Redox Transformations, Complexation and Soil/Sediment Interactions of Inorganic Forms of Arsenic and Selenium in Aquatic Environments: Effects of Natural Organic Matter

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Patsy Buckley, Ph.D. Student, Department of Chemistry and Geochemistry,
Kaylene Ritter, Ph.D. Student, Department of Chemistry and Geochemistry

Most of the work reported here is due to Aaron. More recent work by all three students is reported in the posters to be shown this afternoon.
The ultimate justification for this research is the presence of mining and industrial sites where As and Se cause serious problems. Many of these sites are characterized by active formation of solid metal oxyhydroxides. Adsorption of As and Se to these oxides provides a major removal mechanism for these metals. Natural organic matter (NOM) has a Ubiquitous presence in natural and artificial aquatic systems. Therefore the effects of NOM on the adsorption of As and Se (and anionic forms of other metals such as Cr, and Sb) is of critical concern.
**NOM and As Geochemistry**

**NOM properties:**
- Molecular origins (allochthonous)
  - Condensation, polymerization
  - Detritus or old leaves
  - Inherently complex mixture
- Characteristic functional groups
  - Alcohols
  - Carboxylic acids
  - Ethers
  - Aromatic moieties
  - Amino groups
  - Sulfhydryl groups
- Surface and redox active, solute complexant

**As properties:**
- Anionic As(V) (arsenate, $H_3AsO_4$):
  - $pK_{a,1}$ 2.2; $pK_{a,2}$ 6.9; $pK_{a,3}$ 11.0
- Neutral As(III) (arsenite, $H_3AsO_3$):
  - $pK_{a,1}$ 9.2
- Surface active

Possible NOM molecule
Conceptual Model

Considerations:

- NOM forms strong inner-sphere ligand-like complexes with metal-oxide surfaces
  - Spectroscopic evidence (Redman et al., 2002; Gu et al., 1994)
  - Multiple surface, aqueous structures possible

- Competitive behavior towards arsenic adsorption
  - Less As adsorbed to metal oxides in the presence of humic and fulvic acids (Xu et al., 1988, 1991; Bowell 1994)

- NOM forms aqueous complexes with cationic metals
  - Possibility of ternary complex formation of Al-NOM with As (Bloom 1981)
Supporting Evidence

Field Sites in Bangladesh
- suggestive correlations

- High DOC correlates with high As in geographically diverse areas
  - Oxic conditions
- Supports competitive adsorption
- Other explanations:
  - dissolution of minerals
  - aqueous complexes

Industrial Site in California

Sources:
- Anawar et al., 2002 and personal communication;
- E. Mack personal communication 2001
Experimental Approach

Experimental method: batch systems

- NOM first
  - 12h colloidal hematite
  - add As
    - 100h colloidal hematite
    - resuspend in NOM
    - 48h colloidal hematite
- As first
  - 12h colloidal hematite
  - resuspend in NOM
  - 48h colloidal hematite

Conditions:
- 1µM (75 ppb) As(V) or As(III)
- NOM = 10mgC/L
- [metals in NOM] = 6 - 0.01 ppm
- 300mg/L hematite
- I = 10mM NaCl
- pH 6.0
- gentle rocking
- darkness
- 25°C
- HPLC-ICP-MS

By the Numbers:
- 1 µM As(V) or As(III)
- Estimated 140 µM NOM-RCOOH
- 20 µM sorption sites

The key to success: Chromatographic separation of As species

HPLC-ICP-MS

HPLC mobile phase = 5 mM Malonate:Acetate mixture, pH 4.8 with a strong anion exchange resin
Can As Adsorb onto NOM-Coated Hematite?

NOM First: As(V) adsorption to NOM pre-treated hematite

- Reduction to As(III) in presence of NOM and hematite
- As still exhibits a high affinity for hematite
- Other concerns:
  - Dissolution of Hematite by organic acids
  - Other competitive solutes: sulfate, carbonate

NOM First: As(III) adsorption to NOM pre-treated hematite

- Oxidation to As(V) observed in the presence of NOM
- More As mobilized in As(III) system due to better competition?

- Motivation: NOM pre-coated sediments in rivers and streams receiving AMD; wetlands (PRB’s)
Can NOM Mobilize Adsorbed As?

**As(V) First: NOM adsorption to As(V) pre-treated hematite**

- NOM promotes desorption of As from hematite
- NOM promotes reduction of As(V)
- Actual AsTOT is greater than measurable free As! (stay tuned)

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<thead>
<tr>
<th>Location</th>
<th>Free As(III)</th>
<th>Free As(V)</th>
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<tbody>
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<td>Rio Negro</td>
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<td>MW-6 Suwannee River</td>
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<td>Inangahua River</td>
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<td>No NOM</td>
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**As(III) First: NOM adsorption to As(III) pre-treated hematite**

- NOM promotes desorption of As from hematite
- NOM promotes oxidation of As(III), unknown though similar mechanisms?

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Aqueous Complexation

Aqueous complexation of As(V) with NOM

- Up to 80% aqueous complexation achieved (MW-6 NOM)
- Reduction of As(V) by Inangahua River NOM

Aqueous complexation of As(III) with NOM

- Similar pattern of complexation as seen for As(V) --> similar processes?
- All NOM samples oxidized As(III)
- Slow oxidation of As(III) by molecular O₂
- NOM as redox buffer, As₅TOT vs Free As
Aqueous Complexation Continued:
Al-(III) Dose Response

**As-Al-DI water**

Dose Response: As(V) + Al-DI water

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<th>[Al] (μM)</th>
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HPLC-ICP-MS Chromatograms of As-Al-DI water solutions

- As(III)
- As(V)
- Unknown

**As-Al-NOM**

Dose Response: As(V) + Al-NOM

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HPLC-ICP-MS Chromatograms of As-Al-NOM solutions

- As(III)
- As(V)
- Unknown

**Note:** Different scales

- Reduction of As(V) observed in high Al-NOM conditions
- Smooth chromatogram peaks in Al-NOM systems indicate organic-As species
- Irregular chromatogram peaks in Al-DI water systems indication Al-colloidal bound As dissolution and desorption
Redox Activity and Mechanisms

• Mechanism of NOM redox activity not well understood, but high activity is observed under many different conditions

• NOM acts as a redox buffer:
  – While slowly oxidized by molecular oxygen, NOM will rapidly reduce oxidized metals in oxic solutions (Macalady 1994)

• Rate of As(V) reduction in aqueous systems seems to be very fast (minutes) and the role of metals in these systems seems to be important
  – Promising results in experiments where EDTA is added to stop the reactions
  – Biological activity cannot be ruled out yet using: autoclaving, bioinhibitors and aseptic technique in addition to filtration (0.2 µm)
Conclusions

1. NOM exhibits competition adsorption towards As on hematite.

2. Rates of As adsorption dramatically slowed by the presence of NOM on hematite.

3. Aqueous complexes are possibly important environmental species of As affecting fate, transport and perhaps toxicity of As.

4. NOM accelerates the redox transformations of As under many environmentally relevant conditions.
Acknowledgements

In addition to funding through the EPA RMRHSRC, this work was made possible by:

• The HPLC-ICP-MS analytical methods used here were largely developed by Dr. John Garbarino and Tony Bednar at the U.S. Geological Survey. We are indebted to them for their assistance and for making their instrumentation and facilities available to us.

• Junji Akai (second author of Anawar et al., 2002) and Erin Mack kindly shared with us information on As-impacted sites

• Additional funding came through a DuPont Young Professor Grant to Dr. Ahmann
Arsenic and Old Leaves:
Interactions among Inorganic Arsenic, Hydrous Metal Oxides and Natural Organic Matter.

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Rates of Adsorption

Individual species adsorption to hematite (note scale: < 10 hours)

As adsorption to NOM-coated hematite (note scale: near 100 hours)

- Mass transfer limitations
  - site availability: competition and coagulation
- surface charge
- Implications into As transport in streams, lakes, PRBs, groundwater...
Aqueous Complexation Continued

Free vs Total As in As(V)-treated MW-6 systems

- Higher As$_{TOT}$ in bulk liquid than what is measured as Free As
  - Green bars as measured by HPLC-ICP-MS (Free As(V) + Free As(III))
  - Red bars as measured by GF-AAS (Free As(V) + Free As(III) + As-NOM)

Possible structures of As-NOM complexes:

- Adsorption onto NOM-Metal Oxide Colloids
- Metal Bridge
Toxicological Implications

- Anawar et al., 2002 --> As in the presence of humic acids exhibit variable and conflicting toxicity towards humans
  - Based on epidemiological studies in Bangladesh, Chile, Japan and other countries
- Variable and conflicting toxicity of As in the presence of humic acids towards enzyme activities also observed
- How is this possible?
  - Redox activity of NOM towards As species
  - Aqueous complexation of As with NOM may reduce bioavailability
  - Toxic, physiological impacts of NOM
- Small scale toxicity tests (Microtox, Daphnia, BSA enzyme activity) may help answer these questions