Geochemical Perspectives Linking Arsenic Fate and Retention to Iron and Sulfur Cycling

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Arsenic in the Environment

• Arsenic not rare in the environment
  – “average soil”: about 10 mg As/kg

• Toxic environmental effects associated with arsenic not rare.
  – Effects of arsenic significant even at very low dissolved levels
  – Effects of arsenic are widespread
Natural Sources: Arsenic in Groundwater

- Arsenic concentrations in sediments in Bangladesh and Cambodia are not high. In fact, they are frequently below average.

- **Chemical Conditions** create elevated dissolved arsenic concentrations.
  - LANDFILLS (lined and unlined) are not unique, but are reactors in which pH and redox conditions are modulated by a combination of biological, chemical, and physical processes
    - Microbes
    - Electron Source (organic matter, H₂)
    - Terminal Electron Acceptors (Oxygen, Iron(III), Sulfate, CO₂)
Protect Your Health

The soils and sediments in this area contain harmful levels of lead and other metals. Small children and pregnant women are at the greatest risk from exposure.

KEEP CLEAN! Wash your hands and face before you eat anything. Wash toys, bottles, and pacifiers if they have been in contact with soil or dust. Remove loose soil from your clothing, camping equipment, and pets before leaving the area. Wash all items when you return home.

EAT CLEAN! Drink, cook, and wash only with water from home or other approved source. Do not use river water. Always eat at a table or clean surface off the ground. Clean fish thoroughly and eat only fish fillets.

PLAY CLEAN! Children should play in grassy areas and avoid loose soil, dust, and muddy areas. No mud pies.

Healthy Choices......Healthy Kids!

For more information call Panhandle Health District / Kellogg at (208) 783-0707
What Controls Dissolved Arsenic Concentrations in Wells?

- Arsenic is normally strongly retained by iron minerals
- *Microbes change (metabolize) the minerals in the soil and sediment, thereby releasing arsenic into groundwater.*
- Conditions usually are reducing (usually +100 to -100 mV) where dissolved arsenic is found.
- Organic carbon quality and content critical to the development of reducing conditions
Arsenic, Iron, and Sulfur Cycling


CDA Lake Porewater Concentrations

Data from Toevs, Bostick, Morra, & Fendorf (2006) *ES&T*
Trace Metal Retention and Release

Reduction:
\[ \text{Me-Fe(OH)}_3 + \text{OM} \rightarrow \text{Me(aq)} + \text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \]

\[ 8\text{Me-Fe(OH)}_3 + \text{HS}^- + 15\text{H}^+ \rightarrow 8\text{Me(aq)} + 8\text{Fe}^{2+} + \text{SO}_4^{2-} + 20\text{H}_2\text{O} \]

However…

\[ \text{Fe(OH)}_3\text{-Me(sorb)} \rightarrow \text{FeOOH-Me(sorb)} + \text{H}_2\text{O} \]

\[ \text{Me(aq)} + \text{Fe}^{2+} + \text{HS}^- \rightarrow \text{FeS-Me(sorb)} + \text{H}^+ \]

\[ 2\text{As(aq)} + 3\text{HS}^- \rightarrow \text{As}_2\text{S}_3 + 3\text{H}^+ \]

\[ \text{Pb}^{2+} + \text{HS}^- \rightarrow \text{PbS} + \text{H}^+ \]
Arsenic Sequestration and Mobilization in Model Systems

- Oxic systems: Fe(III) oxides and sulfate

- Suboxic Systems: Fe(III) oxides $\rightarrow$ Fe(II)$_{aq}$, sulfate

- Anoxic Systems: Sulfate $\rightarrow$ sulfide, possibly Fe(III) oxides $\rightarrow$ Fe(II)$_{aq}$

- Field-Based Studies of As Cycling
Arsenic-Iron-Sulfur Cycling in 3 Field Sites

• Coakley Superfund Site (NH)
• Coeur d’Alene Mining District (ID)
• Cambodian Groundwater Systems

Collaborators (Dartmouth): Carl E. Renshaw, Jamie L. deLemos, Stefan Stürup, Xiahong Feng

Reference: de Lemos et al. (2005) ES&T
As Source: Overburden-Clay Aquitard

- Log (As) in mg/L
- Bedrock
- Overburden
- p < 0.05

3-10m Thick Clay Layer
K = 7 \times 10^{-7} \text{ cm/s}
[As] \sim 20 \text{ ppm}
As Source: Characterization

Ferrihydrite

FT Magnitude

Fe
3 Fe-O @1.99 Å
3 Fe-O @2.11 Å
2 Fe-Fe @ 3.04 Å
2 Fe-Fe @ 3.45 Å

As
4 As-O @1.68 Å
1 As-Fe @ 2.84 Å
1 As-Fe @ 3.27 Å

Bidentate As(V)
Coakley: Arsenic Mobilization & Natural Attenuation

$30\text{Fe(OH)}_3 + \text{C}_6\text{H}_6 + 60\text{H}^+ \rightarrow 30\text{Fe}^{2+} + 6\text{CO}_2 + 78\text{H}_2\text{O}$ \hspace{1cm} \Delta G^o = -2359.96 \text{ kJ}$

\begin{figure}
\centering
\begin{minipage}{.5\textwidth}
\centering
\includegraphics[width=\textwidth]{benzene_arsenic_correlations}
\caption*{Post Cap correlations}
\label{fig:benzene_arsenic_correlations}
\end{minipage}
\begin{minipage}{.5\textwidth}
\centering
\includegraphics[width=\textwidth]{benzene_arsenic_correlations}
\caption*{Post Cap correlations}
\end{minipage}
\end{figure}

$\Delta[\text{Arsenic}]$ in ppb

$\Delta[\text{Benzene}]$ in ppb

$\log[\text{Fe}]$ in ppm

$\log[\text{benzene}]$ in (ppb)

$R^2 = 0.86$

$R^2 = 0.88$
Coakley: Batch Experiments and Field Data

![Diagram showing changes in Eh and concentration over time](image-url)
Coakley: Batch Experiments and Field Data

- Eh (volts) vs pH diagram
- Fe+++ and Fe++ redox states
- Fe(OH)₃, Fe(OH)₂, Fe(OH)₄⁻ phases
- Pyrite (FeS)
- As Concentration (As Conc.) ranges: 0 - 10 ppb, 10 - 50 ppb, 50 - 100 ppb, 100 - 320 ppb

25°C condition
Arsenic-Iron-Sulfur Cycling in 3 Field Sites

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- Cambodian Groundwater Systems

Collaborators: Gretchen Gehrke (Dartmouth), Gordon Toeves and Matt Morra (Univ. Idaho), Scott Fendorf and Matt Polizzotto (Stanford)
Coeur d’Alene (CDA) Mining District, ID

Downstream of the Lateral Lakes
CDA: As Distribution (mg/kg)

Legend

As (mg/kg)
- 0 - 31
- 31 - 121
- 121 - 288
- 288 - 620
- 620 - 979

CDA river

wetlands

0  2.5  5  10 Kilometers
Selected contaminants often are correlated spatially, but in no obvious way with distance from source.
Cataldo: Fe Speciation

- Most Fe is present as amorphous Fe (hydr)oxides
- About 20% maximum fluctuation with season
Cataldo: As Speciation

- Large seasonal variation in the occurrence of reduced arsenic phases in Cataldo Wetland sediments
Experimental Studies of Sulfate Redox Transformations Coupled to As Levels: Coeur d’Alene Mining District

Students:
Andrew N. Quicksall
Samantha Saalfeld
Joshua D. Landis

Coeur d’Alene River
At Swan Lake, ID
Incubations

Soil Collection

Microcosms

+ Media

Microbial Analysis

Aliquots

Solids: Bulk XAS

Solids: Micro XRF, XRD & XAS

Solution Analysis: ICP-OES

Solids: SEM

Sampling
CDA Cataldo
Lactate+Molybdate Amended

Plotted as Change from T=0
Solids: As Speciation

Determined using As XANES, SSRL 2-3
Solids: Fe Speciation

Fe(II) mineralization

Siderite present in SRB suppressed with net loss in FeS

Determined using Fe EXAFS, SSRL 2-3
Temporal Change

Paired Fe and As Release in SRB Suppressed Microcosms

Fe and As were sequestered when FeRB and SRB were active

Changes as seen in representative microcosms

Time=0

SRB Suppressed

Full Community

[Images of containers showing changes in conditions]
Soil Chemistry Cataldo Site

Determined via µXRF, NSLS x26A

Fe-Pb Decoupling

"hot spot" generation

Distance (mm)

Log Pb Intensity

Time=0

$R^2=0.68$

Time=10d

$R^2=0.21$

Log Fe Intensity

Determined via µXRF, NSLS x26A
Microbial Ties

- The suppression via molybdate yields strong evidence for SRB involvement in trace element retention

- Can we explain this observation via direct methods to identify specific microbial populations?

Sequencing of cloned 16S rDNA soil extracts
Dominant Microbial Species

Lactate (Full Community)

Clostridia (89-91%)

Obligate Anaerobes
Many Can Reduce Fe

Desulfitobacterium hafniense (89%)

Can Reduce $\text{SO}_4^{2-}$

Lactate + Molybdate (SRB Suppressed)

Anaeromyxobacter dehalogenans (100%)

Metal Reducer
Particularly Fe
No S Reducers
Observations:
- Iron reduction is central to the release of trace metals
- Mineral transformations govern trace metal sequestration

Implication:
- Solution Concentrations are ultimately governed by balanced Fe and S Reduction
PRIMARY EXPERIMENTAL METHODS

Flow-through experiments

Influent

Iron-coated sand (and/or arsenic and/or microbes)

Effluent (to fraction collector)
Incubations

- Mixed constantly for life of experiment
- Represent stagnant or low-flow end-member of groundwater systems
- Products accumulate, reactants are depleted – system approaches equilibrium
How does sulfate input concentration affect mineralogy in *D. desulfuricans* columns?

5 µM  
0.8 mM  
10 mM  
20 mM
By what mechanisms does flow rate affect mineralogy in iron oxide-sulfide columns?

Flow rate ~3.5 mL/hr

Flow rate ~6 mL/hr
What determines which minerals form in SRB/FeRB systems?

- Magnetite formation
- Magnetite + iron sulfide formation
What mineral transformations occur under stagnant conditions in *D. desulfuricans* incubations?

SRBs, 10 mM SO$_4$  
No bugs

Only modest changes in Fe mineralogy  
(not enough carbon to reduce all Fe)
Sulfide formation in *D. desulfuricans* incubations

What mechanisms regulate arsenic release from *D. desulfuricans* columns?
What causes differences in patterns of Iron and Arsenic release caused by SRBs and FeRBs?
How do changes in $\delta^{34}\text{S}$ reflect sulfur cycling?
A more complete description of As fate

- It is necessary to include sulfate reduction to adequately describe arsenic concentrations.
- Kinetic processes are critical to regulating arsenic levels
Arsenic-Iron-Sulfur Cycling in 3 Field Sites

Coakley Superfund Site (NH)
Coeur d’Alene Mining District (ID)
Cambodian Groundwater Systems

Collaborators:
Mickey Sampson (Resources Development International, Cambodia)
Elizabeth Hadzima
Gretchen Gehrke
Nick Papacostas
Joshua Landis
Jamie de Lemos
• Typical As, S and Fe levels
• Hard to determine composition of aquifer materials based on surficial environment
Arsenic and Regional Surficial Geology

- 0-10 ppb
- 11-25 ppb
- 26-50 ppb
- 51-100 ppb
- >100 ppb

- Beach ridges and levees
- Floodplains
- Organic deposits (swamps)
- Water

water_concentration_join
AS1890
Redox Processes: Sulfate and Iron reduction

- Redox Conditions indicate that sulfate reduction and/or Fe reduction is thermodynamically viable, concentration information indicates the extent to which they have occurred.
Arsenic is associated with waters high in Fe and low in sulfate.

- Highly elevated As levels are most notably associated with waters high in Fe and low in sulfate.