Influence of adsorption on the transport of inorganic contaminants: conceptual and quantitative models

USGS Toxic Substances Hydrology Program
National Point Source Research Meeting
January 26-29, 2009
San Diego, CA
Outline

• Background
• Adsorption and chemical speciation
• Quantitative modeling of the influence of variable chemistry
• Critical issues and future research
Why mineral surfaces drive adsorption

Coordination of ions interrupted at surface

The hydrated oxide surface

Adsorption of water

Chemisorption of water molecules

Dissociation of water to form surface hydroxyl groups
Solutes bind to surface sites
Cape Cod aquifer sediments

>90% quartz
Coston et al. (1995)

~5% feldspars
Wood et al. (1990)
Zinc adsorption on quartz and sediments

- Adsorption of metal ions like zinc vary with pH.
Cape Cod aquifer sediments

>90% quartz
Coston et al. (1995)

~5% feldspars
Wood et al. (1990)
Coating on quartz grain

Goethite, 5-10 nm

Major components: Al, Si, Fe

Banfield and Hamers (1997)
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Effect of speciation on transport

- Strongly sorbed solutes
- Weakly sorbed solutes

\[ \text{M}_1^{z+} \quad \text{Complexation} \quad \text{M}_1 L_1, M_1 L_2, \ldots, M_1 L_x \]

\[ \text{M}_2^{z+} \quad \text{Redox} \quad \text{M}_2^{z-1+} \]
Direction of Ground water Flow

S469
S521
S473
Copper and zinc prior to source cessation
Fate of zinc post cessation

Graph showing the change in zinc concentration (Zn) in μM over years after source cessation. The pH is also depicted over the same time period. The graph includes data points for ZnT and pH with a notable peak around year 8.
Fate of copper post cessation

![Graph showing the fate of copper over time, with DOC (μmoles C/L) on the y-axis and Years after source cessation on the x-axis. The graph illustrates a decrease in copper concentration over time.]
Complexed copper

![Graph showing the relationship between years after source cessation and concentrations of Cu, DOC, and complexed Cu. The graph includes lines for CuT, DOC, and complexed Cu, with labels for each line in the legend.](image-url)
Copper and zinc prior to source cessation

Graph A: Zn (μM) vs. Altitude, meters to sea level.
Graph B: Cu (μM) vs. Altitude, meters to sea level.

- Complexed Cu
- pH

Data from 11/95.
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Zinc adsorption on quartz and sediments

- Cape Cod sediment
- Quartz powder

176 m²/L; 10 μM Znₜ

% Zn Adsorbed vs pH

- One site-one proton
- One site-two proton
Modeling Zn adsorption

Surface-complexation modeling approach

One-site SCM

\[ \text{Zn}^{2+} + \text{>SOH} = \text{>SOZn}^+ + \text{H}^+ \]  Parameters: 
\[ \text{>SOHT, log}K \]

Two-site SCM

\[ \text{Zn}^{2+} + \text{>S}_s\text{OH} = \text{>S}_s\text{OZn}^+ + \text{H}^+ \]
\[ \text{Zn}^{2+} + \text{>S}_w\text{OH} = \text{>S}_w\text{OZn}^+ + \text{H}^+ \]  Parameters: 
\[ \text{>S}_s\text{OHT, >S}_w\text{OHT} \]
\[ \text{log}K_s, \text{log}K_w \]
Zinc adsorption on Cape Cod sediments

![Graph showing zinc adsorption data with pH values and model predictions.](image-url)
Dissolved Zn: 2-3 μM
Adsorbed Zn: 85-120 μM
Tracer test design

- Natural gradient (0.4 m/d)
- Inject pulse of groundwater with KBr (2 mM) and pH 4.5 (CO$_2$)
- Injected groundwater had no Zn
Model calibration: surface ionization and major cation adsorption or ion exchange reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>logK</th>
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</thead>
<tbody>
<tr>
<td>$&gt;S_s\text{OH} + H \rightarrow S_s\text{OH}_2$</td>
<td>3.99</td>
</tr>
<tr>
<td>$&gt;S_w\text{OH} + H \rightarrow S_w\text{OH}_2$</td>
<td>3.99</td>
</tr>
<tr>
<td>$\text{Na} + \text{XH} = \text{H} + \text{XNa}$</td>
<td>-4.65</td>
</tr>
<tr>
<td>$\text{K} + \text{XH} = \text{XK} + \text{H}$</td>
<td>-3.63</td>
</tr>
<tr>
<td>$\text{Mg} + 2\text{XH} = \text{X}_2\text{Mg} + 2\text{H}$</td>
<td>-6.72</td>
</tr>
<tr>
<td>$\text{Ca} + 2\text{XH} = \text{X}_2\text{Ca} + 2\text{H}$</td>
<td>-6.72</td>
</tr>
</tbody>
</table>

$X_{\text{HTOT}} = 0.5 \text{ meq/100 g} \rightarrow 20 \text{ meq/L}$

$>SO_{\text{HTOT}} = 3.84 \ \mu\text{moles/m}^2 \rightarrow 5 \text{ mM}$

Non-electrostatic model
Breakthrough 4.6 meters downgradient

![Graphs showing observed vs predicted values for various parameters including pH, Zn, K, Alkalinity, Phosphate, and Ca over days after injection.](image-url)
Other applications

• Ligand-enhanced metal-ion mobility: Kent et al. (2008)
• Lead and nickel tracer tests at Cape Cod: Gillian Fairchild’s poster
• Uranium at DOE UMTRA sites: Curtis et al. (2006)
• Cr(VI) reactive barrier: (Uli) Mayer et al. (2001)
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Hanford, Washington

South Pit 1
South Pit 2
North Pit 2
North Pit 1
Dissolved U(VI) speciation

pH = 7.87; calcite equilibrium assumed
U(VI)$_{\text{tot}}$ = 2 x $10^{-6}$ M

Columbia River

300 Area Groundwater
Surface Complexation Model

The graph shows the relationship between Log U(VI) Sorption $K_d$ (L/kg) and Alkalinity (meq/L) for different samples and models.

- **Sample NPP1-16**
- **Sample NPP1-20**
- **Sample SPP2-18**
- **Sample SPP1-18**
- **Sample SPP2-16**

The models are categorized as:
- Model all data
- Model NPP data
- Model SPP data

Chemical reactions shown:

1. $>\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = >\text{SOUO}_2\text{OH} + 2\text{H}^+$
2. $>\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = >\text{SOUO}_2\text{OH} + 2\text{H}^+$

Columbia River

300 Area Groundwater
Particle-scale diffusion

Temporally-variant bulk water concentrations, \((\text{H}^+, \text{U(VI)}, \text{Ca}^{2+}, \text{HCO}_3^-)\)_b

Iron oxide precipitate

Calcite

Local Chemical equilibrium

Surface Charge

Diffusive flux

\(\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0\)

\(\text{Ca}^{2+}\)

\(\text{HCO}_3^-\)

\(\text{HCO}_3^-\)
Adsorption coupled to other reactions

- Abiotic arsenic(III) oxidation
- Microbial arsenic and iron oxidation, reduction, precipitation, dissolution: Poster by Kent and others
- Tractable approach to modeling
Further information