Speciation, Fate, and Cycling of Arsenic in Subsurface Environments

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Mechanistic understanding of arsenic speciation can help predict its behavior in subsurface environments

- Can we use geochemical scenarios to categorize potential As mobilization?
- How do we optimize kinetics of biogeochemical processes to enhance natural As attenuation?

Geochemical Parameters:
- Amount of labile iron
- Amount of sulfur available for reduction/oxidation
- pH & Eh (local and gradients)
- Role of nitrogen species?
Arsenic Speciation in the Environment

**Inorganic Arsenic**

Arsenious acid or Arsenite (As\textsubscript{III}(OH)\textsubscript{3})
\[ pK_{a1,2,3} = 9.23, 12.13, 13.40 \]

Arsenic acid or Arsenate (H\textsubscript{3}As\textsubscript{V}O\textsubscript{4})
\[ pK_{a1,2,3} = 2.20, 6.97, 11.53 \]

**Methylated Arsenic Compounds**

Monomethylarsonous acid or MMAs(III) (As(OH)\textsubscript{2}CH\textsubscript{3})

Dimethylarsinous acid or DMAs(III) (As(OH)(CH\textsubscript{3})\textsubscript{2})

**Organoarsenic Compounds**

Arsenocholine (CH\textsubscript{3})\textsubscript{3}As+CH\textsubscript{2}CH\textsubscript{2}OH)

Arsenobetaine (CH\textsubscript{3})\textsubscript{3}As+CH\textsubscript{2}COO\textsuperscript{-}

**Arsenic Minerals**

Orpiment (As\textsubscript{2}S\textsubscript{3})
Realgar (As\textsubscript{4}S\textsubscript{4})
Arsenopyrite (FeAsS)
Scorodite (FeAs\textsubscript{V}O\textsubscript{4.2}H\textsubscript{2}O)
Oxides, Arsenites, Arsenates

**Organoarsenic Lipids**

Arsenobetaine (CH\textsubscript{3})\textsubscript{3}As+CH\textsubscript{2}COO\textsuperscript{-}

\[ R = \text{OH} \]
\[ R = \text{OP(O)(O\textsuperscript{-})OCH}_2\text{CH(OH)CH}_2\text{OH} \]
\[ R = \text{SO}_3\textsuperscript{-} \]
\[ R = \text{OSO}_3\textsuperscript{-} \]
Arsenic Speciation & Partitioning: Tied to Major Element Chemistry

• Precipitation important for sulfides and sulfates

• Adsorption: Strongly associates with Iron hydroxides/oxides; competitive sorbates?

• Organic carbon and microbial activity

• Microbial coupling/competition with Nitrogen species?
Haiwee Reservoir, Owens Valley

- Aqueduct water dosed with FeCl₃ to remove As
- Deposition of high Fe, low S sediments with sorbed As(V)
Haiwee Reservoir, Owens Valley
Haiwee Reservoir: Core Sediments
High Iron, low Sulfur, Carbon System

Dixit & Hering (2003) ES&T 37, 4182-4189
High Iron, low Sulfur, Carbon System

- Reductive dissolution of sorbent Fe(OH)$_3$ releases As
- Low potential for Sulfur reduction -- no removal by sulfides
- Reduction of As(V) to As(III) -- may remain sorbed
- As(III) sorption depends on pH, competitive sorbates, available sorbents
Bay Road Site East Palo Alto CA.

- Tidal influence
- Sulfate reducing
Bay Road Site, East Palo Alto (CA, USA):
Subsurface plume below former sodium arsenite herbicide & pesticide manufacturing facility (1926-71)

**Contaminant Plume:**
- **[As\textsubscript{T}] in Groundwater**
  - Up to 100 mg l\textsuperscript{-1}
- **[As\textsubscript{T}] in Sediments**
  - Up to 1000 mg kg\textsuperscript{-1}

**Down-gradient of Plume:**
- **[As\textsubscript{T}] in Groundwater**
  - <0.01 mg l\textsuperscript{-1}
- **[As\textsubscript{T}] in Sediments**
  - Natural Background
Seasonal variation in well water level compared to tidal variation and rainfall (8/15/01-1/15/02)
Sediment Arsenic, Iron, & Organic Carbon

Within Plume

CORE 1

As(s) mg/kg
0 100 200 300 400

Fe(s) x10^3 mg/kg
0 20 40 60 80

%TOC mg/kg
0 20 40 60 80

In Tidal Marsh

CORE 2

CORE 3

AsS, As_2S_3

Adsorbed As(III), As(V)

Adsorbed As(V)

Transition

Root, 2003
As-Fe-S Speciation

Green Rust: GRII: Fe$^{II}$_6Fe$^{III}$_2(OH)_{16}(SO_4)\cdot4H_2O
Deciphering biotic vs. abiotic reaction rates

\[
[\text{As}]_T = 100 \text{ uM} \\
[\text{SO}_4^2-]_T = 28 \text{ mM} \\
\text{pH} = 7
\]

O’Day et al. (2004) PNAS 101, 13703-13708
Soil Amendments for As Stabilization
Bay Road Site

Amendments:
Ferrous sulfate (3% w/w)
Portland Cement (Type V, 10% w/w)

As Concentrations:
500-5000 mg/kg

Treatments:
1-9 m depth
surface capped
Microfocused Synchrotron XRD: Bay Road Field Samples
Soil Amendments for As Stabilization

- Arsenate incorporated into crystalline sulfate phases
- No evidence for reduction to As(III) after 10+ years
- High pH stabilized
- Aging process relatively rapid -- weeks? (experiments in progress)
-- Rates?
-- Sorption Capacity?

-- Limited by rate of sulfate reduction
Assessing the Potential for Arsenic Mobilization

- Rates of reductive dissolution of Fe(III) and Fe(II,III) (hydr)oxides and potential release of sorbed As
- pH-dependent desorption and competitive effects (phosphate, sulfate, silica)
- Rates of sulfate reduction and production of As-bearing sulfides; rates of re-oxidation
- Influence of N species on As-Fe-S redox rates
- Cost/benefit of amendment stabilization
- Validation of reactive transport models: accurate coupling of biogeochemical and hydrologic processes