MNA of Metals and In Situ Bioremediation

Richard T. Wilkin and Robert G. Ford
Outline of Topics

• Introduce MNA Framework Document for Inorganics in Ground Water
• Regional Training and Technical Assistance Activities
• Overview of In Situ Bioremediation for Inorganics
  – Strategies for Degradable versus Non-degradable Contaminants
• Research Activities
Acknowledgments - MNA

- Ron Wilhelm (OAR/ORIA)
- David Bartenfelder, Stuart Walker, Matthew Charsky, Ken Lovelace (OSWER/OSRTI)
- Robert Puls, Steve Acree, Chunming Su, Ann Azadpour-Keeley, Kirk Scheckel (ORD)
- Steve Mangion (Region 1)
- Pat Brady (Sandia NL), Craig Bethke (U. Illinois), Jim Amonette (Pacific Northwest NL), Paul Bertsch (Savannah River NL), Doug Kent (USGS), Dan Kaplan (Savannah River NL)
OSWER Directive 9200.4-17P

Concepts described in Directive:

- Stable or shrinking plume
- Source control measures
- Identify mechanism(s) of attenuation
- Demonstrate irreversibility of attenuation process ("sorption") – recognizes that many inorganic contaminants will persist in subsurface
Generalized Site Scenario

Contaminant Release

Seepage into Surface Water

Water Supply Well

Contaminant Plume

Contaminant Concentration (above MCL or ARAR)

High

Low
1. Reduce contaminant flux in subsurface...

2. Use of MNA to remediate dilute portion of plume...

Source Removal/Isolation

In-Situ Treatment (ISB, PRB)

MNA

Contaminant Concentration (above MCL or ARAR)

High

Low

Contaminant Plume
Conceptual Distinction for Inorganic vs. Organic contaminants

Organic

Original Plume Boundary
Mobile Contaminant
Immobile Contaminant

Inorganic

Mobile plume shrinkage due to degradation or immobilization onto aquifer solids

Immobilized inorganic contaminant still present on aquifer solids
Contrast with MNA for Organics

- Existing protocols do not include metals and metalloids
- “Immobilization” will likely dominate over “transformation” (with some exceptions…)
  - Nitrate/perchlorate reduction
  - Radioactive decay
- Non-destructive mechanisms necessitate extensive characterization
  - Q: Where did the contaminant go?
- Few “complete” case studies
Volume I – Technical Basis

- Regulatory Overview
- Tiered Analysis Approach (TAA)
- Role of Modeling in TAA
- Technical Basis for NA in Ground Water
- Site Characterization to Support Evaluation of MNA
Tiered Analysis Approach

Tier 1: Evaluation of plume stability

Tier 2: Evaluation of rate and mechanism(s) of attenuation

Tier 3: Demonstrate capacity & stability

Tier 4: Development of long-term monitoring plan, contingencies
Impacts of Improper Preservation of In-situ Mineralogy/Microbiology

• Transformations in sediment mineralogy
  ➢ Misleading identification of mineral(s) controlling contaminant immobilization
  ➢ Changes in chemical speciation of contaminant(s) leading to misidentification of attenuation process(es)

• Loss of viable organisms that can be cultured to determine microcosm degradation rates
Ground Water Issue Paper

Mineralogical preservation of solid samples collected from anoxic subsurface environments

(http://www.epa.gov/ada/publications/html)

EPA/600/R-06/112

Study Parameters:

- Examine preservation methods
- Evaluate & develop freezing protocol
- Iron, Sulfur, and Arsenic

Introduction

Solid-phase samples may be collected for physical, chemical, or biological testing, although characterization and morphological parameters may also be studied. This study focused on examining physical and chemical properties of solid-phase samples, including their preservation under anoxic conditions. Solid-phase samples were collected from anoxic subsurface environments, where they undergo complex transformations. Under these conditions, solid-phase samples may exhibit unique properties that are not observed in aerobic environments. Therefore, understanding the preservation of solid-phase samples is crucial for interpreting environmental data accurately.}

Background

Preservation of solid-phase samples is essential for determining their physical and chemical properties. Under anoxic conditions, solid-phase samples may undergo significant transformations. Thus, it is crucial to develop effective preservation methods to maintain their integrity. In this study, we examined various preservation methods to determine their effectiveness in maintaining the physical and chemical properties of solid-phase samples. Additionally, we evaluated and developed a freezing protocol to improve the preservation of solid-phase samples under anoxic conditions.
Comparison of Preserved versus Unpreserved Adsorption Tests

Uptake capacity of As (unpreserved > preserved)
Uptake capacity of Zn (preserved > unpreserved)
Volume II – NA of Non-Rads

- Reviews on As, Cd, Cr, Cu, Pb, Ni, NO₃, ClO₄, and Se
- Occurrence and Distribution
- Geochemistry & NA Processes
- Site Characterization
- Long-Term Stability & Capacity
- Tiered Analysis
- References
**Arsenic – Chemical Characteristics**

- **Inorganic and organic forms (methylated and organosugars)**
- **Inorganic forms most common** – typically present as negative or neutral ions in GW
- **Arsenic bound to O and/or S in aqueous and solid species**
- **Microbial oxidation-reduction documented for inorganic forms**
- **Microbial methylation-demethylation possible, but less common in GW**

**Oxic**
- **Aqueous** → $\text{H}_3\text{As(V)}\text{O}_4$
- **Solid** → $\text{As}_2\text{O}_5$, $\text{FeAsO}_4$

**Iron Reducing**
- $\text{H}_3\text{As(III)}\text{O}_3$
- $\text{As}_2\text{O}_3$

**Sulfate Reducing**
- $\text{H}_3\text{As(III)}\text{S}_3$
- $\text{As}_2\text{S}_3$
Arsenic Attenuation

1) **Coprecipitation** commonly occurs near plume edge where there is rapid change in redox.

2) **Adsorption** is more prevalent at pH<7, since As is anionic and mineral surfaces neutral or positively charged.

<table>
<thead>
<tr>
<th><strong>Im mobilization Mechanism</strong></th>
<th><strong>Types of Solid Species</strong></th>
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<tbody>
<tr>
<td>Precipitation</td>
<td>Metal arsenates/arsenites Sulfides</td>
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<tr>
<td>Coprecipitation</td>
<td>Trace component in oxyhydroxides or sulfides of Fe and Mn</td>
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<tr>
<td>Adsorption</td>
<td>Surfaces of iron oxyhydroxides, iron sulfides, clay minerals</td>
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</table>
Arsenic - Precipitation

Direct precipitation not anticipated except at very high As concentrations.

Stability region for these precipitates does not overlap significantly with common Eh-pH range for GW.
Arsenic Adsorption

Aqueous As

Aquifer Fe-bearing Minerals

- Adsorption of arsenic in aquifers shows a common link to the abundance of Fe-bearing minerals
- Ferric oxyhydroxides (ferrihydrite, goethite) in oxic conditions
- Ferrous sulfides (mackinawite, pyrite) in sulfate-reducing conditions
- As mobility highest under Fe-reducing conditions in the absence of sulfate reduction
Arsenic – Characterization Data

- **Geochemical characteristics of GW – especially “redox condition” & pH**
  - Changes in these parameters may dictate re-mobilization (solid phase dissolution, As speciation)

- **Mineralogical composition of aquifer**
  - Solid phase association critical for understanding capacity & stability

- **Chemical speciation of arsenic**
  - As(V) & As(III) oxyanions common, but others can be significant (thioarsenic, organoarsenic)

![Plume around ZVI PRB](chart.png)
Arsenic – Sample Integrity

Solid samples – preservation of redox condition
- Oxygen exposure usually most critical

Water samples (laboratory or field analysis)
- Prevent precipitation of dissolved constituents, e.g., Fe(II)
- Preserve arsenic speciation
  1) Minimize air exposure
  2) Acidify, unless sulfide present (precipitates As$_2$S$_3$)
  3) Filter and light exclusion (microbial, photocatalyzed reactions)

Field methods for species analysis and/or separation are available, but need to be tested under site-specific conditions.

Region 4 (Atlanta, GA) June 19, 2007  
Presenters: Steven Acree (ORD-Ada), Robert Ford (ORD-Cincinnati)  
Coordinator: Felicia Barnett (ORD/OSP STL)

Region 5 (Chicago, IL) July 31, 2007  
Presenters: Steven Acree (ORD-Ada), Robert Ford (ORD-Cincinnati)  
Coordinator: Charles Maurice (ORD/OSP STL)

Region 8 (Denver, CO; Helena, MT videoconference) August 2, 2007  
Presenters: Rick Wilkin (ORD-Ada), Steven Acree (ORD-Ada)  
Coordinator: Brian Caruso (Chief – Wetlands & Watershed Unit)

Region 1 (North Chelmsford, MA) September 10, 2007  
Presenters: Randall Ross (ORD-Ada), Robert Ford (ORD-Cincinnati)  
Coordinator: Steve Mangion (ORD/OSP STL)
# ORD Workshop Synopsis

## who attended

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<tr>
<th>Region 4</th>
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<td>28 Regional Office Staff</td>
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<tr>
<td>8/8 State Offices (23 Staff)</td>
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<tr>
<td>4 Georgia</td>
<td>3 Tennessee</td>
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<tr>
<td>4 Kentucky</td>
<td>1 North Carolina</td>
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<td>3 South Carolina</td>
<td>2 Mississippi</td>
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<td>5 Alabama</td>
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<td>2 Wyoming</td>
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<td>1 Region 3</td>
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<td>4/6 State Offices (18 Staff)</td>
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<td>11 Massachusetts</td>
<td>4 New Hampshire</td>
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<tr>
<td>2 Connecticut</td>
<td>1 Rhode Island</td>
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In Situ Bioremediation for Metals

- MNA Principles: F&T, Site Characterization, Monitoring
- Maximizing Rates & Capacity
- Control & Manipulation of the Subsurface
- Redox Manipulation
  - Direct biodegradation
  - Indirect biogeochemical process, solubility
- Related technologies: PRBs, In situ injections
  - Delivery of Substrate
Microbial sulfate reduction and metal attenuation in pH 4 acid mine water

EPA-USGS
IAG at Penn Mine (CA)

Geochemical Transactions, 2007, v. 8

Geochemistry
Stable Isotopes (S, C, O)
Dissolved gases
Molecular Biology
Solid Phase Studies

ZnS spherule
Biogenic

DGGE scans
In–Situ Biodegradation

- System Characterization & Design Tree Approach
- Design and Testing
- Monitoring and Evaluation
- Inorganics: nitrate and perchlorate

PRB Installation/Biowall for Nitrate
Nitrate

- Average % removal ranges from 42 (T1) to 91 (T2), based on influent & effluent
- Nitrate removal within PRB is 92 – 100%
- Transect 1 PRB wells show subtle increases in nitrate starting at 35 months; no nitrate detection in Transect 2 PRB wells
- Declining source term?
Denitrification

\[ 2\text{NO}_3^- \rightarrow 2\text{NO}_2^- \rightarrow 2\text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]

Nitrate ions (+5) \nNitriTE ions (+3) \nNitric oxide (+2) \nNitrous oxide (+1) \nDinitrogen gas (0)

Dissimilatory Nitrate reduction to ammonia (under low electron acceptor conditions, i.e., C>>>NO_3^-)

\[ 2\text{NH}_4^+ \]

Denitrification trend
Heterotrophic Denitrification

\[ 5CH_2O + 4NO_3^- = CO_2 + 2N_2 + 3H_2O + 4HCO_3^- \]

Mean DOC values in transect wells, \( n = 14 \)

Decrease in capacity from \(~2200\) to \(38\) mg/L Nitrate-N to \(N_2\), based on reaction stoichiometry
Biodegradation - perchlorate

Wilkin et al. (2007)
Indirect Biogeochemical Process

- Carbon/Sulfate addition to drive SR
- Low solubility of, e.g., Pb, Cd, Ni, Zn, & Cu sulfides.
- Precipitation as MeS or
- Precipitation of FeS and metal/metalloid interaction
Metal Sulfide Solubility

pH 6

$log \text{Me}^{2+} (M)$ vs $log \text{H}_2\text{S} (M)$

- $\text{Ni}^{2+}$
- $\text{Zn}^{2+}$
- $\text{Pb}^{2+}$
- $\text{Cd}^{2+}$
- $\text{Cu}^{2+}$

MCLs

NA ISB

$\text{Cu}$ $\text{Pb}$ $\text{Cd}$
Arsenic Sulfide Solubility

Contrasting Behavior of As

Multiple Factors:
- pH
- Total Sulfide
- Arsenic speciation
- Surfaces
In Situ Injections

- Calcium Polysulfide
- Sodium Dithionite
- Ferrous Sulfate
- Sodium Phosphate
- Aluminum Hydroxide
- Zerovalent Iron
  - Precipitation
  - Adsorption
Tiered Analysis Approach

Tier 1: Evaluation of plume stability

Tier 2: Evaluation of rate and mechanism(s) of attenuation

Tier 3: Demonstrate capacity & stability

Tier 4: Development of long-term monitoring plan, contingencies
Final Remarks

• Need for improved conceptual understanding of element behavior; biogeochemical processes
• Technology verification for inorganics
  – Where did the contaminant go?
• Improved: site characterization methods; sample characterization practices; model input parameters
• Coupling MNA with source control/in situ remediation
• Case studies