

**Metal Oxides, Inorganic
Arsenic and Natural Organic
Matter:
Interactions and
Transformations**

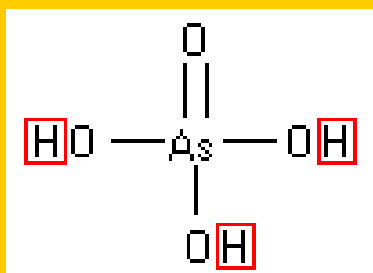
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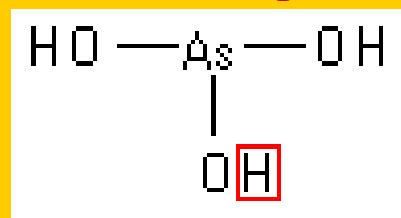
Relevant Arsenic Chemistry

Acid-Base Chemistry

As(V): $pK_1 = 2.2$, $pK_2 = 6.9$, $pK_3 = 11.5$



As(III): $pK_1 = 9.2$



Redox Chemistry



$$E_{\text{H}} = 0.093 \text{ @ pH} = 6, [\text{As(IV)}] = [\text{As(III)}]$$

MnO₂ (s), O₂, and Fe(III) and a host of other natural oxidants are thermodynamically able to oxidize As(III) to As(IV)

Microbial As(V) reduction is common

Mobilizes great quantities of As(III). Even in the presence of NO₃⁻, and dissolved O₂

Redox disequilibrium and kinetic controls on speciation are the rule.

Environmental Considerations

Adsorption is the primary control on arsenic mobility in aqueous systems. As(V) is less mobile than As(III)

Other specifically adsorbing anions(NOM, PO₄) may compete with As(V) and As(III)

As(III) is more toxic than As(V)

Carcinogenic

Drinking Water Standards

Proposed: 10 ppb total As

Current: 50 ppb total As

1 μM As(V) or As(III) = 74.92 ppb As

Sources of As(V) and As(III) contamination

Anthropogenic: Smelters, mine tailings

Natural: Bangladesh Arsenic Crisis, Chili, Japan

Natural Organic Matter (NOM)

- NOM is an inherently complex mixture of polyfunctional organic acids with variable aromatic and aliphatic character.
- **At essentially all environmental pH's, NOM “molecules” exhibit a net negative charge**
- NOM is present in all natural waters. Typical surface waters show 2-10 mg C/L of NOM.

Hydrous Metal Oxides

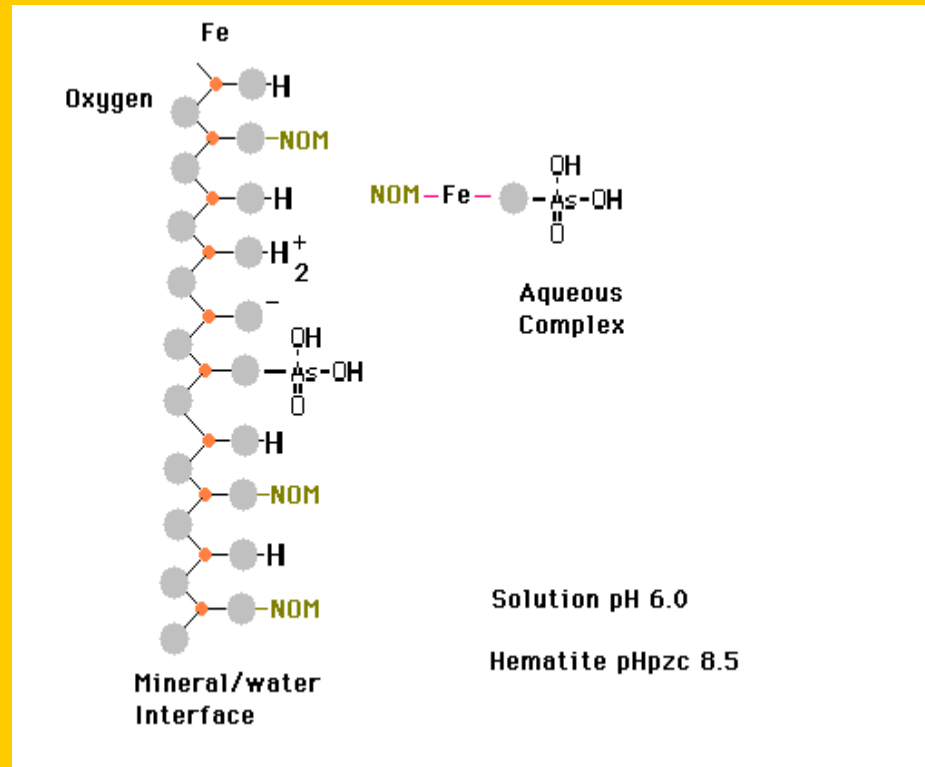
- Iron and aluminum oxyhydroxides are common in many soils (e.g. oxisols) and natural waters, especially those contaminated by acid mine water.
- **The surfaces of Al and Fe (also Ti) hydrous oxide particles show net positive charges at most environmental pH values.**
- These surfaces are effective adsorbents for anions, but also for cations such as Cu^{2+}
- **Dissolved As(V) and As(III) can be essentially totally (bdl) removed from solution in the presence of iron oxide particles.**
- Fe and Al oxyhydroxides are also effective at adsorbing NOM from solution, though not as completely as for As species.

Hypotheses

- 1. NOM and As(III) or As(V) compete for surface sites on hydrous iron oxide particles
- 2. NOM will displace adsorbed As and vice versa.
- 3. NOM will alter the redox chemistry of As species
- 4. NOM will form solution-phase complexes with As species
- 5. All of the above observations will vary in extent depending upon the NOM source
- 6. Soils and sediments rich in Al and Fe oxides will show behavior similar to our model Fe oxide (hematite)

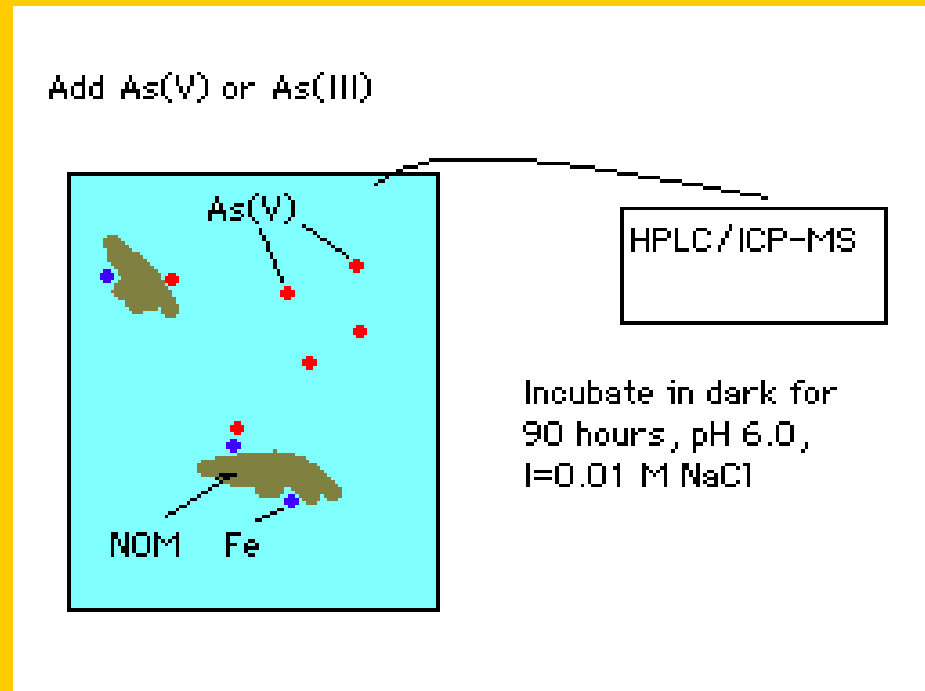
Conceptual Model

- 1) NOM competes with As(V) and As(III) for sorption sites
- 2) NOM forms bridging solution complexes with As(V) and As(III)



Experimental Design I

Does NOM form Aqueous Complexes with 1 μM As(V) or As(III)?

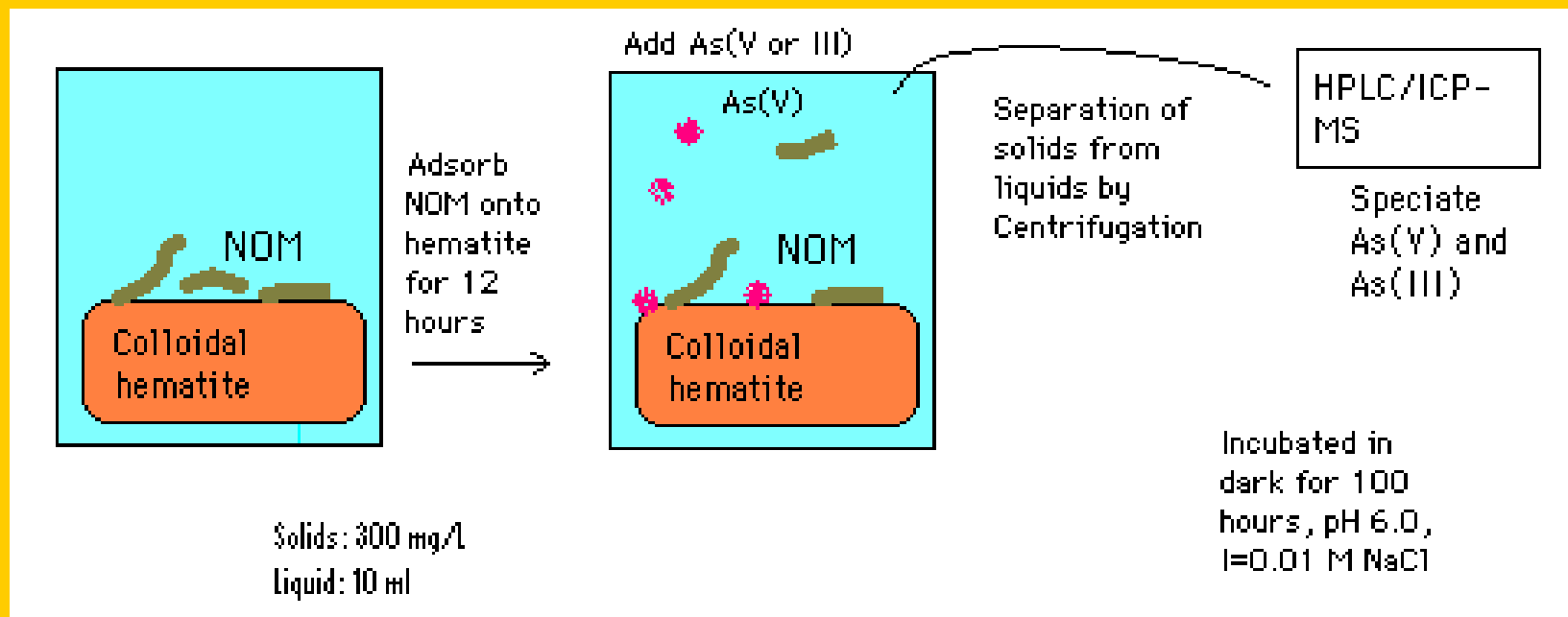


HPLC separation method: Strong anion exchange resin separates complexed As(V or III) from free As(V) from As(III). Complexed As is not eluted from the column.

Experimental Design II

NOM First: As(III or V)

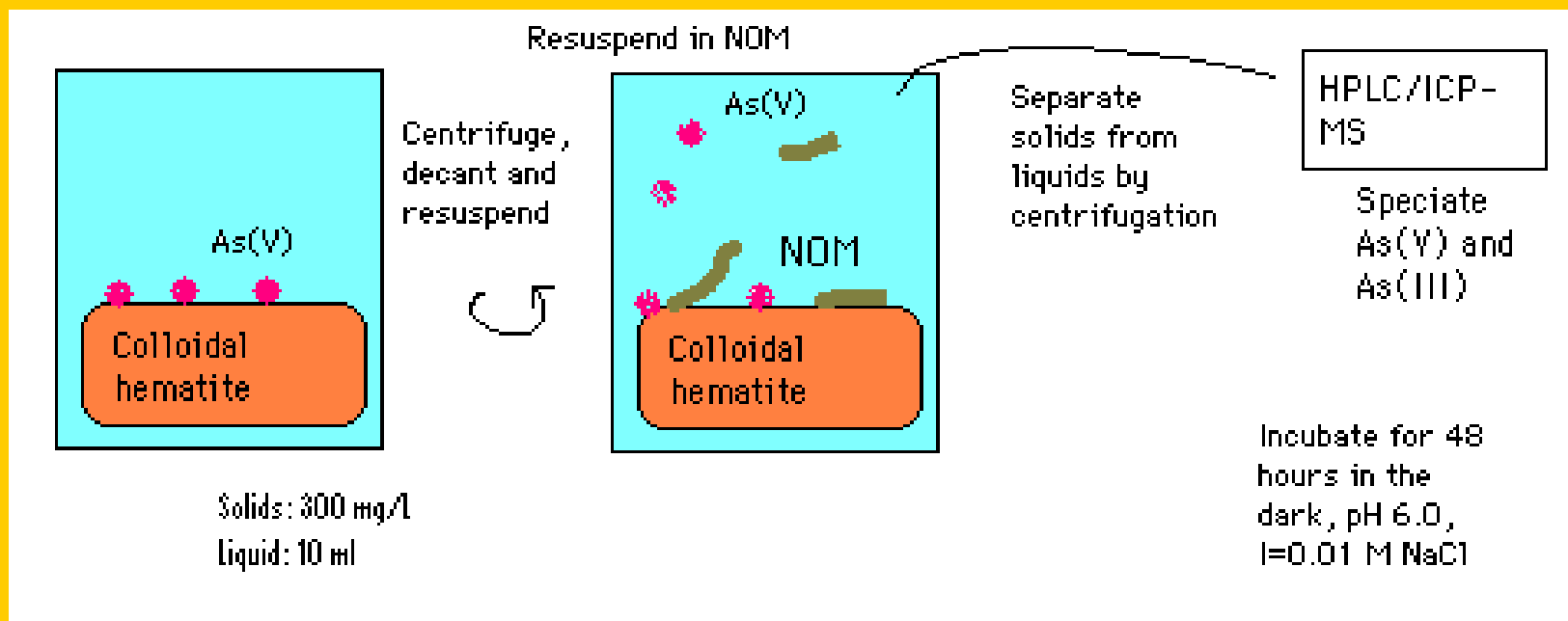
Does 1 μM As(V or III) adsorb onto
NOM-coated hematite?



Experimental Design III

As(V or III) First

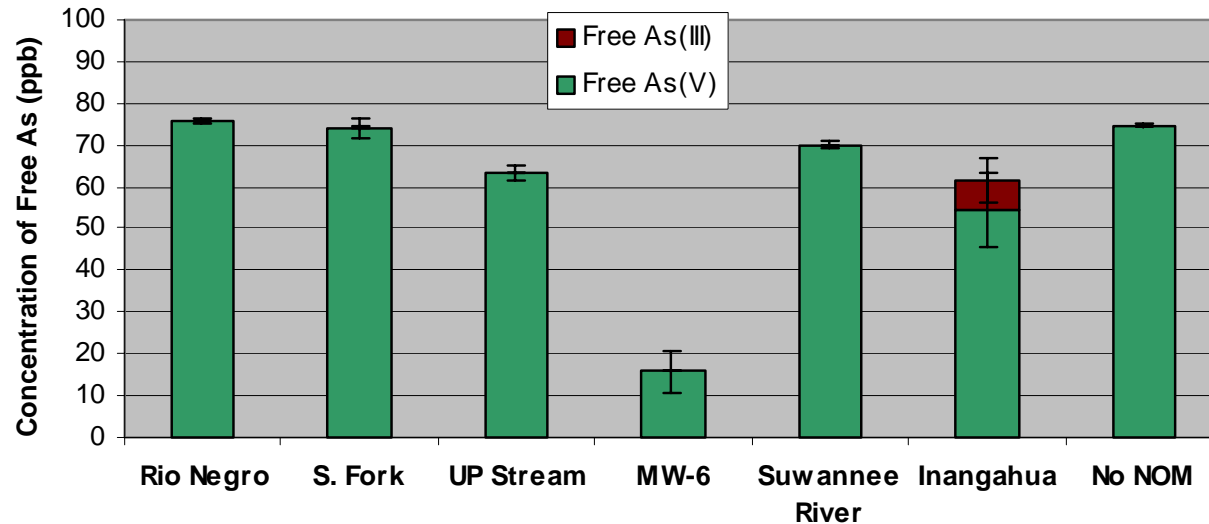
Does NOM displace adsorbed As(V or III)?



Experimental Results

Aqueous Complexation of As(V)

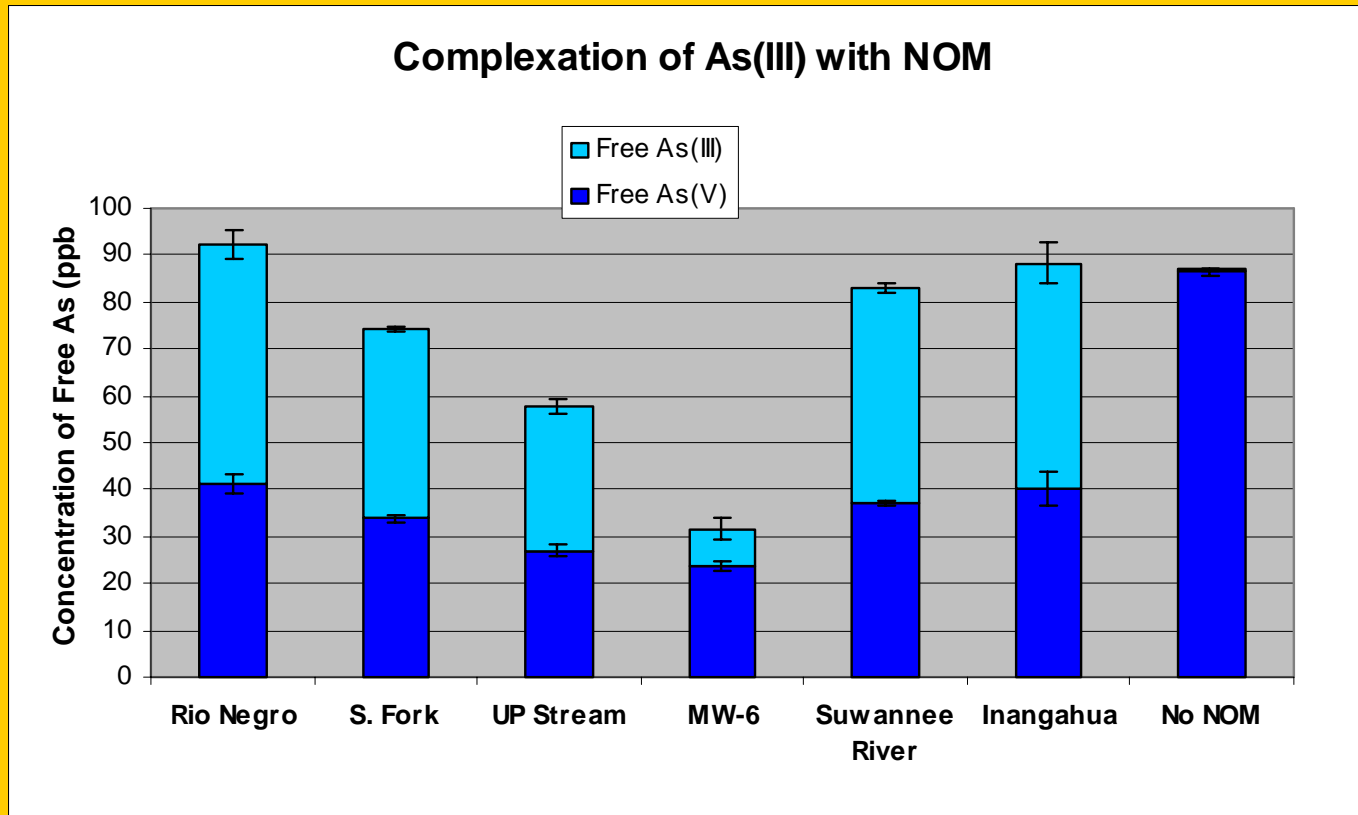
As(V) Complexation with NOM



Duplicate samples; error bars represent the range of data

1. Reduction of As(V) by Inangahua River NOM!!
2. Aqueous complexation by MW-6 and others
3. 90 hours of incubation in dark, equilibrium is assumed

Aqueous Complexation of As(III)



Duplicate samples, error bars represent the range of data

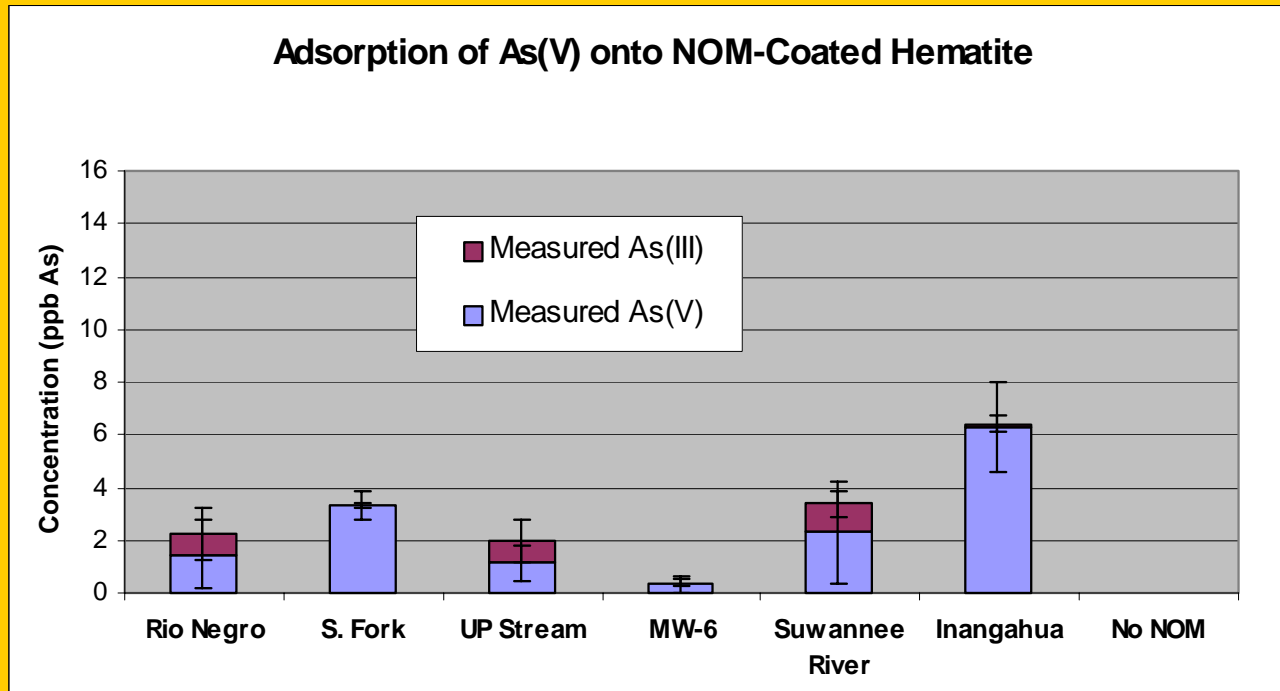
NOM appears to accelerate the oxidation of As(III):

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)



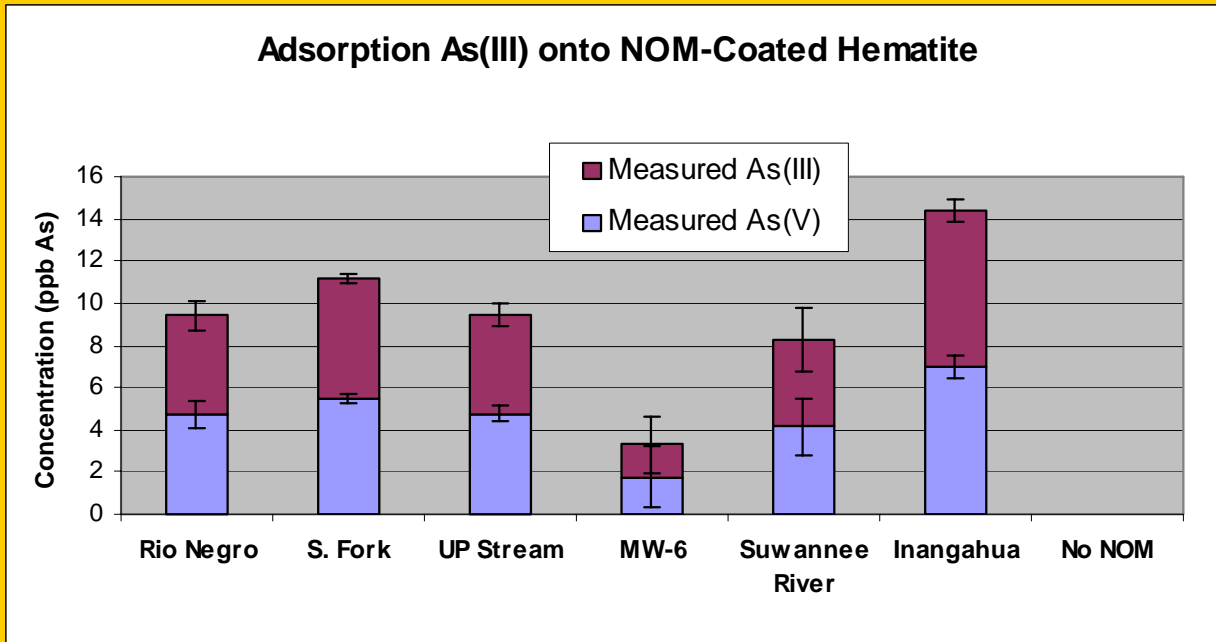
Triplicate samples, error bars represent the range of data

Significant amounts of free As in system As(V)

Significant As(III)! Surface-catalyzed reduction??

100 hours of incubation in dark

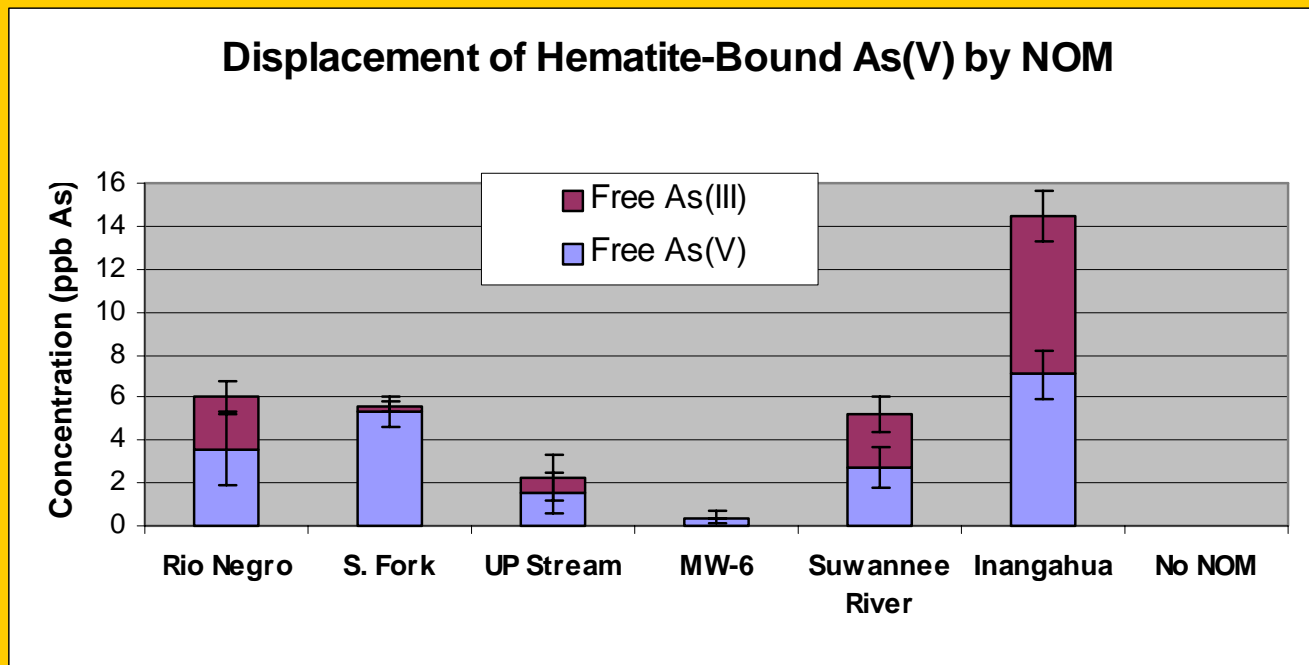
Results of NOM First: As(III)



Triplicate samples, error bars represent the range of data

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

As(V), Then 10 mg/L NOM

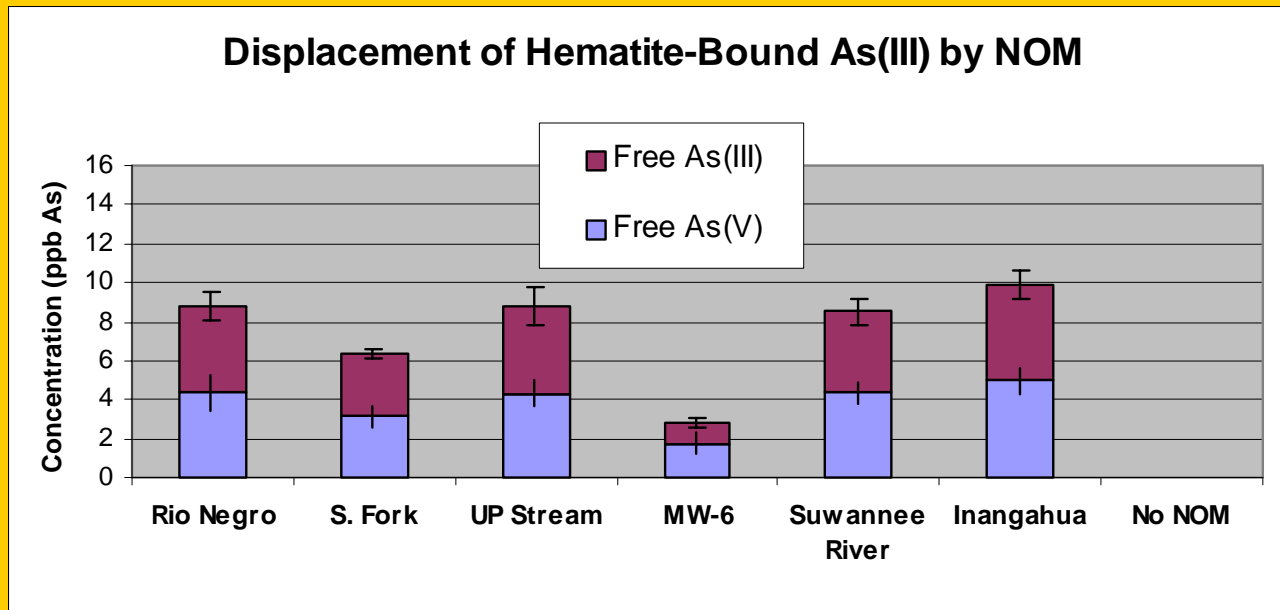


Triplicate samples, error bars represent the range of data

Surface-catalyzed reduction??

Lots of reduction by Inangahua river NOM
[re-oxidation of As(III) takes >48 hours]

As(III), Then 10 mg/L NOM

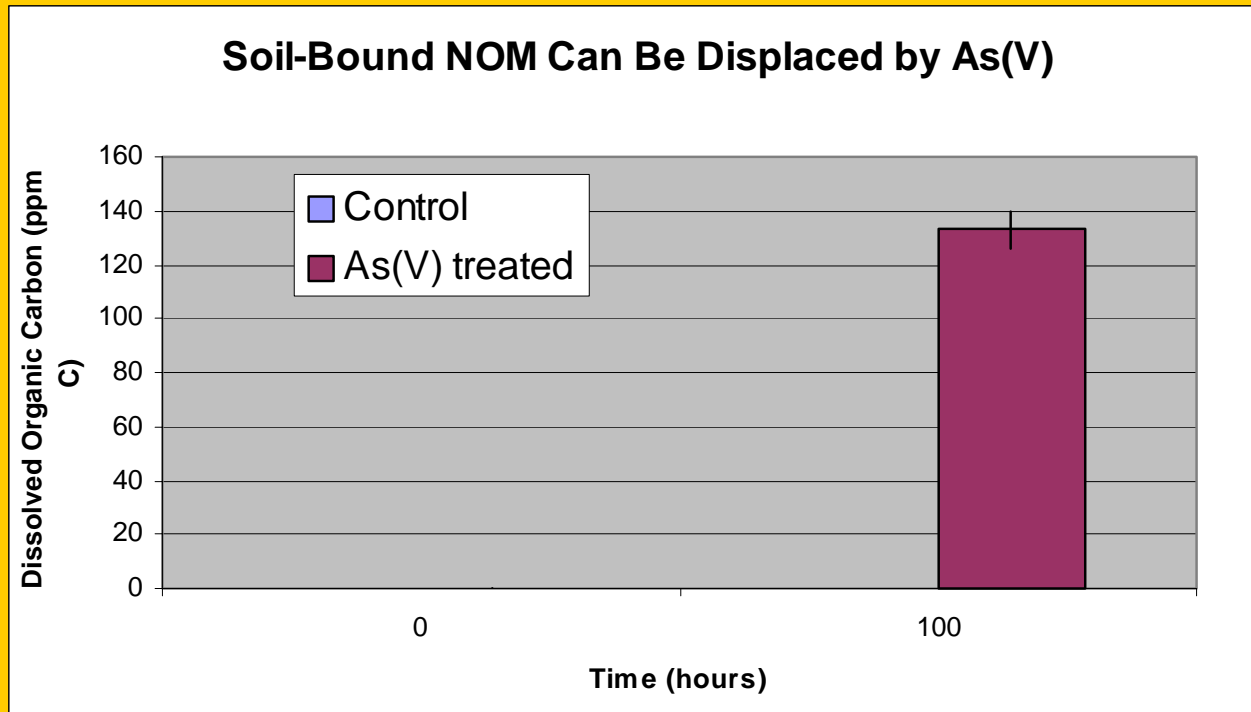


Triplicate samples, error bars represent the range of data

Higher values of free total As are observed in As(III) systems.

48 hours of incubation in the dark

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

Significant findings

- 1. NOM can mobilize adsorbed As(V) and As(III)**
- 2. As(V) can mobilize adsorbed NOM, which can compete further in the soil column.**
- 3) Aqueous “complexation” can be very important.**
- 4) NOM can facilitate redox transformations of As(V) and As(III).**

ONGOING RESEARCH

- **Investigations of the nature of the solution phase As-NOM complexes**
- **Verification of hematite findings using field sediments and soils**
- **Extension to studies of Selenium (Chromate, Antimony???)**
- **Studies of the implications for metal-removal treatment systems.**
- **Further investigations of the role of the nature of the NOM source.**

Acknowledgements

Based in part on the M.S. research of Aaron Redman, Division of Environmental Science and Engineering, CSM, supported by a grant from the Dupont Company.

Thanks to John Garbarino, U.S. Geological Survey and Tony Bednar, CSM for Analytical help

Thanks also to James McQuillan, Keith Hunter, Rich Wanty, Larry Gough and Rui Ribero for samples and advice