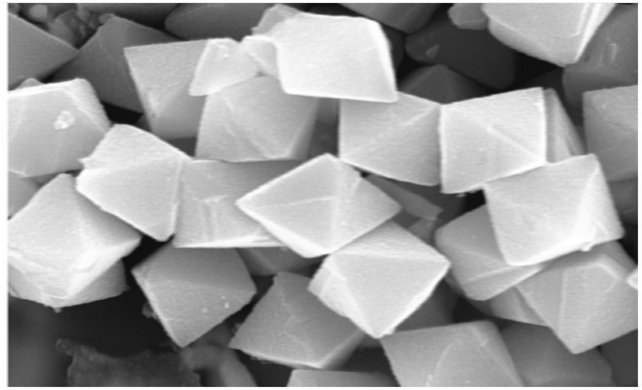
MNA of Metals and In Situ Bioremediation

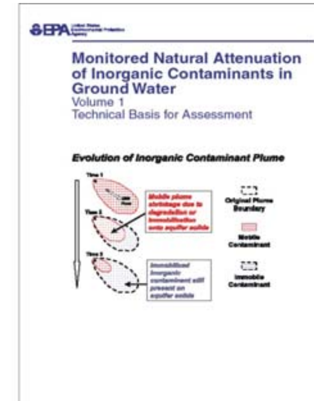
Richard T. Wilkin and Robert G. Ford



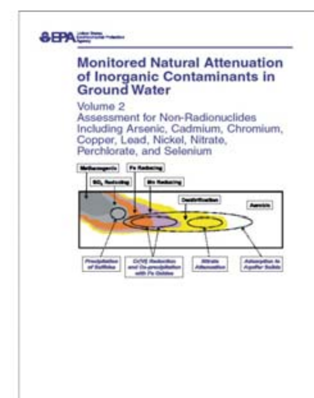
Office of Research and Development
National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, Ada, OK

November 15, 2007
Washington DC

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

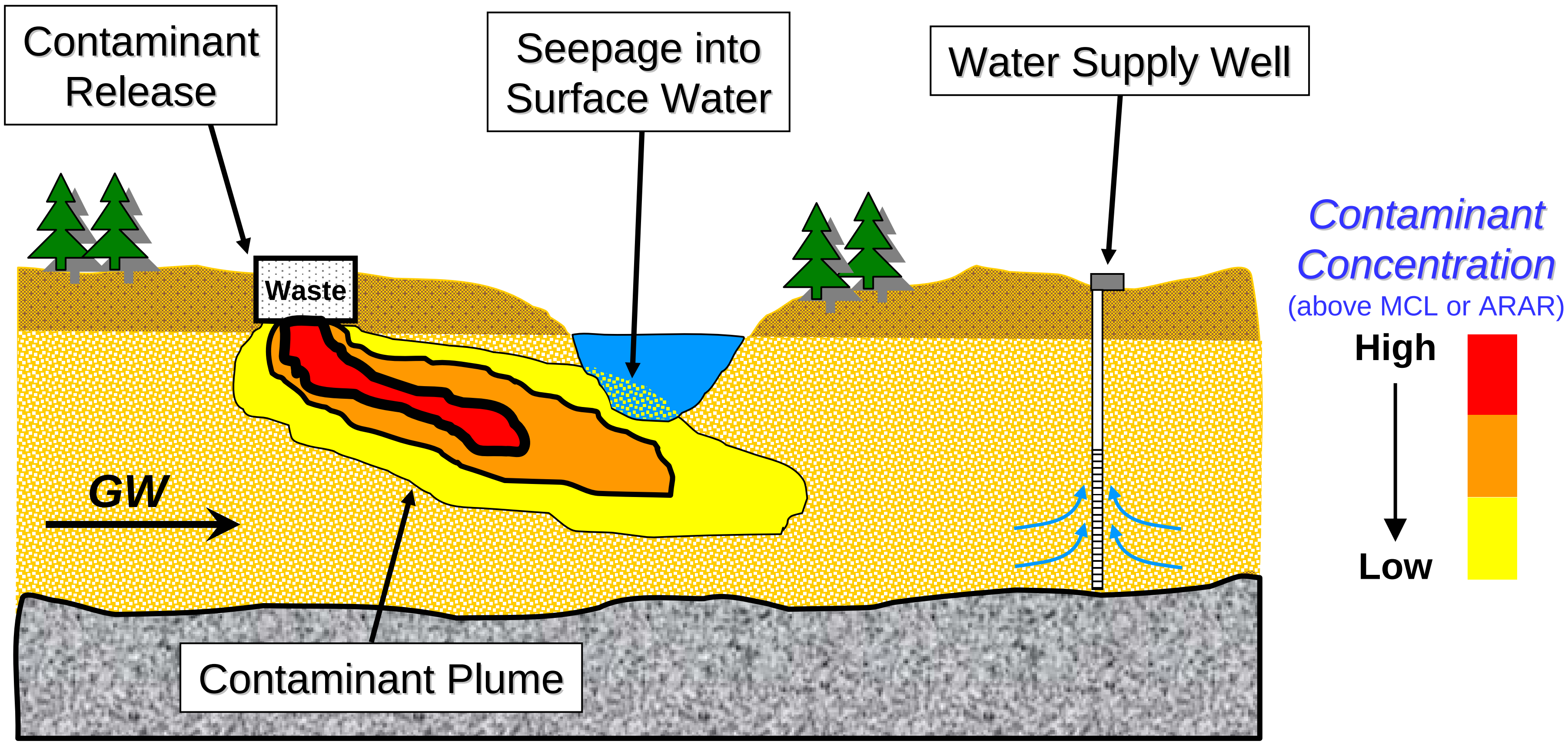
- Ron Wilhelm (OAR/ORIA)
- David Bartenfelder, Stuart Walker, Matthew Charsky, Ken Lovelace (OSWER/OSRTI)
- Robert Puls, Steve Acree, Chunming Su, Ann Azadpour-Keeley, Kirk Scheckel (ORD)
- Steve Mangion (Region 1)
- Pat Brady (Sandia NL), Craig Bethke (U. Illinois), Jim Amonette (Pacific Northwest NL),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

OSWER Directive 9200.4-17P

Concepts described in Directive:

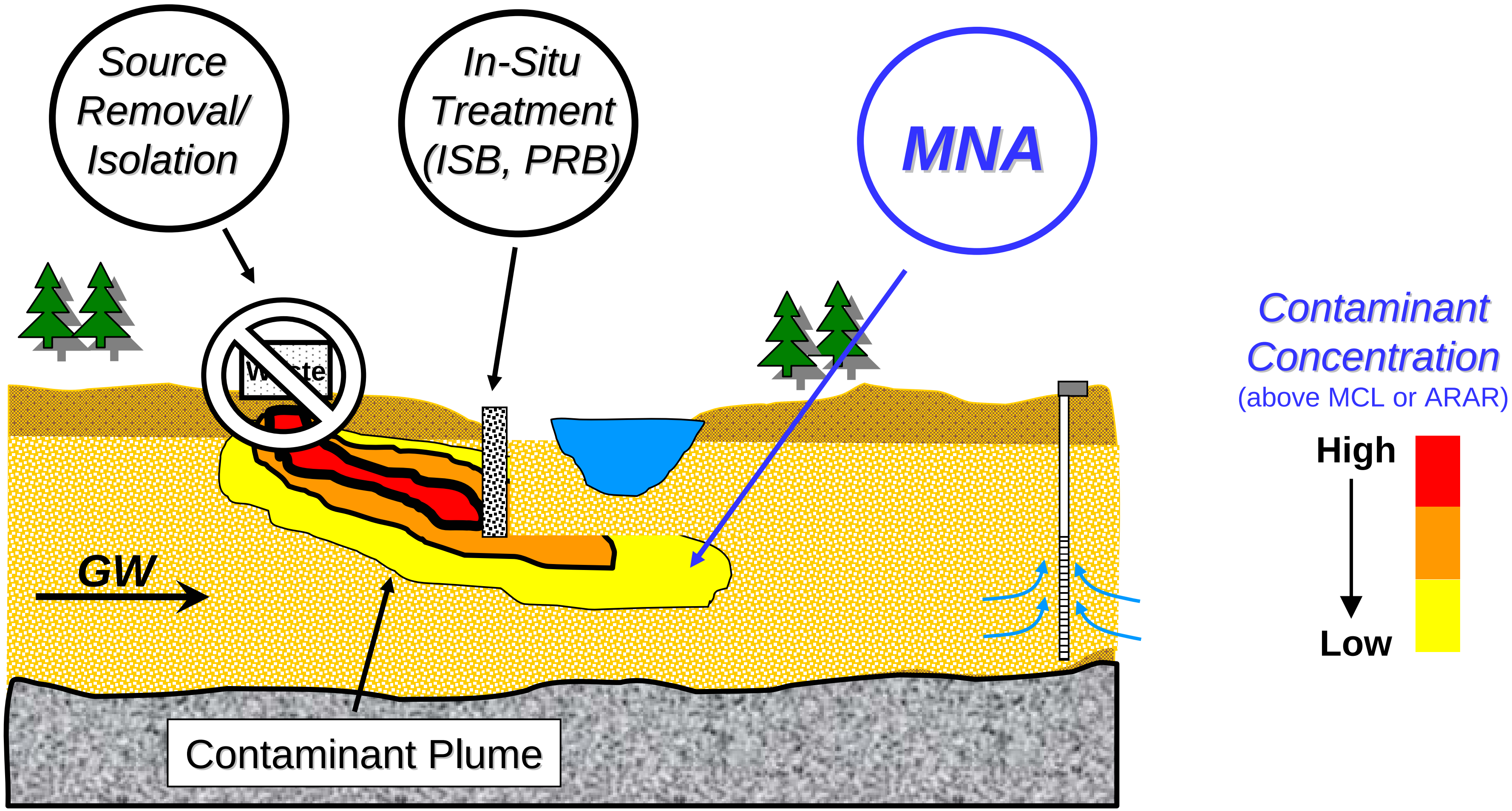
- Stable or shrinking plume
- Source control measures
- Identify mechanism(s) of attenuation
- Demonstrate irreversibility of attenuation process ("sorption") – *recognizes that many inorganic contaminants will persist in subsurface*

Generalized Site Scenario

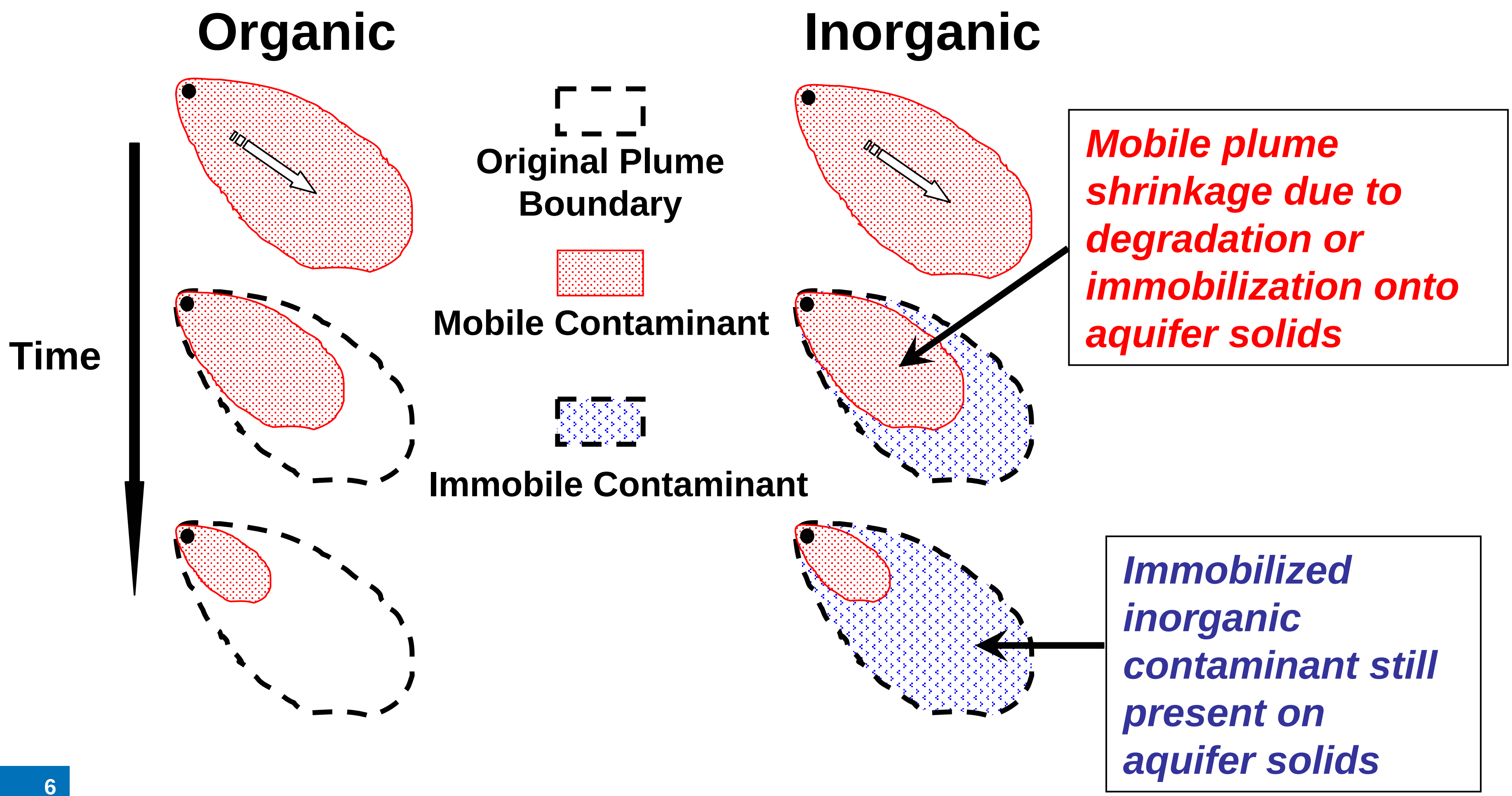


1 Reduce contaminant flux in subsurface…

2 Use of MNA to remediate dilute portion of plume…



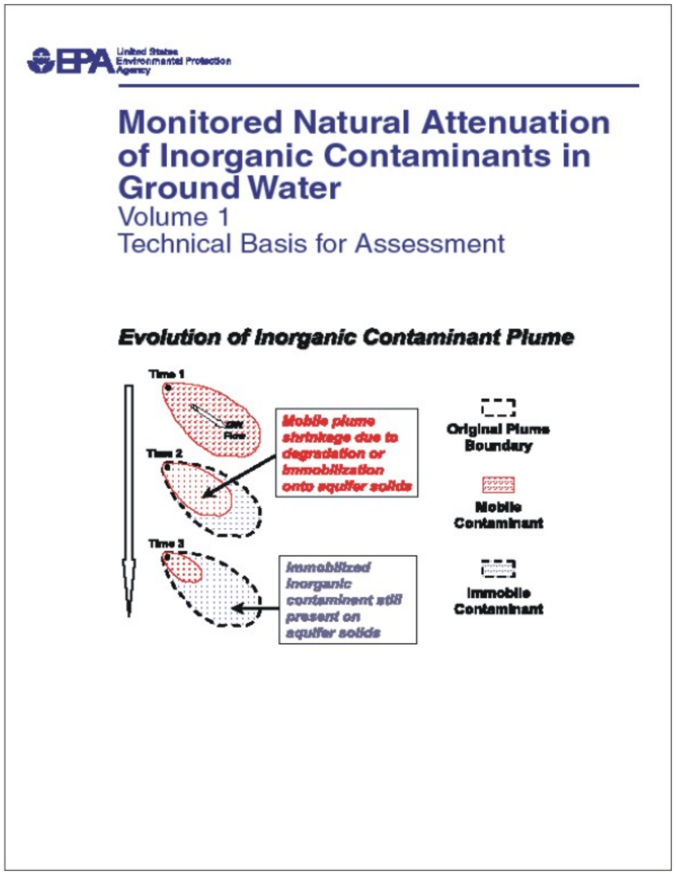
Conceptual Distinction for Inorganic vs. Organic contaminants



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

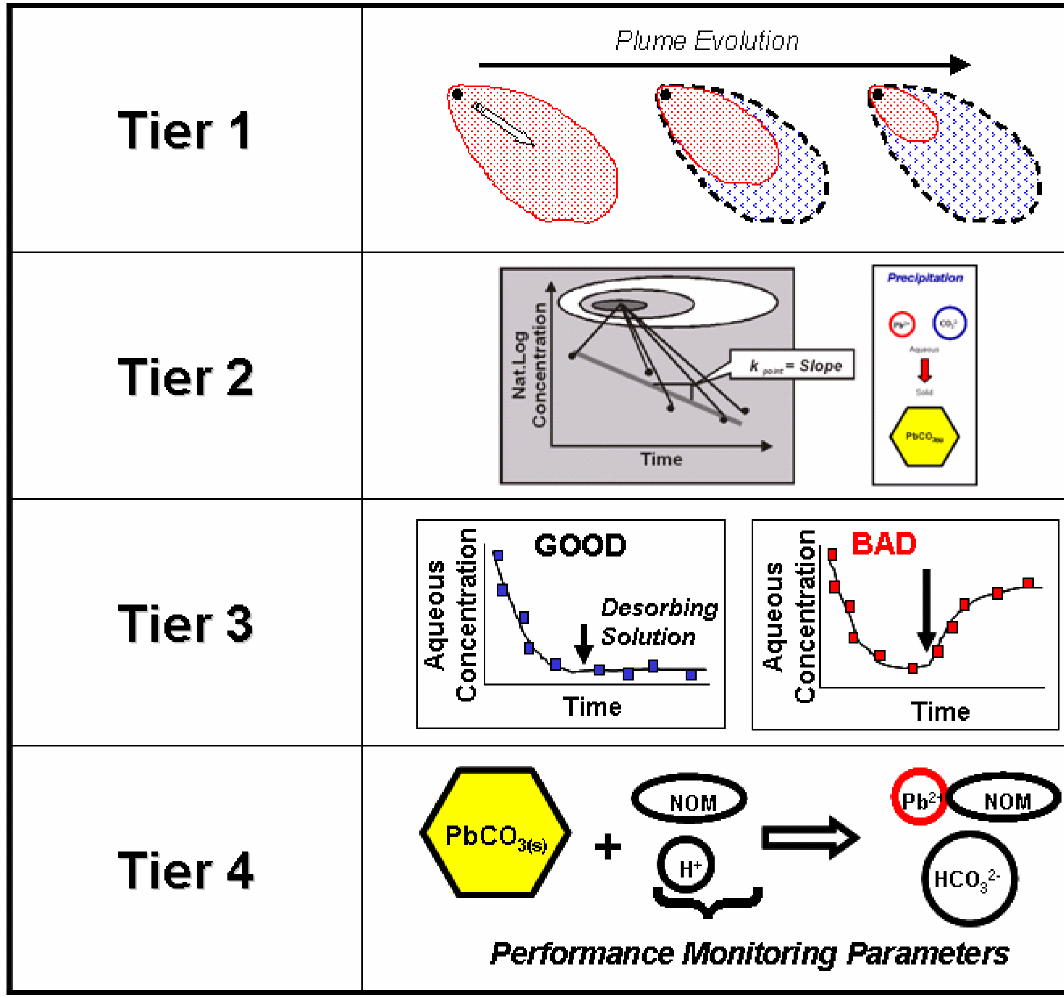
Tiered Analysis Approach

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



United States Environmental Protection Agency

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

EPA United States Environmental Protection Agency

Ground Water Issue

Mineralogical Preservation of Solid Samples Collected from Anoxic Subsurface Environments

Richard T. Wilkin

Background

Remedial technologies utilized at hazardous waste sites for the treatment of metal and metalloid contaminants often take advantage of reduction-oxidation (redox) processes to reach ground water clean up goals (Barcelona and Holm, 1991; U.S. Environmental Protection Agency, 2002). This is because redox reactions, in many cases, govern the biogeochemical behavior of inorganic contaminants by affecting their solubility, reactivity, and bioavailability. Site characterization efforts, remedial investigations, and long-term post-remedial monitoring often involve sampling and analysis of solids. Solid-phase studies are needed to evaluate contaminant partitioning to various mineral fractions, to develop site conceptual models of contaminant transport and fate, and to assess whether or not remedial mechanisms are occurring as expected. Measurements to determine mineralogical compositions, contaminant-mineral associations, and metal/metalloid uptake capacities of subsurface solids or reactive media used for *in situ* treatment of the subsurface all depend upon proper sample collection and preservation practices. This Issue Paper discusses mineralogical preservation methods for solid samples that can be applied during site characterization studies and assessments of remedial performance. A preservation protocol is presented that is applicable to solids collected from anoxic subsurface environments, such as soils, aquifers, and sediments.

The preservation method evaluated and recommended here for solids collected from anoxic environments involves sample freezing (-18 °C), transportation of frozen samples on dry ice, and laboratory processing of solids in an anaerobic glove box. This method was found to preserve the redox integrity of reduced iron- and sulfur-bearing compounds, which are typically predominant redox-sensitive inorganic constituents in environmental materials and are important in controlling contaminant behavior at hazardous waste sites. A selection of solid-phase measurements was carried out on preserved anoxic sediments collected from a contaminated lake and compared to identical measurements on sample splits in which no preservation protocol was adopted, i.e., the unpreserved samples were allowed to oxidize in ambient air. An analysis of results illustrates the importance of proper sample preservation for obtaining meaningful solid-phase characterization. This Issue Paper provides remedial project managers and other state or private remediation managers and their technical support personnel with information necessary for preparing sampling plans to support site characterization, remedy selection, and post-remedial monitoring efforts.

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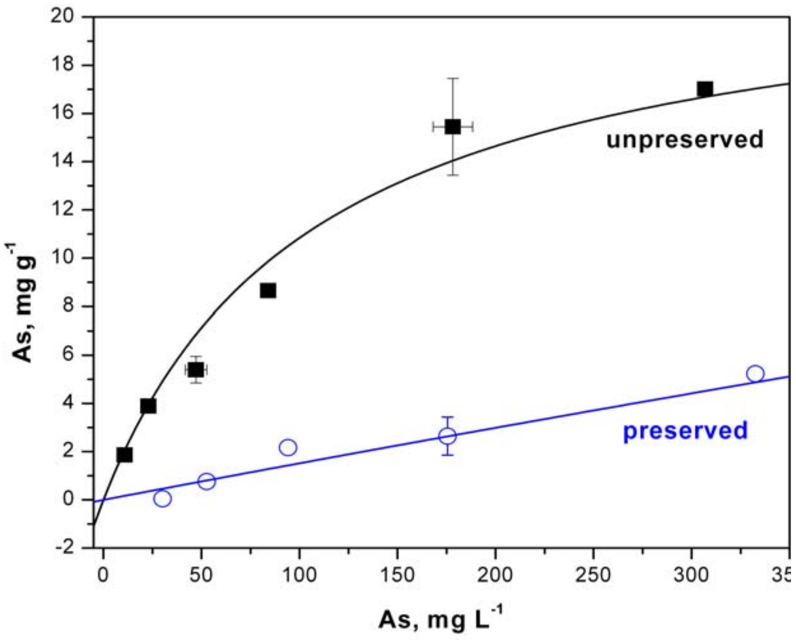
Introduction

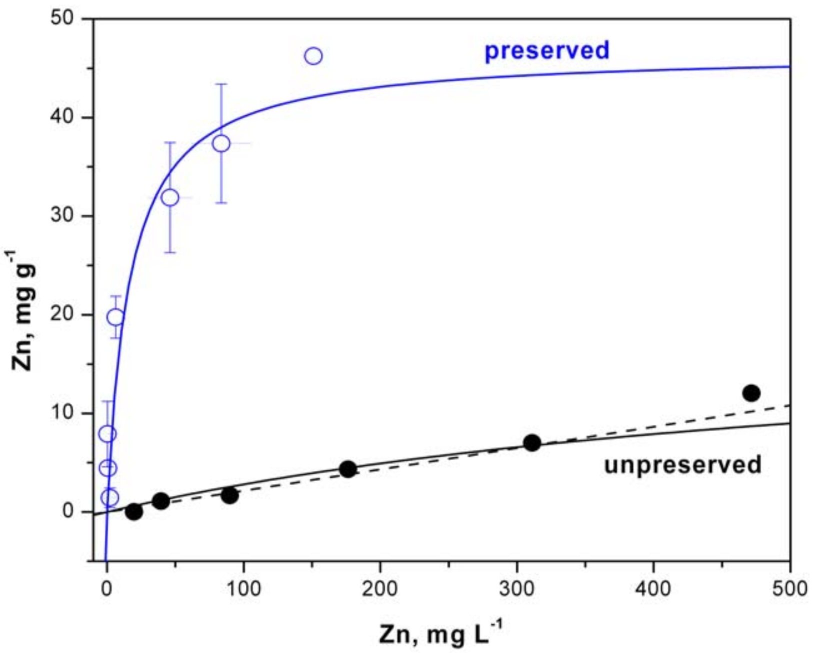
Solid phase samples may be collected for physical, chemical, or biological tests during site characterization and remedial performance monitoring studies. The principal objective of any sampling program is to collect and deliver materials to the laboratory that are representative of the original material present in the environment. If samples are collected for the purpose of determining total element concentrations, then the mode of preservation may not be important unless the contaminant is a volatile or semi-volatile component. However, when solid samples are collected for more sensitive or detailed analyses, such as sequential extraction tests, solid-phase speciation tests, or batch adsorption tests, preservation methods become critical and may direct the outcome of all subsequent analyses and interpretations. For samples collected from anoxic subsurface environments, oxidation is the primary reaction process that leads to unrepresentative samples. Therefore, proper sample preservation will ideally minimize the undesirable effects of oxidation. Unfortunately, the literature is not extensive on the assessment of procedures for handling anoxic materials. Lacking general guidance, sampling and preservation protocols are usually developed to best suit needs on a project-by-project basis.

Redox-sensitive elements commonly important in environmental studies include iron, manganese, sulfur, chromium, copper, uranium, and arsenic (U.S. Environmental Protection Agency, 2002). Reduction-oxidation processes involving iron and sulfur compounds, in particular, have significant impacts on the partitioning of metals to solids and these impacts must be considered when collecting and preserving field samples. For example, minerals containing ferrous iron (e.g., siderite, $FeCO_3$; mackinawite, FeS; pyrite, FeS_2) may undergo rapid oxidation reactions during air exposure and transform to ferric-iron phases (e.g., ferrihydrite, $Fe(OH)_3 \cdot nH_2O$; lepidocrocite, γ-FeOOH; goethite, α-FeOOH). Subsequently during batch adsorption tests or sequential extraction tests, ferric-bearing phases should behave differently than the original, unoxidized material representative of the natural environment. Oxidative mineral transformations may result in changes in reactive surface area, influence precipitation and co-precipitation reactions, and/or trigger different surface adsorption reactions. Similarly, sulfide minerals are in general highly susceptible to

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, 919 Kerr Research Drive, Ada, OK 74820 (wilkin.rick@epa.gov)

Comparison of Preserved versus Unpreserved Adsorption Tests

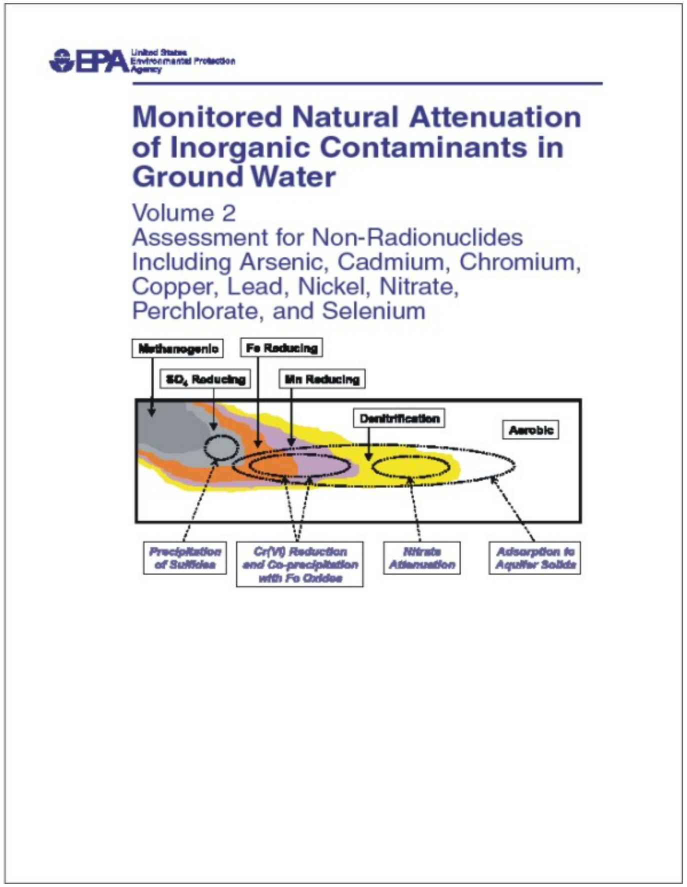




Uptake capacity of As (unpreserved > preserved)
Uptake capacity of Zn (preserved > unpreserved)

United States
Environmental Protection
Agency

Volume II – NA of Non-Rads


United States Environmental Protection Agency

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 2
Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium

- Reviews on As, Cd, Cr, Cu, Pb, Ni, NO_3, ClO_4, 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

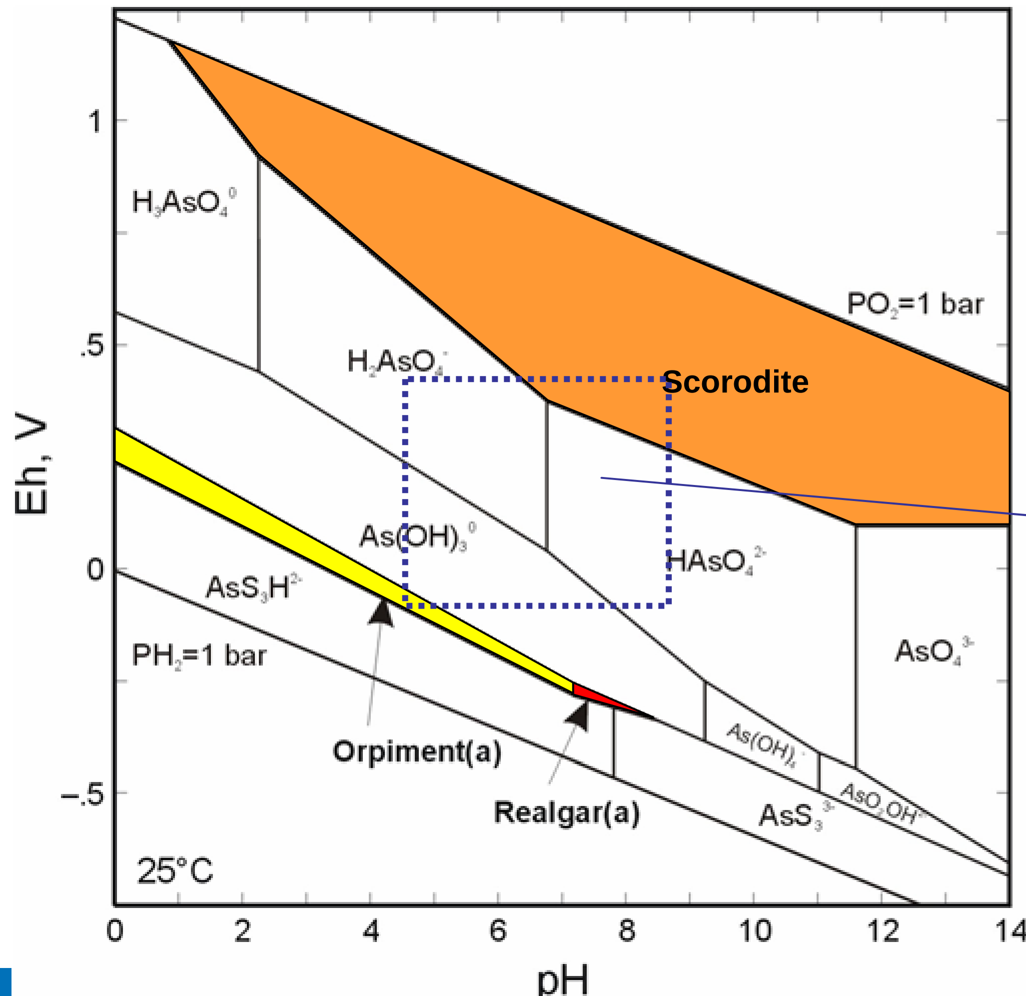
	Oxic	Iron Reducing	Sulfate Reducing
Aqueous →	$H_3As(V)O_4$	$H_3As(III)O_3$	$H_3As(III)S_3$
Solid →	As_2O_5, $FeAsO_4$	As_2O_3	As_2S_3

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

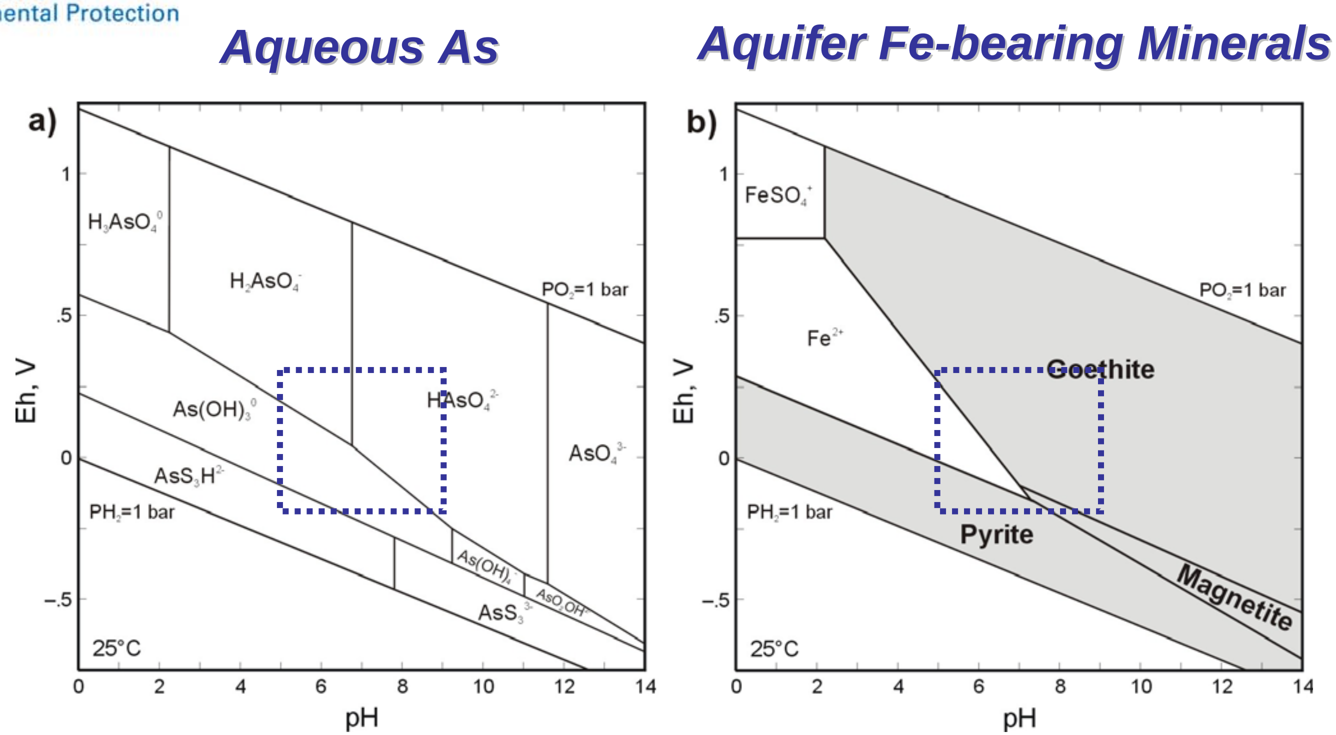
Immobilization Mechanism	*Types of Solid Species*
Precipitation	Metal arsenates/arsenites Sulfides
Coprecipitation	Trace component in oxyhydroxides or sulfides of Fe and Mn
Adsorption	Surfaces of iron oxyhydroxides, iron sulfides, clay minerals

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

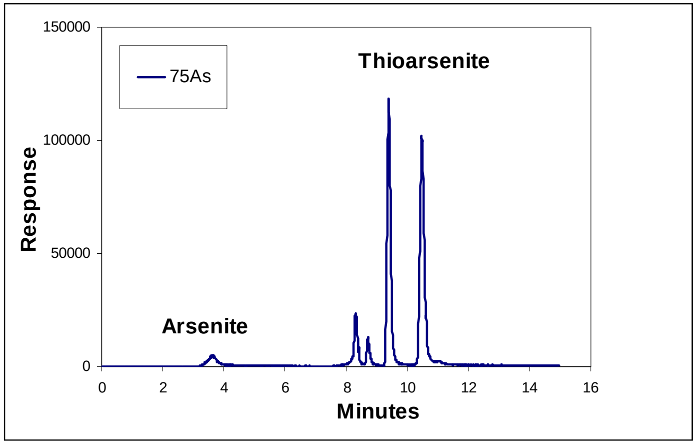
Arsenic - Adsorption



- 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

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_2S_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.

⇨ http://cluin.org/download/char/arsenic_paper.pdf

ORD Workshop Synopsis

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

Region 4 (51 total)
28 Regional Office Staff

8/8 State Offices (23 Staff)

4 Georgia	3 Tennessee
4 Kentucky	1 North Carolina
3 South Carolina	2 Mississippi
5 Alabama	1 Florida

Region 5 (33 total)
24 Regional Office Staff

3/6 State Offices (9 Staff)

4 Indiana	4 Wisconsin
1 Ohio	

Region 8 (33 total)
17 Regional Office Staff
1 USGS-EPA Liason

3/6 State Offices (15 Staff)

10 Colorado	3 Montana
2 Wyoming	

Region 1 (38 total)
19 Regional Office Staff
1 Region 3

4/6 State Offices (18 Staff)

11 Massachusetts	4 New Hampshire
2 Connecticut	1 Rhode Island

In Situ Bioremediation for Metals

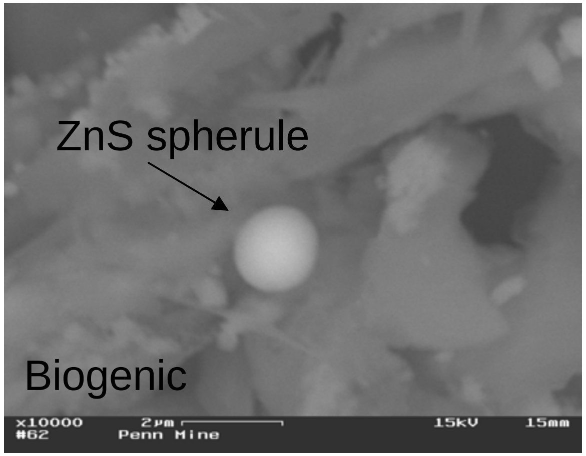
- MNA Principles: F&T, Site Characterization, Monitoring
- Maximizing Rates & Capacity
- Control & Manipulation of the Subsurface
- Redox Manipulation
  - Direct biodegradation
  - Indirect biogeochemical process, solubility
- Related technologies: PRBs, In situ injections
  - Delivery of Substrate

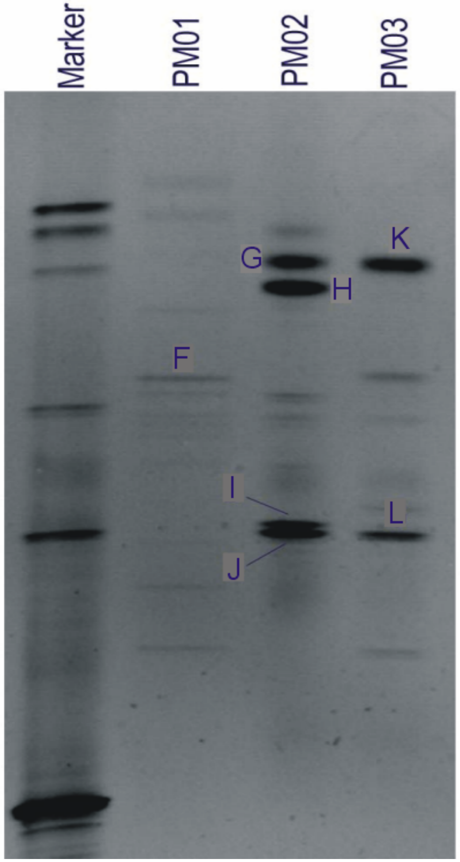
Microbial sulfate reduction and metal attenuation in pH 4 acid mine water

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

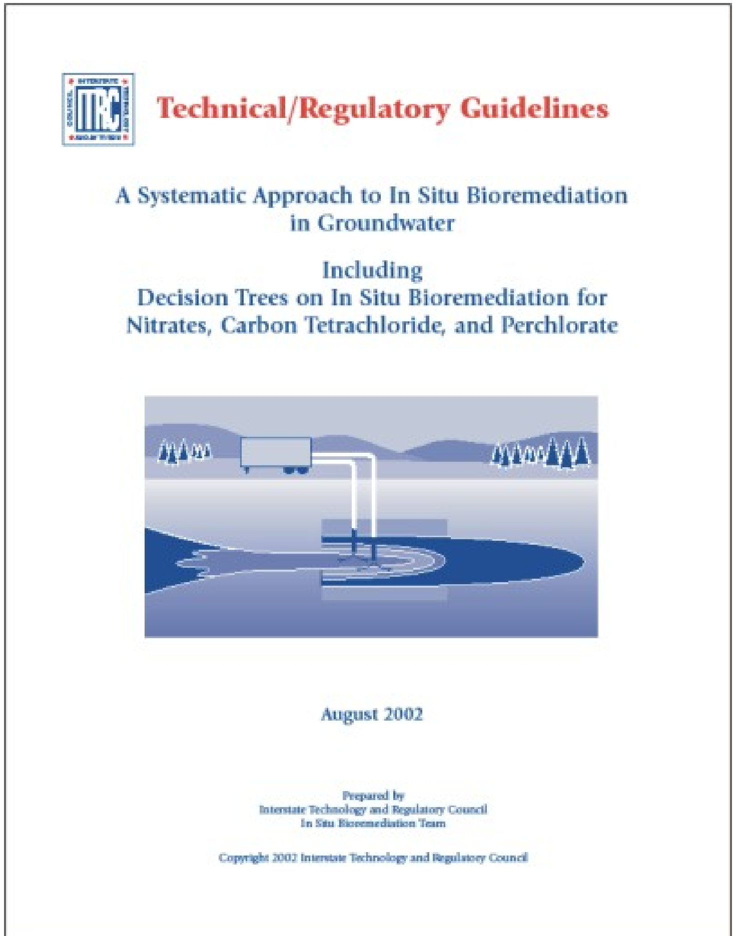




DGGE scans

United States
Environmental Protection
Agency

In–Situ Biodegradation


Technical/Regulatory Guidelines

A Systematic Approach to In Situ Bioremediation
in Groundwater

Including
Decision Trees on In Situ Bioremediation for
Nitrates, Carbon Tetrachloride, and Perchlorate

August 2002

Prepared by
Interstate Technology and Regulatory Council
In Situ Bioremediation Team

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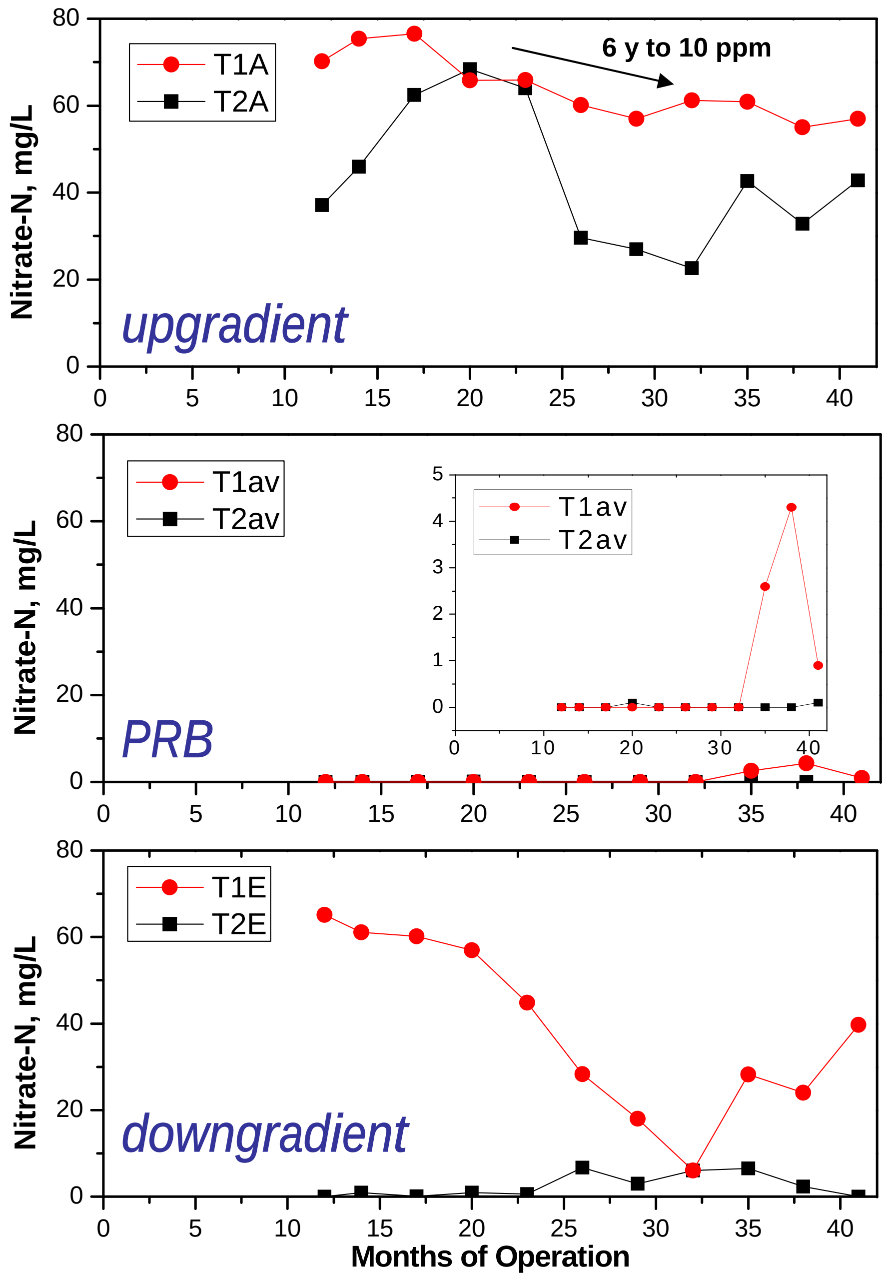
www.itrcweb.org/Documents/ISB-8.pdf

- 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?

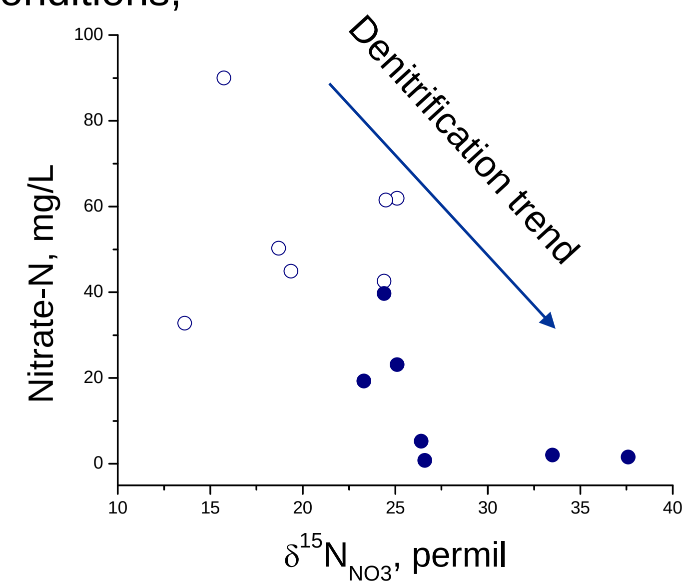
Denitrification

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2$$

Nitrate ions (+5)	Nitrite ions (+3)	Nitric oxide (+2)	Nitrous oxide (+1)	Dinitrogen gas (0)

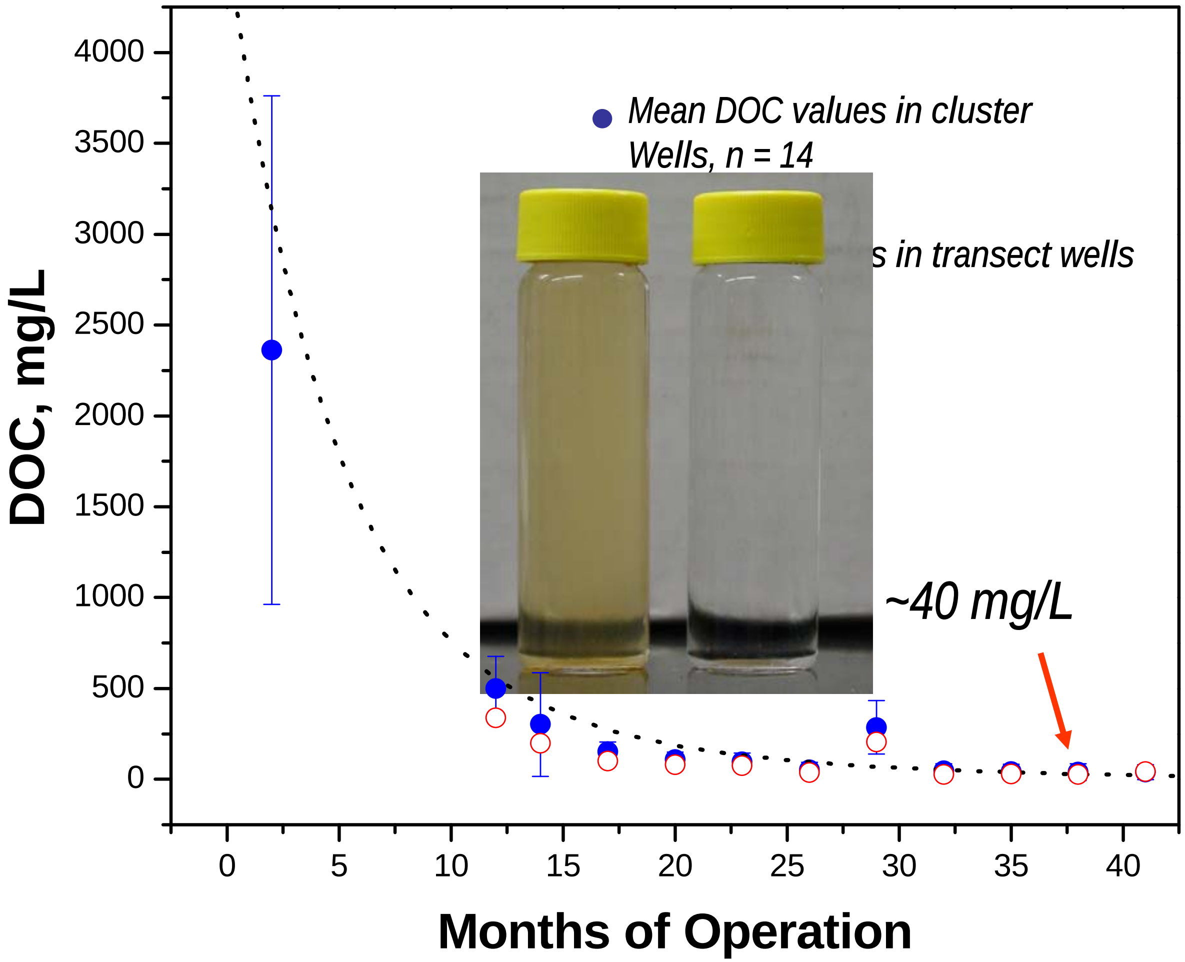
Dissimilatory
Nitrate reduction
to ammonia
(under low electron acceptor conditions, i.e., C>>>NO_3^-)

$$2NO_2^- \rightarrow 2NH_4^+$$



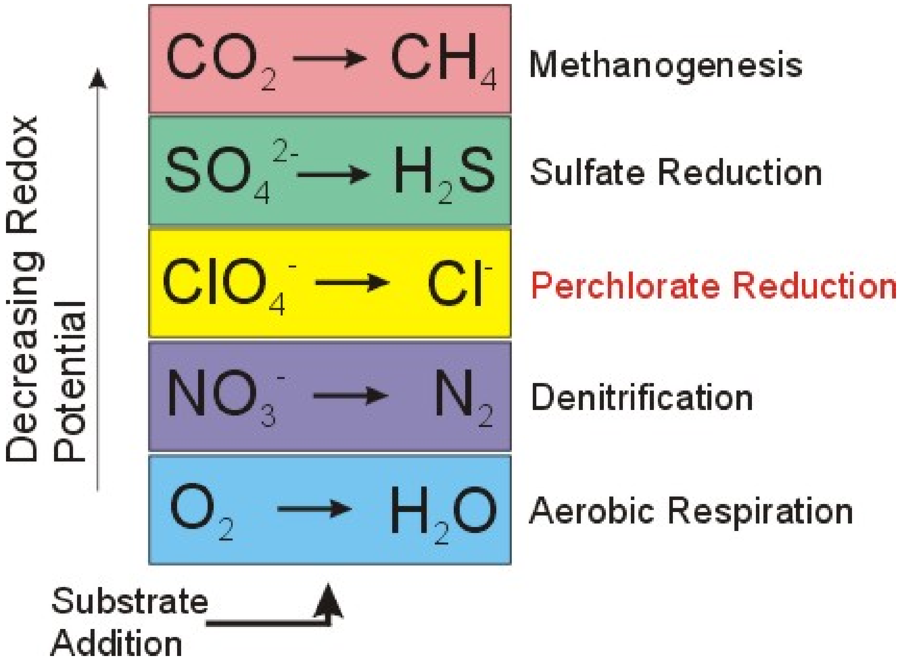
Heterotrophic Denitrification

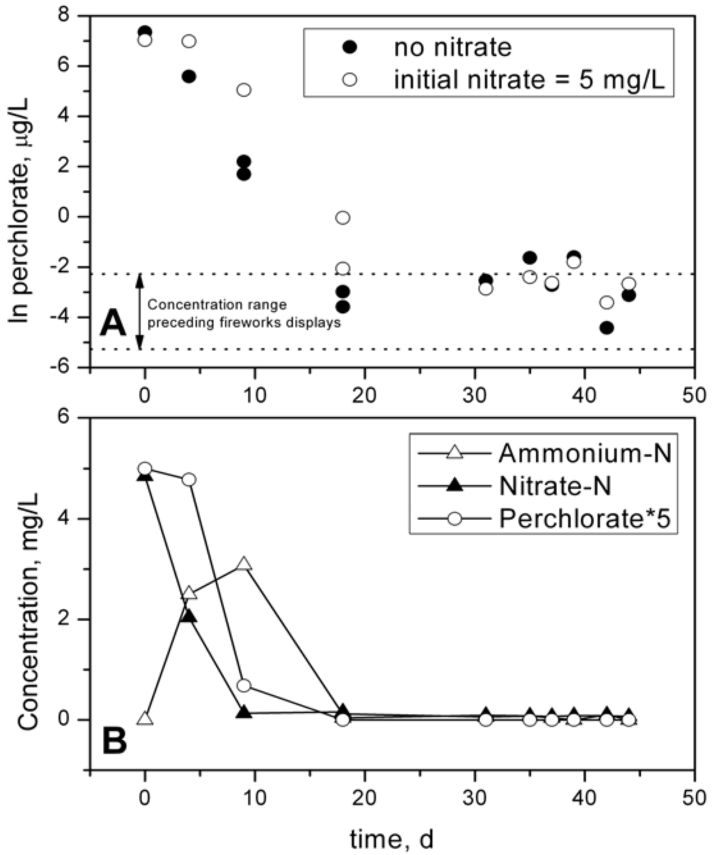
$$5CH_2O + 4NO_3^- = CO_2 + 2N_2 + 3H_2O + 4HCO_3^-$$



Decrease in capacity from ~2200 to 38 mg/L Nitrate-N To N_2, based on reaction stoichiometry

Biodegradation - perchlorate

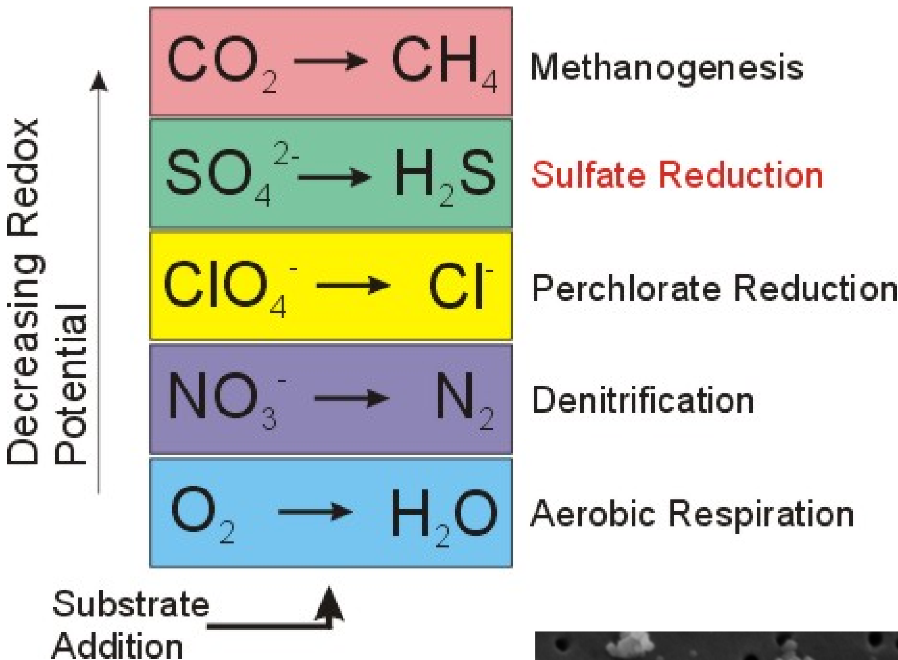




Wilkin et al. (2007)
ES&T, v. 41, p. 3966-3971.

EPA United States Environmental Protection Agency

Indirect Biogeochemical Process

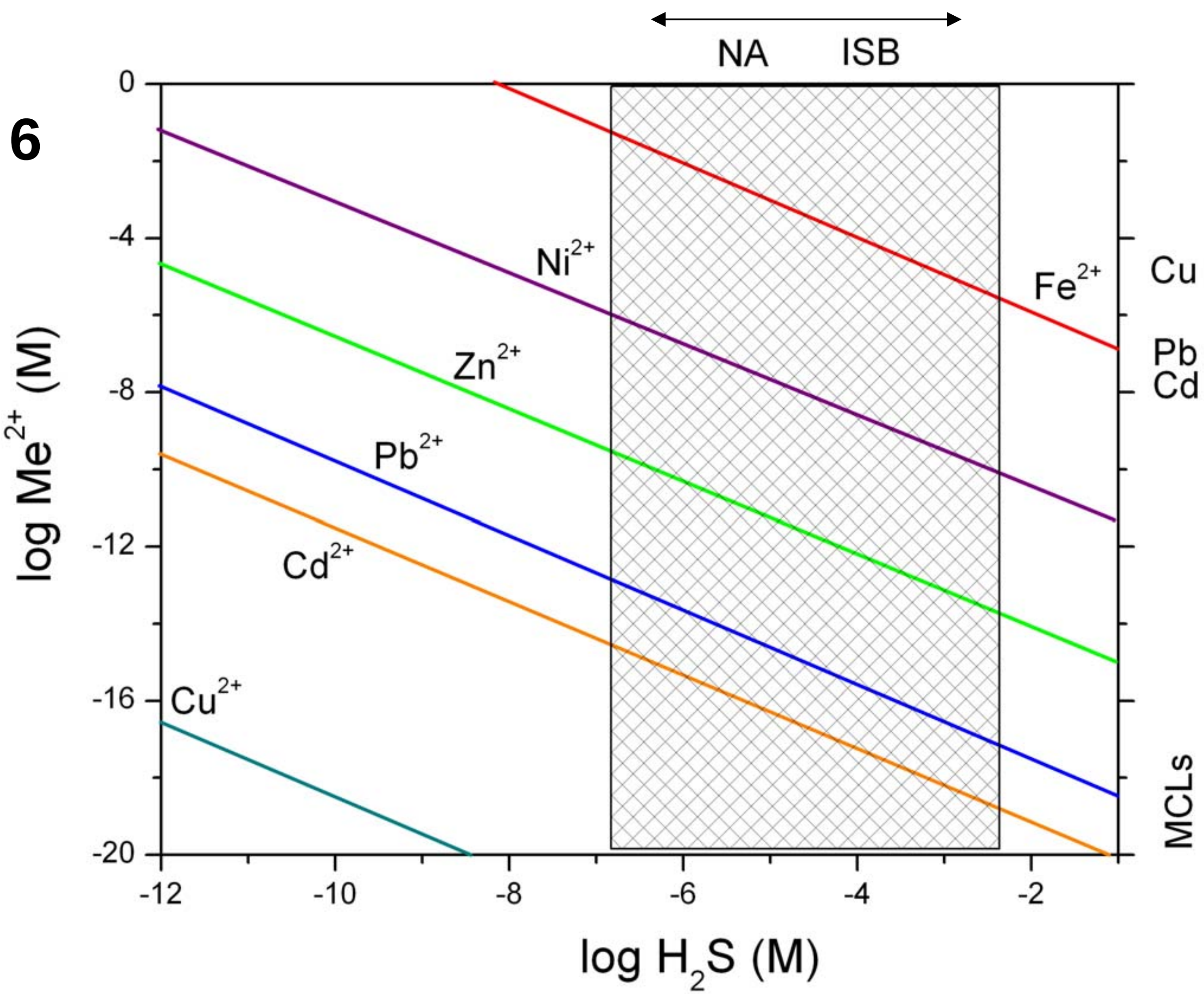


- Carbon/Sulfate addition to drive SR
- Low solubility of, e.g., Pb, Cd, Ni, Zn, & Cu sulfides.
- Precipitation as MeS or
- Precipitation of FeS and metal/metalloid interaction

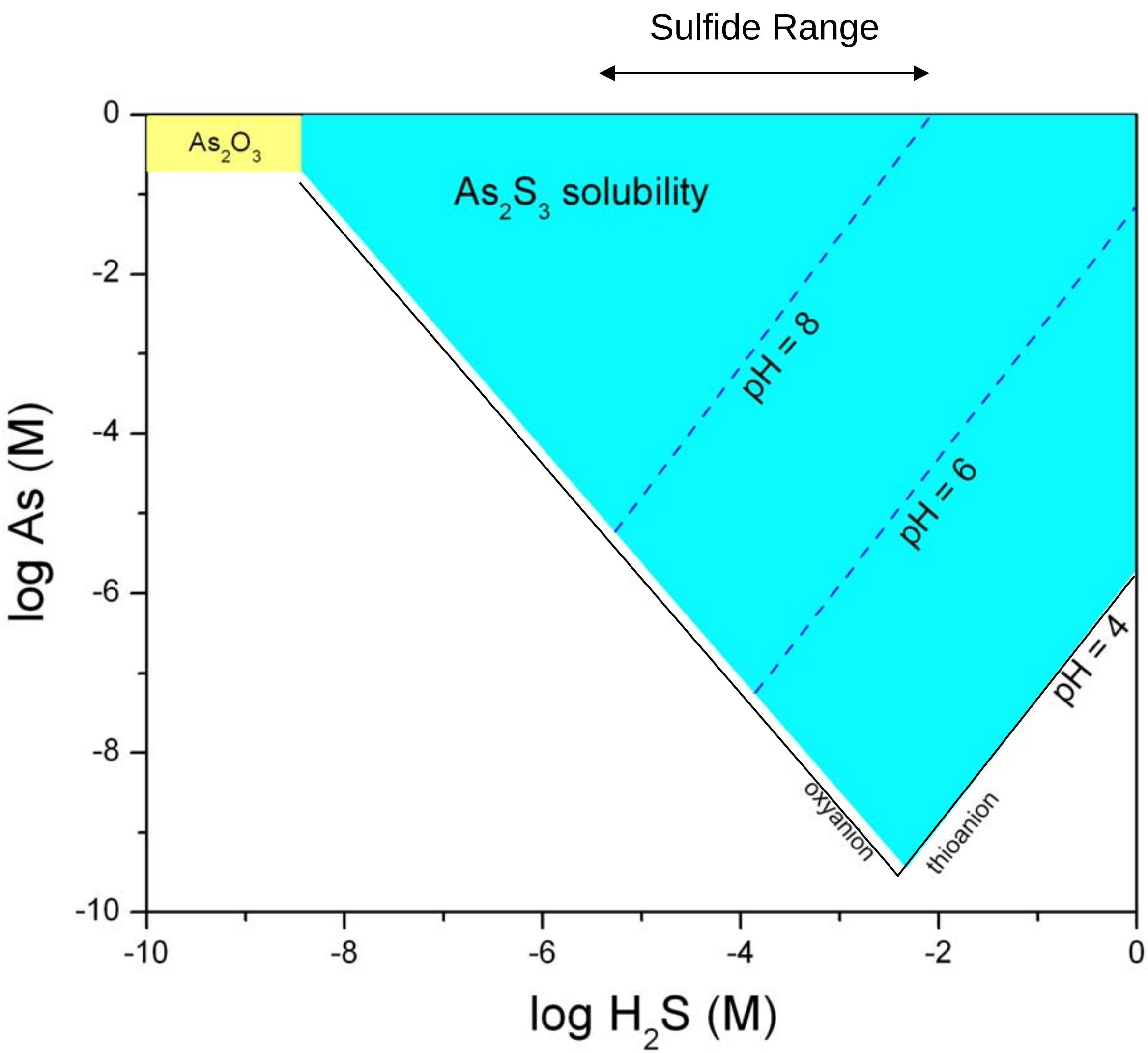
Desulfovibrio

Metal Sulfide Solubility

pH 6



Arsenic Sulfide Solubility



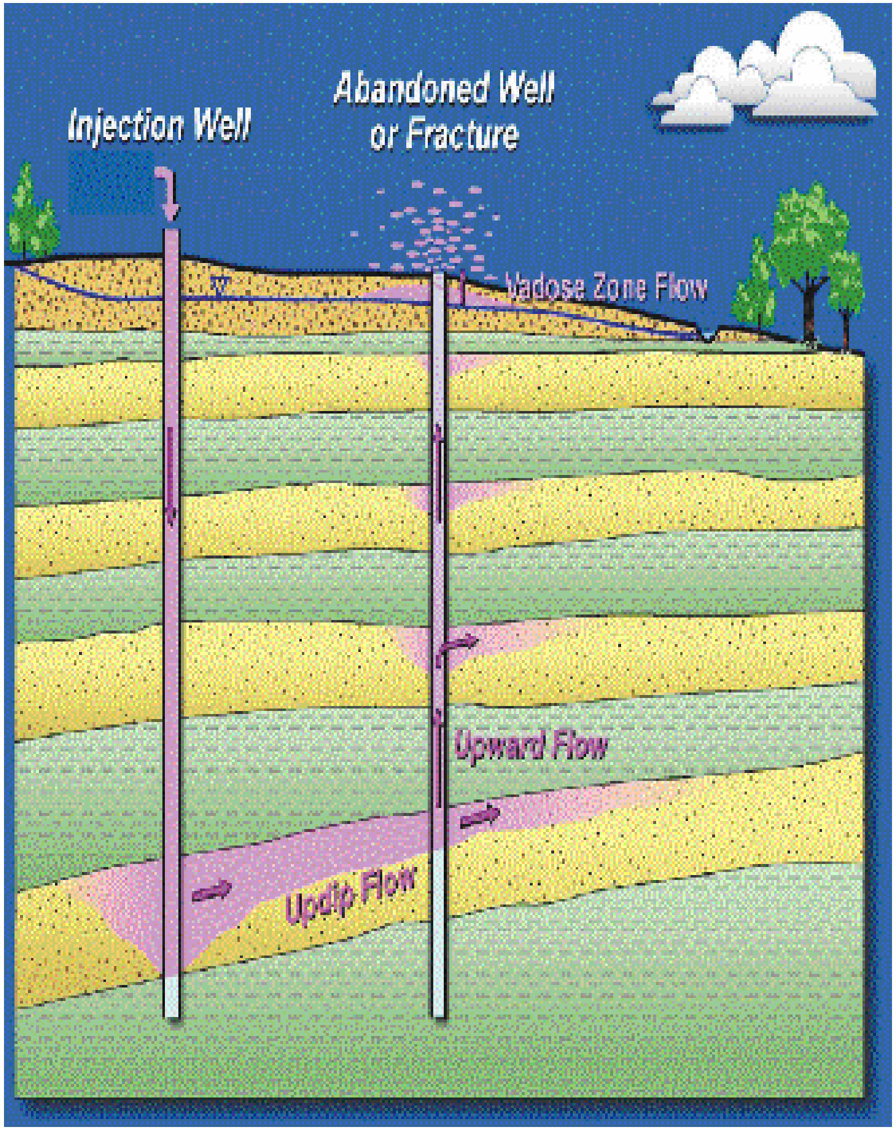
Contrasting Behavior of As

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

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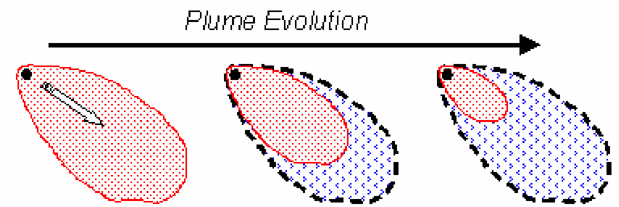
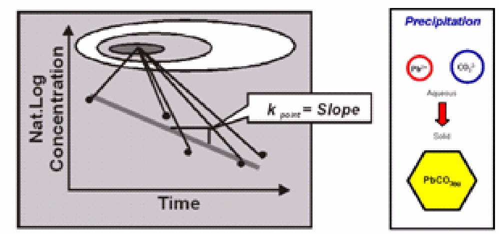
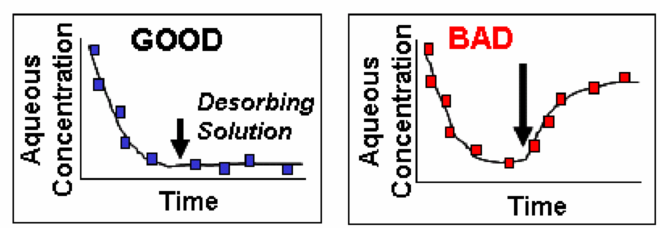
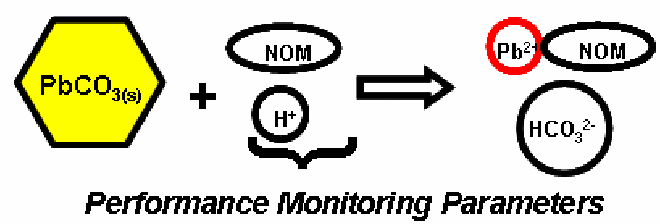
Tier 2: Evaluation of rate and mechanism(s) of attenuation

Tier 3: Demonstrate capacity & stability

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

Tier 1	
Tier 2	
Tier 3	
Tier 4	

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