of heavy metal cation adsorption by oxides

**Adsorption Edge** = pH at which adsorption increases from very low to very high

**Adsorption Edge Occurs at pH = pK$_{\text{metal}}$ – 1 (or 2)**
Specific Adsorption of Oxyanions to hydrous oxide sorption sites

Chemisorbed Phosphate

PO₄³⁻: Phosphate
AsO₄³⁻: Arsenate
SO₄²⁻: Sulfate
MoO₄²⁻: Molybdate
COO⁻: Organic acid anions

Soil pH dependence of oxyanion adsorption by oxides

Acids that loose one proton
HF, silicic acid have a maxima at their pK₁ value

Polyprotic acids have an inflection point at their pK values

This behavior is termed the anion’s Adsorption Envelope

Adsorption by Goethite
Chemical Specific Adsorption Models
Constant Capacitance Model

- Finite number of specific adsorption sites on oxide
- Only inner sphere complexes

\[
\sigma = \sigma_H + \sigma_{IS}
\]

- SOH + H\(^+\) = SOH\(_2^+\)
- SOH = SO\(^-\) + H\(^+\)
- SOH + M\(^{n+}\) = SOM\(^{(n-1)}\) + H\(^+\)
- 2SOH + M\(^{2+}\) = (SO)\(_2\)M\(^{(n-2)}\) + 2H\(^+\)
- SOH + L\(^{q-}\) = SOL\(^{(q-1)}\) + OH\(^-\)
- 2SOH + L\(^{q-}\) = S\(_2\) L\(^{(q-2)}\) + 2OH\(^-\)

Charge of all surface species = \(\sigma\)
Constant Capacitance Model accounts for changes in surface charge for variable charge oxide surfaces

\[ \text{Total Charge} \]

\[ \text{Soil pH} \]

- \[ \text{SOH}_2^+ = \text{SO}^- = \text{SO} \]
- \[ \text{SOH} \]
- \[ \text{SOH} + \text{H}^+ = \text{SOH}_2^+ \]
- \[ \text{SOH} = \text{SO}^- + \text{H}^+ \]
- \[ \text{SOH} + \text{M}^{n+} = \text{SOM}^{(n-1)} + \text{H}^+ \]
- \[ 2\text{SOH} + \text{M}^{2+} = (\text{SO})_2\text{M}^{(n-2)} + 2\text{H}^+ \]
- \[ \text{SOH} + \text{L}^{q-} = \text{SOL}^{(q-1)-} + \text{OH}^- \]
- \[ 2\text{SOH} + \text{L}^{q-} = \text{S}_2\text{L}^{(q-2)} + 2\text{OH}^- \]

Each reaction has an equilibrium expression

\[
K_+ = \frac{[\text{SOH}_2^+]}{[\text{SOH}][\text{H}^+]} \exp \left( \frac{F\Psi_i}{RT} \right)
\]

K values for each reaction calculated (computer model)
Used to predict adsorption species to oxide surface
Application of the Constant Capacitance Model

Quantity-Intensity (Q-I) Curves

Soil CEC

- Potentially available K
- Available K

Predict the effect of solution chemistry on adsorption or desorption of K

[Graph showing metal adsorption as a function of pH]
(Ca,Mg)$_{\frac{1}{2}}$X + K$^+$ = KX + $\frac{1}{2}$ (Ca,Mg)$^{2+}$

\[
\frac{K_{\text{ads}}}{(Ca + Mg)_{\frac{1}{2}}X} = K_{\text{ex}} \sqrt{\frac{(K)}{(Ca + Mg)}}
\]

Quantity | Intensity
---|---
$K$ | $K_{\text{ex}} AR^K$

$K_{\text{ex}}$ = exchangeable K in soil (Quantity term)

$K_x$ = specific adsorbed (inner sphere) K – fixed K

$\Delta K = \text{exchangeable K adsorbed (+) or desorbed (-)}$

$PBC^K = \text{potential buffer capacity for K}^+$

$\Delta K^o = \text{Exchangeable K in soil (Quantity term)}$

Slope = $\frac{\Delta(\Delta K)}{\Delta AR^K} = PBC^K$

$AR^K_{\text{eq}}$ = Intensity

$K = K_{\text{ex}} AR^K$
Chemical Adsorption Models
Triple Layer Model

from Essington 2004
from Essington 2004
### Other Chemical Adsorption Models

Sparks – Chapter 5, p.165

\[ \sigma_p = \sigma_0 + \sigma_H + \sigma_{IS} + \sigma_{OS} \]

- **Particle charge**
- **Permanent charge**
- **Variable charge**
- **Inner sphere charge**
- **Outer sphere charge**

**Modified Triple Layer Model**
\[ \sigma_0 + \sigma_H + \sigma_{IS} \]

**Stern VSC-VSP**
(4-layer model)
\[ \sigma_0 + \sigma_H + \sigma_{IS} \]

More complex models will have better fits but
–but they are more complex to work with
Better fit due to “statistics” – more parameters – better statistical fit

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### Adsorption vs. Surface Precipitation

A and B – low surface coverage of metal
**True adsorption**

C, D – high surface coverage of metal
**Surface precipitation**
Is it adsorption or precipitation?

Data fitting an adsorption model is **not proof** the process is adsorption.

Surface precipitation will fit a Langmuir or Freundlich Model but spectroscopic study of surface can provide evidence.

**Surface Loading with Adsorbate**

- Adsorption Monolayer
- Surface Precipitation
- Mineral Precipitation

- Adsorption Isotherm controls ion activity
- "unsaturated" conditions below adsorption maxima
- Mineral $K_{sp}$ controls ion activity