

WELCOME

Two-Part Webinar Series Featuring
Madeline Gotkowitz, PG, U. of Wisconsin and Maddy Schreiber, PhD, Virginia Tech University

Arsenic in Ground Water, Part 1

10 November 2010

Arsenic Geochemistry: Demystifying
the Complexities and "Conventional Wisdom"

This Webinar will begin at 1pm (Central Time).

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10 November 2010

Arsenic Geochemistry: Demystifying
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Madeline Schreiber
Virginia Tech



Madeline Gotkowitz
Wisconsin Geological and
Natural History Survey

1.5 Professional Development Hours

1.5 PDHs

0.15 Continuing Education Units

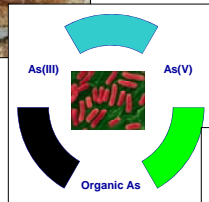
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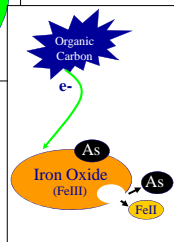
This webinar focuses on biogeochemical conditions that cause solid-phase arsenic to become dissolved or mobile in groundwater. Today's, Part 1, topics include:



Sources and distribution of arsenic in the environment



Arsenic geochemistry



Mechanisms of arsenic release in groundwater

The goal of this webinar is to answer three broad questions:

Where, how much, in what form, is arsenic present in the environment?

How do various geochemical conditions affect solid- and aqueous- phase arsenic?

What geochemical conditions promote arsenic contamination of groundwater?

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Why is there a drinking water standard for arsenic? Arsenic is toxic and causes cancer.



Distribution of documented As in groundwater in major aquifers. Smedley and Kinniburgh, 2002.

Cancer is the primary *long-term* health risk associated with exposure to arsenic in drinking water. Tens of millions of people rely on aquifers with arsenic commonly exceeding the World Health Organization's and the U.S. E.P.A.'s standard, 10 µg/L.

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Sources and distribution of arsenic in the environment (Gotkowitz)



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**Arsenic sources may be naturally-occurring or
a result of anthropogenic activities.**



**Trace amounts of arsenic are ubiquitous in soil, sediment,
rock, and natural waters. Arsenic is concentrated in some
natural environments *and* through human activities.**

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Arsenic is present in many minerals, rocks, and sediments.

Arsenic minerals contain weight percent As

- common to ore deposits
- often in association with Cd, Pb, Au, Moly, nickel, zinc, antimony, tungsten, phosphorous, silver



Arsenopyrite (FeAsS)



Realgar (AsS)



Orpiment (As₂S₃)



Scorodite (FeAsO₄ · 2H₂O)

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Pictures from www.minresco.com, wwwbrr.cr.usgs.gov, www.britannica.com, and personal collection

Many other minerals are arsenic-bearing...

Sulfides: pyrite, marcasite, galena (1's to 10,000s mg/kg)

Oxides: Fe- and Mn- oxides, Fe(III) oxyhydroxides (1,000s mg/kg)

Jarosite, Apatite (up to 1,000 mg/kg)

Smedley and Kinniburgh (2002)



As-bearing pyrite in sandstone



As-bearing iron oxide

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Pictures from www.minresco.com, wwwbrr.cr.usgs.gov, www.britannica.com, and personal collection

Arsenic is present within many rocks and sediments, although often concentrated (as opposed to well-mixed) within host rock or sediment.

Argillaceous rocks have a wide range of As-concentrations. Higher arsenic is associated with greater amounts of sulfides, oxides and organic matter within clays and shale.

Soil and sediment: higher As where the parent material is arsenic rich (soils near sulfide deposits, till derived from shale)



Smedley and Kinniburgh, 2002.

Many rocks and sediments contain arsenic-bearing minerals.

Rocks and their associated arsenic concentration (order of magnitude)

Igneous rocks: 1 – 10 mg/kg

Shale: 10 – 100 mg/kg

Sandstone: 1 – 10 mg/kg

Coal: 1 – 10000 mg/kg

Unconsolidated sediments

Alluvial sand: 1 – 10 mg/kg

Lake sediments: 1 – 10 mg/kg

Glacial tills: 1 – 100 mg/kg

Soils

Various: 1 – 10 mg/kg

Peat: 1 – 10 mg/kg

Soils near ore deposits: 1 – 1000 mg/kg

Compiled from Smedley and Kinniburgh, 2002.

Arsenic-rich rocks are composed of major elements and trace metals...

Whole rock concentrations of selected elements in aquifer materials

Sample	As mg/kg	S %	Fe %	Cu mg/kg	Pb mg/kg	Ni mg/kg	Co mg/kg	Mn mg/kg
sulfide cement	585	17.9	20	129	442	378	241	681
mineral nodule	510	0.5	21	83	585	234	196	168
mineral vein	161	0.02	12	109	53	154	113	387
sandstone, orange-tint	13	<0.01	3	10	12	35	10	138
sandstone	3	<0.01	0.7	8	7	12	3	56

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Arsenic is often concentrated (as opposed to well-mixed) within the host rock or sediment.



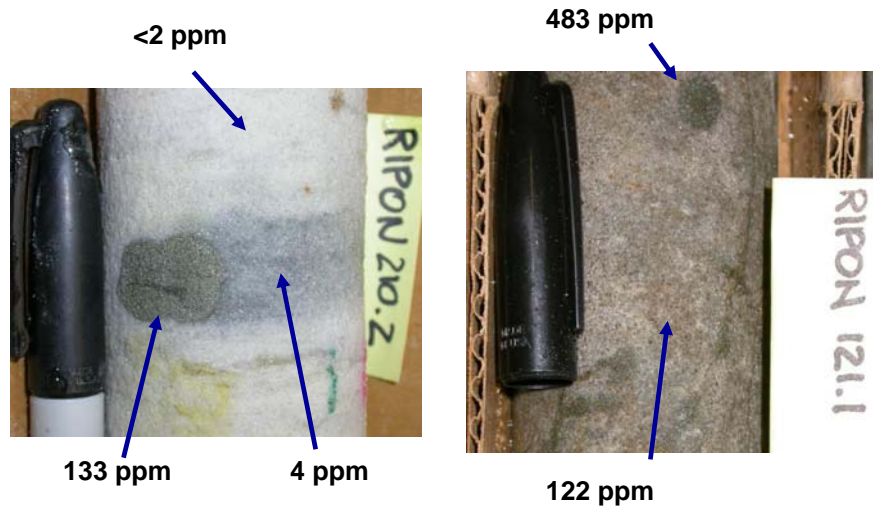
St. Peter Fm., Wisconsin

Depths reported as feet below ground surface

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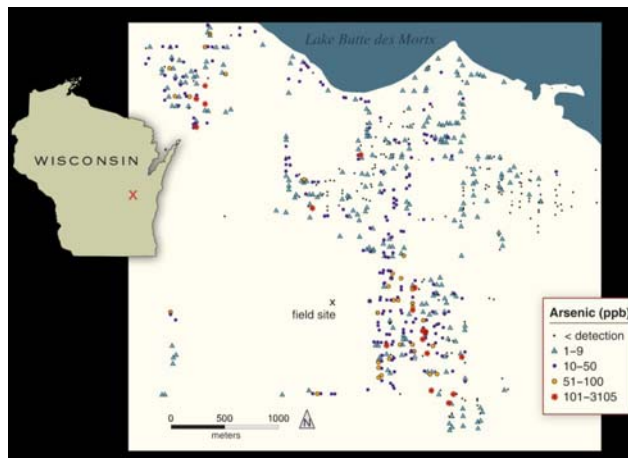
There is a high degree of spatial variability in solid-phase arsenic in this sandstone aquifer.

Whole rock arsenic concentrations of selected material, in mg/kg.



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The spatial variability in groundwater arsenic concentrations reflects that in the solid-phase source (e.g. the sandstone aquifer).



Many anthropogenic activities concentrate elemental and mineral forms of arsenic.

Wood preservative → Chromium copper arsenate (CCA)



Photo by J. Winandy, U.S.F.S., Forest Products Laboratory



Mining → As-rich waste rock

Munitions → manufacturing, storage, and disposal



Bis(diphenylarsine)
p-Phenylene-bis-(diphenylarsine)

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Agricultural sources: arsenic is an effective insecticide, and it controls disease and stimulates growth in poultry.

Insecticide → Lead arsenate



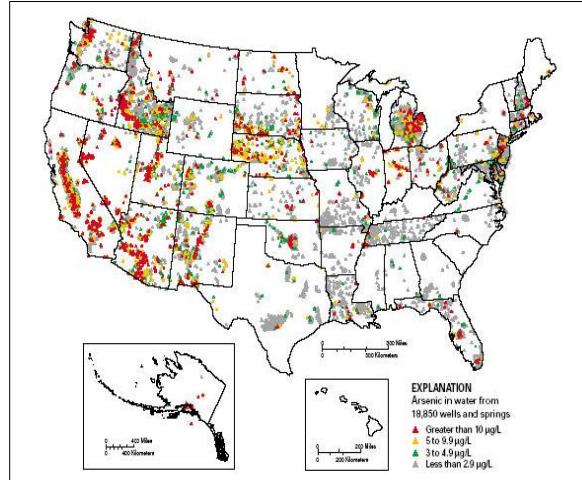
$Pb_5OH(AsO_4)_3$
 $PbHAsO_4$



Animal feed → litter
2-Nitrophenol-4-arsonic acid
(Roxarsone)
 $C_6H_6AsNO_6$

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Most *regions* of elevated groundwater arsenic have naturally-occurring sources. Anthropogenic sources affect conditions at the site- or local-scale.



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U.S.G.S. Water Resources Investigations Report 99-4279

What are the sources of arsenic that you typically encounter in your work?

Are your arsenic-related project(s) at:

- A. Industrial manufacturing sites**
- B. Industrial landfills**
- C. Municipal landfills**
- D. Agricultural facilities**
- E. Mines or mine tailings sites**
- F. Wide-spread “naturally” occurring arsenic**

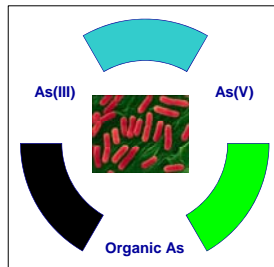
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Arsenic in Ground Water, Part 1

10 November 2010

Arsenic Geochemistry: Demystifying
 the Complexities and "Conventional Wisdom"

Basics of Arsenic Geochemistry (Schreiber)



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Arsenic occurs in a variety of phases and species in water

Phases:

volatile: AsH_3 , methylarsines

dissolved: H_3AsO_4 , H_3AsO_3

solid: FeAsS , AsS , etc.

Speciation:

+5, +3, +1 and -3 oxidation states

But most common in natural waters:

+5 [arsenate, or As(V), H_3AsO_4]

+3 [arsenite or As(III), H_3AsO_3]

Forms:

Inorganic (As(V), As(III), etc)

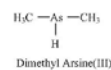
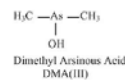
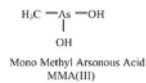
Organic

naturally-occurring: some organic forms are produced by organisms as detoxification processes (e.g. arsenosugars)

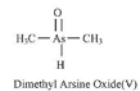
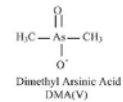
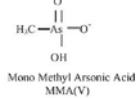
human-made: organoarsenical pesticides/herbicides, animal feed additives

Common arsenic compounds

Trivalent



Pentavalent



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Arsenic species have different toxicities

Toxicity:

$\text{AsH}_3 > \text{As(III)} > \text{As(V)} > \text{org As}$

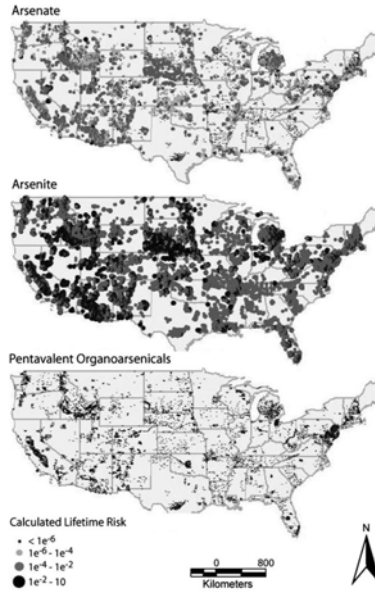
Why?

As(III) binds to thiol groups, which are important for enzymes

As(V) more rapidly excreted, but can interfere with phosphorylation, as it is analog to P(V)

The species does matter, but EPA regulates total As

Fig. 3 Hypothetical chronic exposure risk in USA groundwater based on total arsenic concentration data from Ryker (2001). Chronic exposure risk was calculated for three hypothetical scenarios: arsenic concentrations present as either As^{3+} , As^{5+} , or the oxidized methylated species. Calculations assume adult exposure via oral ingestion of drinking water

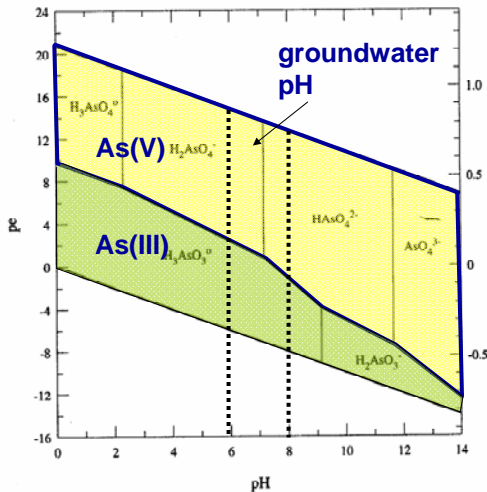


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Markley and Herbert 2009

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In aqueous solutions, arsenic species are controlled by Eh and pH



Eh/pe - measure of redox state (Eh = field measurement)

Most important points

Arsenate (oxidizing)

H_2AsO_4^- , HAsO_4^{2-} dominant (note: negatively charged)

Arsenite (reducing)

H_3AsO_3 dominant (note: uncharged)

Figure 2. pE-pH diagram for predominant aqueous species of arsenic at equilibrium and 298.15 K and 1 atmosphere pressure.

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Nordstrom and Archer 2003

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Recognize that arsenic species are often in thermodynamic disequilibrium

.... As(III) can be found in oxygenated environments and As(V) can be found in reducing environments

Why?

Oxidation of As(III) by air is slow (without bacteria or minerals)

Oxidation rate increases with other redox-sensitive species, e.g. Fe(III)

As(III) can also be oxidized by minerals such as Mn oxides

As(V) can be abiotically reduced by H_2S , H_2 , Fe(II) and humics

Arsenic species can be oxidized and reduced by microorganisms

Main point: Don't assume speciation, measure it! (its not that hard)

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Microorganisms impact As speciation and form

Many microorganisms can biotransform As

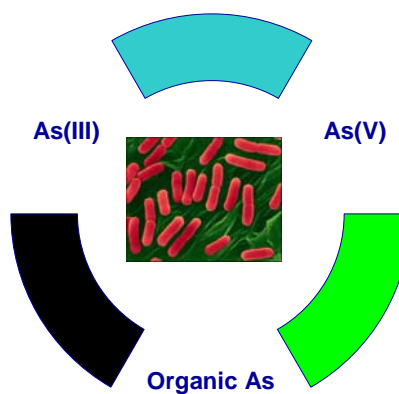
Why?

Detoxification
Respiration

Some can oxidize As(III) to As(V)

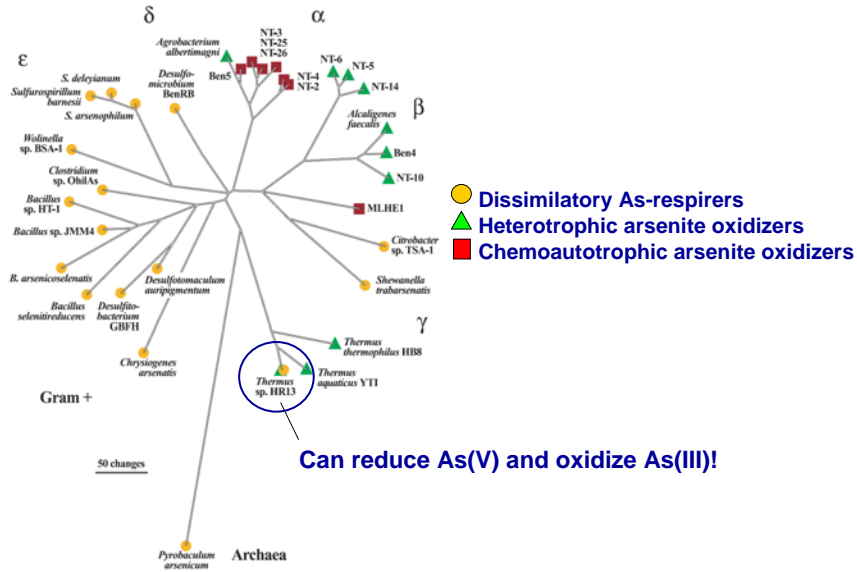
Others can reduce As(V), both for respiration and for detoxification

Others turn inorganic => organic, and vice versa



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Diverse organisms can use arsenic for energy!



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Fig. 1. Phylogenetic diversity of representative arsenic-metabolizing prokaryotes. Dissimilatory arsenate-respiring prokaryotes (DARPs) are indicated by yellow circles, heterotrophic arsenite oxidizers (HAOs) are indicated by green triangles, and chemoautotrophic arsenite oxidizers (CAOs) are indicated by red squares. In some cases (e.g., *Thermus* sp. strain HR13), the microbe has been found able to both respire As(V) and oxidize As(III).

Oremland and Stolz 2003

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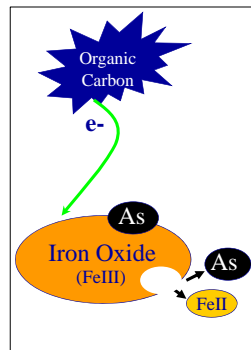
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Release mechanisms (Schreiber)



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How is arsenic released from solids to solution?

Dissolution of As-bearing minerals:

Controlled by thermodynamic properties, presence of oxidants, and microbial influences



Arsenopyrite (FeAsS)

Adsorption and desorption from surfaces:

Controlled by properties of the solid surface, pH, the concentration of As and competing anions, and As speciation



Goethite (FeOOH)

Leaching from human sources (e.g. CCA, pesticides):

Controlled by solubility, surface area, concentration of As in solution



Treated wood

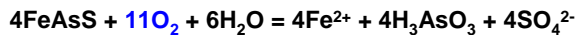
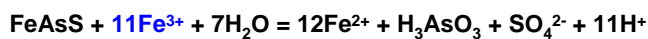
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What mechanisms release As from solid to solution?

Oxidation of As-bearing sulfides

Example: Arsenopyrite oxidation by Fe(III) and O₂



Note: other oxidants can oxidize FeAsS (e.g. nitrate)



Other As-bearing sulfides that can be oxidized: pyrite, realgar, orpiment

Note that at low pH, Fe(II) oxidizers can enhance sulfide oxidation dramatically by continually producing Fe(III)

30 Picture from www.minresco.com, wwwbrr.cr.usgs.gov, www.britannica.com, and personal collection

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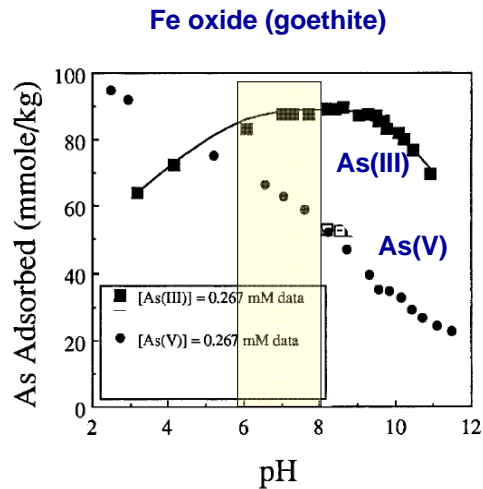
Another process which exerts control on As partitioning between solid and water is adsorption

Both As(V) and As(III) adsorb to metal oxides and clays, but its highly pH dependent!

General trends:

Max As(V) adsorption at low pH, decreases at high pH

Max As(III) adsorption at high pH, decreases at low pH



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Modified from Manning 1998

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The conventional wisdom is that As(III) adsorbs less than As(V) and is thus more mobile

Is this true? It mostly depends on pH, the minerals present, relative concentrations of As and the mineral, and solid:solution ratio

In general,

At low pH, As(V) adsorbs more than As(III) to all oxides and clays

At near-neutral pH (6-8), As(III) adsorbs more than As(V) to Fe oxides, but less to Al oxides and clays

At high pH, As(III) adsorbs more than As(V) to all oxides and clays.

Bottom line for groundwater at near neutral pH:

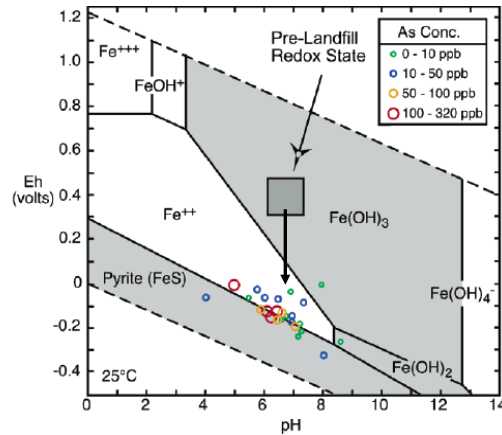
If Fe oxides are the bulk mineral, As(III) may NOT be more mobile than As(V).

But if clays dominate, and Fe oxides are minor (more likely in natural setting), As(III) CAN be more mobile than As(V).

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Example: Arsenic release due to reductive dissolution of iron oxides in a landfill



Prior to landfill, redox state was oxidizing, and Fe was stable as solid phase (see square)

Post landfill, redox dropped into stability field of dissolved FeII – As had nothing left to hold onto!

deLemos et al. 2006

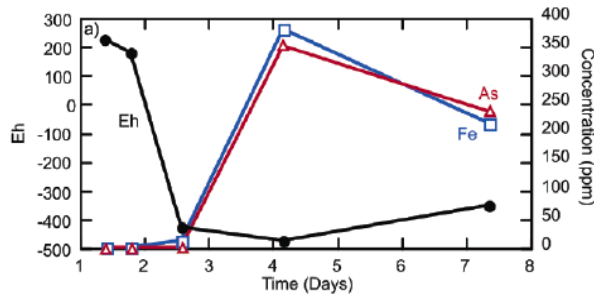
FIGURE 4. Iron stability diagram. Prior to the Coakley landfill, the redox potential and pH of groundwater in the clay layer was within the stability field of ferrihydrite (indicated by the dashed box). Measured redox potential (E_h) and pH of present-day As-contaminated samples from the site are indicative of Fe(III) reduction to dissolved Fe(II). The most reduced samples exhibit the highest arsenic concentrations.

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Addition of organics stimulated Fe and As release

glucose = proxy for organic material



Lab: Added organics (glucose - proxy for organics) to sediment, which stimulated aqueous Fe and As release

FIGURE 3. (a) Coupling of As release to Fe reduction in a batch experiment under a nitrogen atmosphere. Upon the addition of glucose and nutrients to the system, redox potential dropped, leading to the release of dissolved Fe and As. (b) Changes in groundwater dissolved benzene concentrations in overburden wells before and after landfill capping are well correlated with corresponding changes in arsenic concentrations.

deLemos et al. 2006

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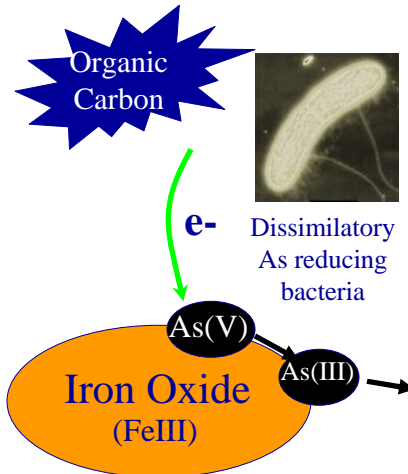
Similar but different: Reductive desorption

Microbial reduction of As(V) to As(III) on mineral surface

Microbes couple oxidation of organic carbon with reduction of electron acceptors
Oxygen quickly depleted => anaerobic

Arsenate-reducing bacteria reduce As(V) on solid surface to As(III)

At low pH, As(III) does not sorb strongly to Fe oxides (refer to previous graph), can be released to solution



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In some cases, reduction of both Fe(III) and As(V) may occur

Bangladesh sediment

Addition of acetate stimulated BOTH Fe(III) and As(V) reduction (panel C)

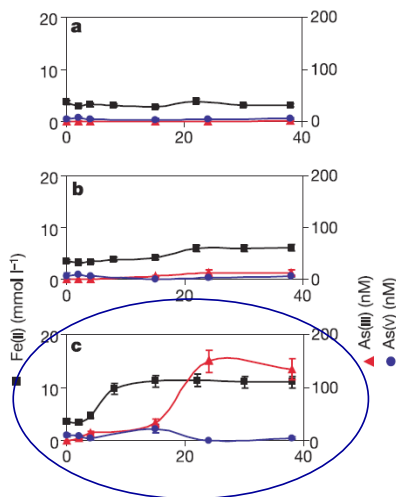


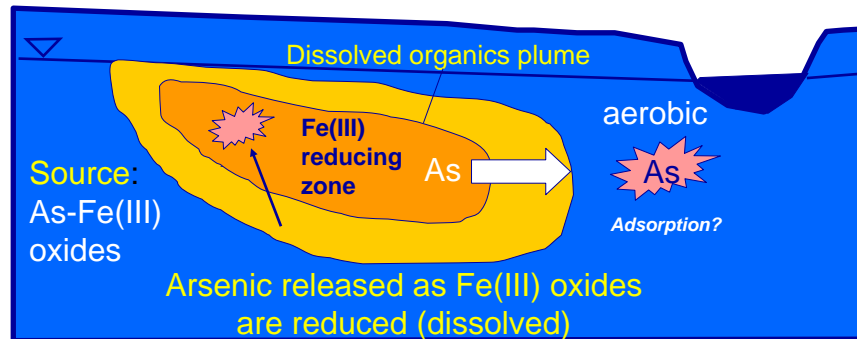
Figure 1 Reduction of Fe(III), and mobilization of arsenic in microcosms containing Bengali sediments incubated under a range of biogeochemical regimes. **a**, Aerobically; **b**, anaerobically; and **c**, anaerobically with 4 g l⁻¹ sodium acetate as a proxy for organic matter. 'Abiotic' control sediments with added acetate were autoclaved before incubation (**d**). Black squares, Fe(III); red triangles, As(III); purple circles, As(V). Each point and error bar represents the mean and standard deviation of three replicate experiments.

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Islam et al. 2004

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Theoretically, once the electron donor has been exhausted and conditions become aerobic downgradient, As can adsorb again to Fe oxides



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Important factor with arsenic contamination of water is the "trigger", not the source concentration

In "problem" aquifers, arsenic content in sediments often NOT exceptionally high

Important factors are the source and the trigger, related to biogeochemical conditions

What are triggers?

Change in pH

pH increase => desorption of As(V); pH decrease => desorption of As(III)

Introduction of organic material => reducing conditions

Promotes reductive dissolution of Fe oxides, reduction of As(V) to As(III)

Competitive anions

Kicks off As(V), to lesser extent As(III)

Introduction of oxidant

Promotes oxidation of arsenic-bearing sulfides

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Addressing arsenic in groundwater systems requires adequate characterization of the biogeochemical conditions.

Naturally occurring arsenic content of rocks and sediments is often NOT exceptionally high, yet causes groundwater concentrations of concern.

Arsenic contamination is complicated by a high degree of spatial variability in arsenic concentrations in geologic materials and geochemical conditions that trigger its solubility and mobility.

Design sampling programs that identify geochemical signatures of arsenic sources, and the processes that mobilize it. This information informs treatment and remediation options.

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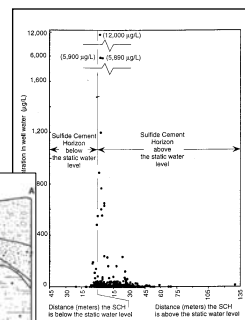
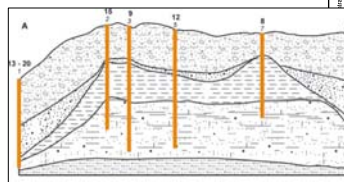
Part 2 of this webinar continues discussion of biogeochemical conditions that cause solid-phase arsenic to become dissolved or mobile in groundwater. Topics will include:



Field and laboratory methods



Case studies



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References

Included with handouts

Contacts

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THANK YOU

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10 November 2010

Arsenic Geochemistry: Demystifying
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This Webinar is complete.

Midwest GeoSciences Group appreciates your attendance
and hopes you have benefited from this online educational event.

We welcome your feedback and also invite you to share your experiences with us in an email following this webinar.

Use the Record of Attendance Form for your own PDH record keeping.

For those who want an official certificate suitable for framing, they will be available for a small administrative fee from Northern Illinois University. Instructions forthcoming in a follow up email to your site coordinator.

Please return the signed **R of A Form** to Dan Kelleher at dan@midwestgeo.com.



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PART TWO NEXT WEEK

Two-Part Webinar Series Featuring
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Arsenic in Ground Water, Part 2

17 November 2010

Advances in Arsenic Site Investigations:
Methods, Data Collection and Interpretation

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Other Upcoming Webinars

Webinar featuring Tim Kemmis, Ph.D., PG.
Co-Author of *The Field Guide for Soil and Stratigraphic Analysis*

Boring Logs

7 December 2010

Making Soil Description that are
Complete, Accurate and Effective

Webinar featuring Dan Kelleher, PG, CIPM and Ken Bradbury, PhD, PG

ROCK CORE LOGGING FOR HYDROGEOLOGIC PROJECTS

10 December 2010

Assessing Recovery, RQD, Fractures and Stratigraphy

Webinar Featuring
C.W. Fetter, Jr., PhD, Author of *Applied Hydrogeology* and *Contaminant Hydrogeology*

How to be an Effective Expert Witness

11 January 2011

for Environmental & Engineering Professionals