The Role of NOM in the Adsorption of As(V) and As(III) onto Metal Oxides

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Environmental Importance and Relevance

• Sources of Arsenate (As(V)) and Arsenite (As(III)) contamination
  – Anthropogenic: Smelters, mine tailings
  – Natural: Bangladesh Arsenic Crisis, Chili, Japan

• Acid mine drainage treated by wetlands
  – Contaminants often adsorbed to soils prior to wetland construction

• Drinking Water Standards
  • Proposed: 10 ppb total As
  • Current: 50 ppb total As
    • 1 µM As(V) or As(III) = 74.92 ppb As
Redox Chemistry

• \( \text{As(V)} + 2e^- = \text{As(III)}, \ E^o = 0.560 \ \text{V} \)
  – CRC: \( \text{Fe(III)} + e^- = \text{Fe(II)}, \ E^o = 0.771 \ \text{V} \)
  – \( \text{MnO}_2, \ O_2 \) are important oxidizers

• Microbial As(V) reduction is common
  – Mobilize great quantities of As(III)
    • Even in the presence of \( \text{NO}_3^- \), and dissolved \( O_2 \)

• As(III) is more toxic than As(V)
  – Carcinogenic
Relevant Arsenic Chemistry

• pH Chemistry
  - As(V): pK₁ = 2.2, pK₂ = 6.9, pK₃ = 11.5
  - As(III): pK₁ = 9.2

• Adsorption is primary control on mobility
  - S-OH + H₂AsO₄⁻ → S-H₂AsO₄ + OH⁻
  - S-OH + H₃AsO₃ → S-H₃AsO₃⁺ + OH⁻
  - Other specifically adsorbing anions (NOM, PO₄) compete with As(V) and As(III)
NOM Chemistry

• Origin: The decomposition of plant/animal/microbial matter

• Composition: Amino acids, aromatic and aliphatic regions, O, N and S functional groups

• Size: Avg. MW between 500-5,000 daltons

• Metal scavengers: Complexes aqueous metals such as Th, Fe, Cu

• Redox activity: Quinone functional groups act as e⁻ shuttles
Conceptual Model

1) NOM competes with As(V) and As(III) for sorption sites
2) NOM forms complexes with As(V) and As(III)
Research Goals

• Competition:
  – 1) Determine whether NOM can remove adsorbed As(V) and As(III)
  – 2) Determine whether As(V) and As(III) can remove adsorbed NOM
    – Is Hysteresis observed?

• Common traits:
  – 3) Determine common traits of NOM that are responsible for competition with As(V) and As(III)
  – 4) Determine common traits that are responsible for the adsorption of NOM
Approach

• Identify 6 NOM’s and analyze for:
  – 1) Aromaticity by UV absorbance
  – 2) Metals content by ICP
  – 3) Acidity (pKa) from potentiometric titrations (I=0.01 M NaCl)

• Normalize all analyses and experiments to 10 mg/L of organic C

• Perform competition experiments at environmentally relevant conditions onto colloidal hematite
  – Hematite: 0.2-0.3 µm spherical particles, 99.+ % hematite by XRD
  – pH 6.0, I=0.01 M NaCl
Definitions

• **As(V or III) First** - Hematite-bound As(V or III) is desorbed with NOM

• **NOM First: As(V or III)** - As(V or III) is adsorbed onto NOM-coated hematite

• **Acidity** - Quantity of base-titrable functional groups of the NOM, between pH 2-6

• **Aromaticity** - Specific UV absorbance at 254 and 280 nm

• **Metals** - Sum of Fe, Al and Mn associated with the NOM

• **Adsorption** - Surface complexation by ligand exchange

• **Complexation** - Metal bridging of As with NOM
# Meet the NOMs

(this is revised data)

<table>
<thead>
<tr>
<th>SUVA, pAcidity*, Metals (mg/L)*</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rio Negro:</td>
<td>Brazil</td>
</tr>
<tr>
<td>.03726, 3.78, 0.225</td>
<td>Sao Paulo, Brazil</td>
</tr>
<tr>
<td>S. Fork:</td>
<td>Alaska</td>
</tr>
<tr>
<td>.02959, N.A., 0.061</td>
<td>Alaska</td>
</tr>
<tr>
<td>UP Stream:</td>
<td>Michigan</td>
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<tr>
<td>.05298, 4.081, 0.581</td>
<td>Upper Peninsula, Mich</td>
</tr>
<tr>
<td>MW-6:</td>
<td>Leadville, Co</td>
</tr>
<tr>
<td>.08876, 4.241, 21.982</td>
<td>Leadville, Co</td>
</tr>
<tr>
<td>Suwannee:</td>
<td>Georgia</td>
</tr>
<tr>
<td>.04303, 4.22, 0.228</td>
<td>Suwannee River, GA</td>
</tr>
<tr>
<td>Inangahua:</td>
<td>New Zealand</td>
</tr>
<tr>
<td>.03498, 3.849, 0.306</td>
<td>Inangahua River, NZ</td>
</tr>
</tbody>
</table>

– normalized to 10 mg C/L, N.A. = data not available
Experimental Design I (batch):
Does NOM form Aqueous Complexes with 1 µM As(V) or As(III)?

HPLC separation method: Strong anion exchange resin separates complexed As(V or III) from free As(V) from As(III)
Experimental Design II (batch):
NOM First: As(III or V)

Does 1 µM As(V or III) adsorb onto NOM-coated hematite?
Experimental Design III (batch): As(V or III) First

Does NOM displace adsorbed As(V or III)?

- Centrifuge, decant and resuspend
- Separate solids from liquids by centrifugation
- Incubate for 48 hours in the dark, pH 6.0, I=0.01 M NaCl
Kinetics of Adsorption

- Individual kinetics are fast (1µM As(V or III), 10 mg C/L UP Stream NOM)
  - Equilibrium reached within 6 hours
Kinetics of As(V or III) Adsorption

- As(V) and As(III) onto NOM-Coated Hematite
  - As must displace NOM or find unoccupied site
  - 40+ hours to remove As(V) below DWS (10 ppb)
- **Isotherm**: Most of surface sites are occupied by NOM at 10 mg C/L
Kinetics of As(V or III) Displacement

- Removal of adsorbed As(V) and As(III) by Up Stream NOM
  - Fast, complete within 10 hours
  - NOM fraction of higher affinity for iron oxides than As(V)?
Aqueous Complexation of As(V)

- Reduction of As(V) by Inangahua River NOM!!
  - Reduced Sulfur groups (cysteine)
- Aqueous complexation by MW-6 and others
- 90 hours of incubation in dark, equilibrium is assumed

Duplicate samples, error bars represent the range of data
Aqueous Complexation of As(III)

- NOM appears to accelerate the oxidation of As(III)
  - Mn, Fe can influence oxidation

- Trace amounts of As(V) in ‘No NOM’ condition
- 90 hours of incubation in dark, equilibrium is assumed
Results of NOM First: As(V)

- Significant amounts of free in system As(V)
- Surface-catalyzed reduction??
- 100 hours of incubation in dark

Triplicate samples, error bars represent the range of data
Results of NOM First: As(III)

- Oxidation of As(III) is significant
- More free total As in solution in As(III) system
- 100 hours of incubation in the dark

### Adsorption As(III) onto NOM-Coated Hematite

<table>
<thead>
<tr>
<th>Location</th>
<th>Measured As(III)</th>
<th>Measured As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rio Negro</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S. Fork</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UP Stream</td>
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<tr>
<td>MW-6</td>
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<td>Suwannee River</td>
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<tr>
<td>Inangahua</td>
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<td></td>
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<tr>
<td>No NOM</td>
<td></td>
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</tbody>
</table>

Triplicate samples, error bars represent the range of data.
As(V) First

Displacement of Hematite-Bound As(V) by NOM

- Surface-catalyzed reduction??
- Lots of reduction by Inangahua river NOM
  - Rate limited re-oxidation of As(III) (48 hours)

Triplicate samples, error bars represent the range of data
As(III) First

Displacement of Hematite-Bound As(III) by NOM

- Higher free total As are observed in As(III) systems
- 48 hours of incubation in the dark

Triplicate samples, error bars represent the range of data
Removal of Soil-bound NOM by As(V)

- 15% adsorption of 20 mM As(V) by soil
- 133 ppm C removed by As(V)
- 3:1 (moles C: moles As(V)) at pH 4.73
Common Thread? Competition

- Correlations are difficult to make
  - Redox activity and metal-bridging complicate analysis
Common Thread? Adsorption

- Higher percentage of aromatic fraction is removed by adsorption
  - No other clear correlations
Conclusions I

1) NOM can mobilize adsorbed As(V) and As(III)

2) As(V) can mobilize adsorbed NOM

3) Aqueous complexation can be very important

4) NOM appears to accelerate redox transformations of As(V) and As(III)
Conclusions II

5) Common threads are difficult to find to describe the adsorption and competition behavior of NOM

6) Hysteresis is not observed for systems with UP Stream NOM
   – Rate limited redox and adsorption reactions may affect the observations of the other NOMs
Future Work

1) The kinetics of the redox transformations of As(V) and As(III)

2) The mechanisms of the redox transformations

3) Adsorption kinetics of As(V) and As(III) onto NOM-coated hematite

4) Kinetics and mechanism of Aqueous complexation of NOM and As(V) and As(III)
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