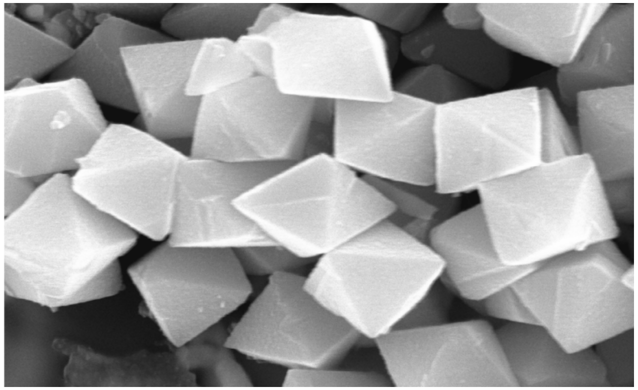
United States Environmental Protection Agency

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

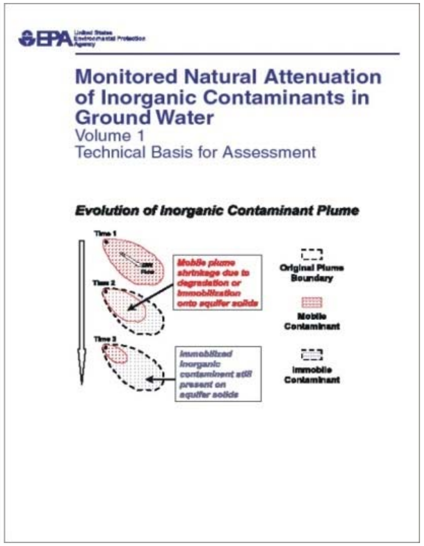


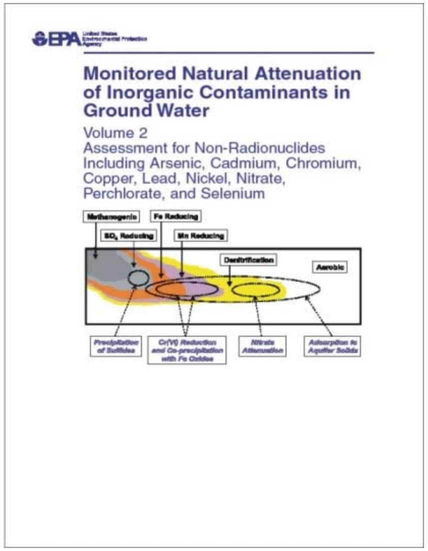
Richard T. Wilkin, U.S. EPA,
Office of Research and Development

MGWA
May 6, 2010
St. Paul, MN

Outline of Topics

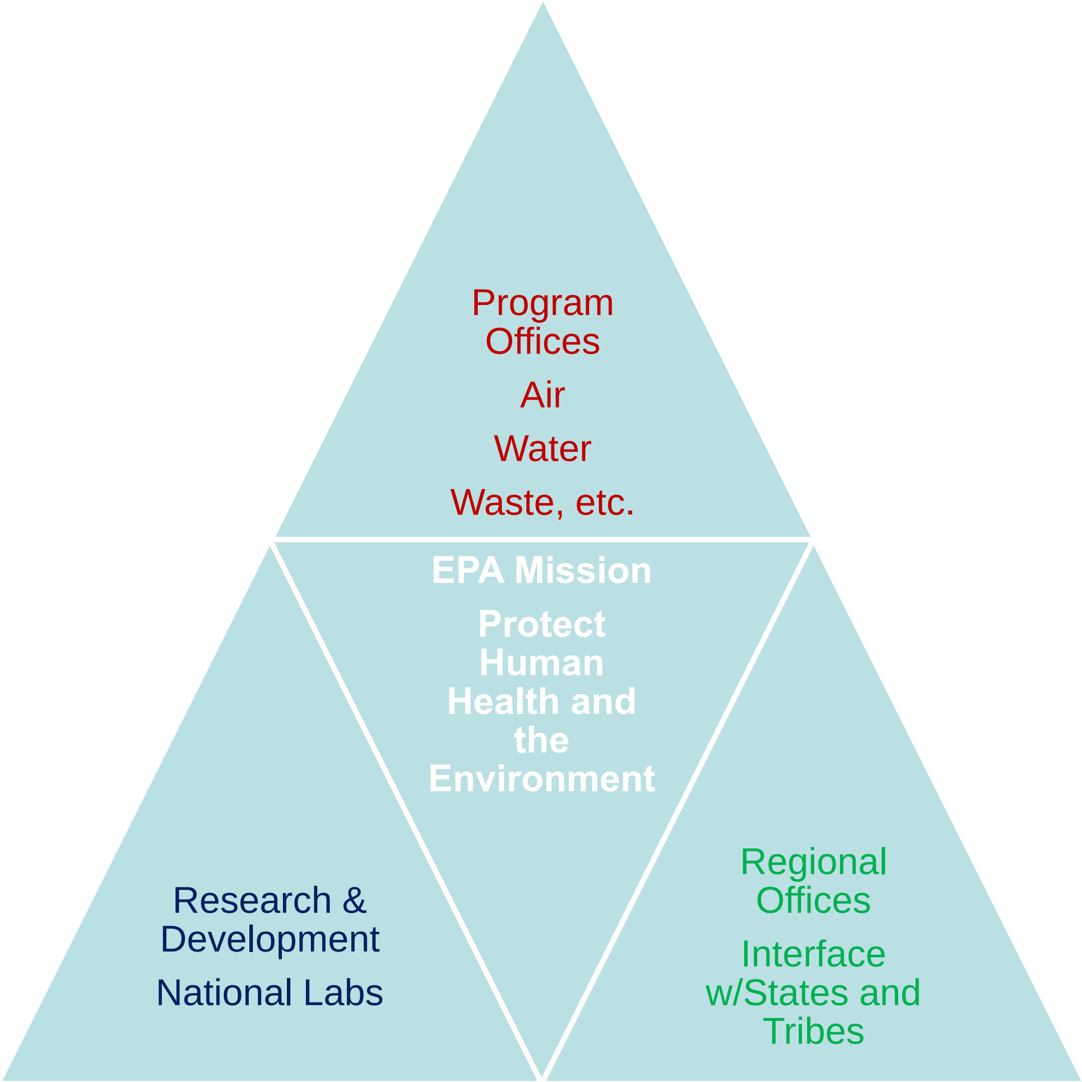
- EPA 101
- Introduce MNA Framework Document for Inorganics in Ground Water
- Discuss MNA for organics vs. inorganics
- Site-specific examples: East Helena SF site, Klau-Buena Vista SF site





http://www.epa.gov/nrmrl/pubs/

EPA Structure



National Risk Management Research Laboratory (Cincinnati, OH)

- Ground Water & Ecosystems Restoration Division (Ada, OK)
- Ground Water Research
  - Contaminant Transport and Fate
  - DNAPL remediation (ISCO, thermal); Metals remediation (reactive barriers, monitored natural attenuation); aquifer storage and recovery; geologic carbon sequestration; CAFOs; nano-particle applications

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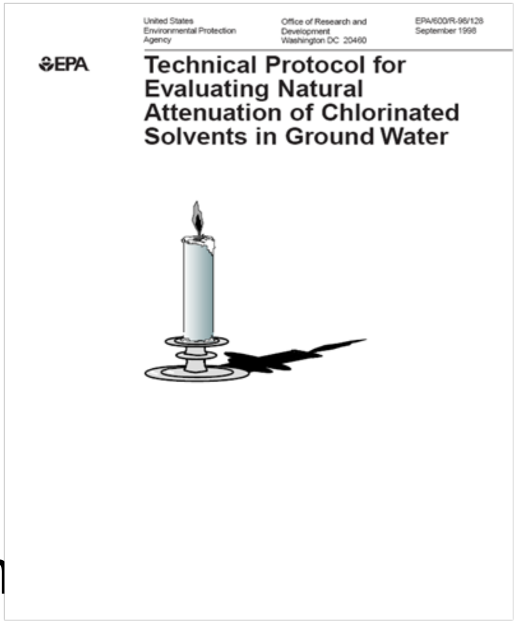
Background

- MNA for organics, technical protocols
- Regional requests for inorganics protocol
- SAB reviews EPA's MNA research program
- MNA inorganics project started in 2002
  - –Expert panel
- Writing completed in 2004
- Review of documents, revision
- Published volume 1 & 2 in 2007/2008, volume 3 in 2010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Office of Research and Development Washington DC 20460

EPA/600/R-98/128 September 1998

EPA

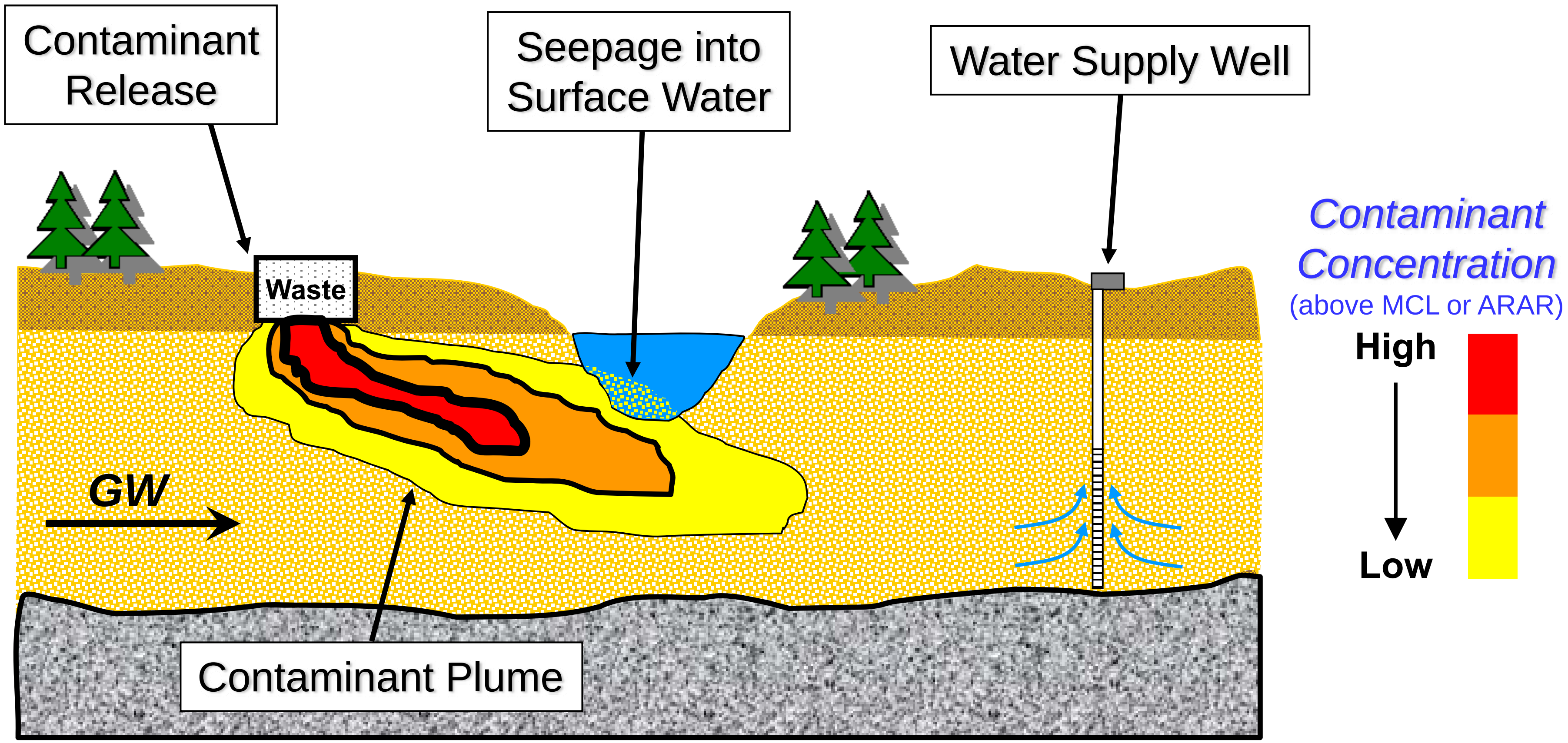
Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

OSWER Directive 9200.4-17P

Concepts described in Directive:

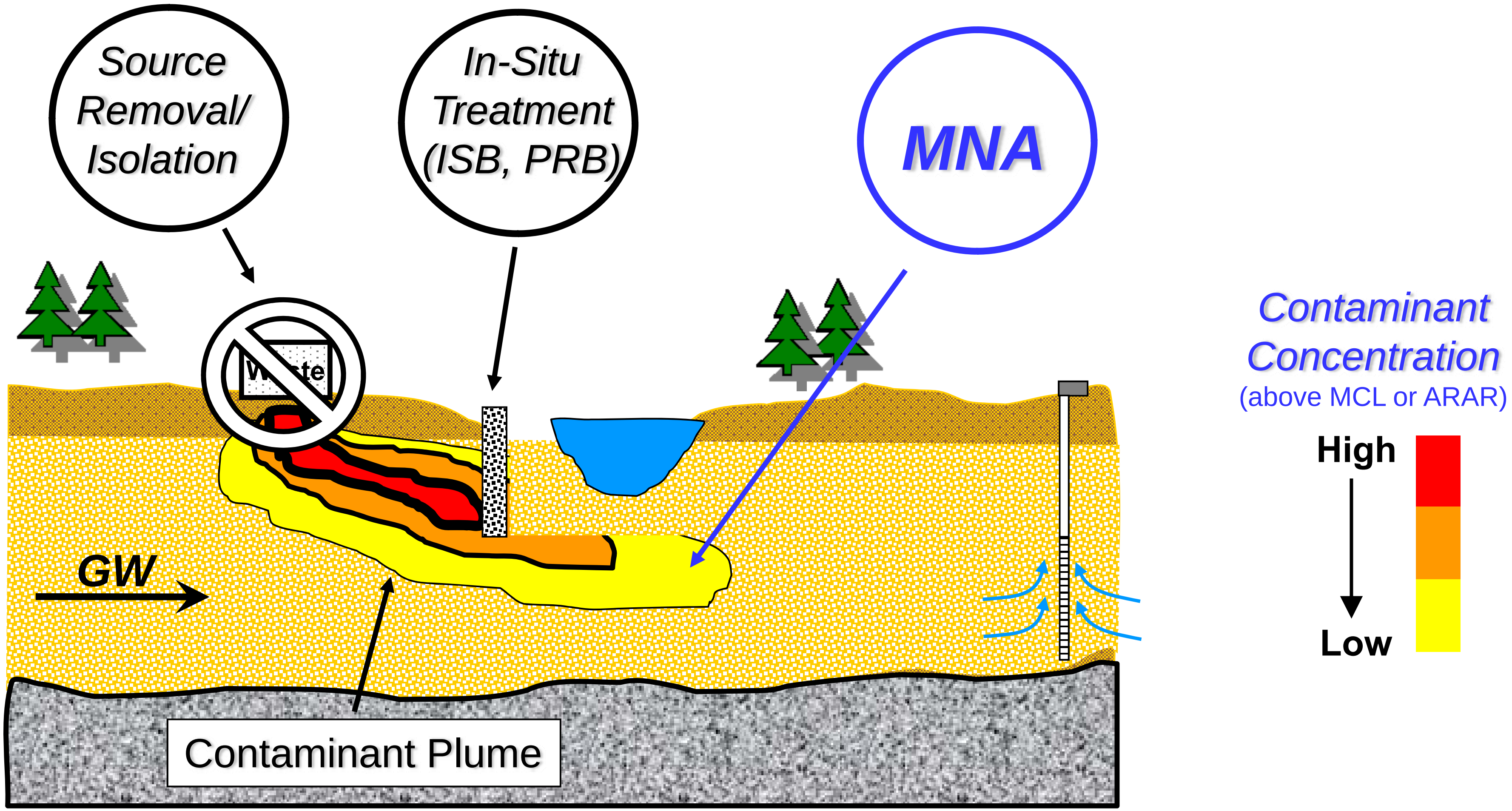
- Stable or shrinking plume
- Source control measures
- Identify mechanism(s) of attenuation
- Demonstrate irreversibility of attenuation process (“sorption”) – *recognizes that many inorganic contaminants will persist in subsurface*

Generalized Site Scenario

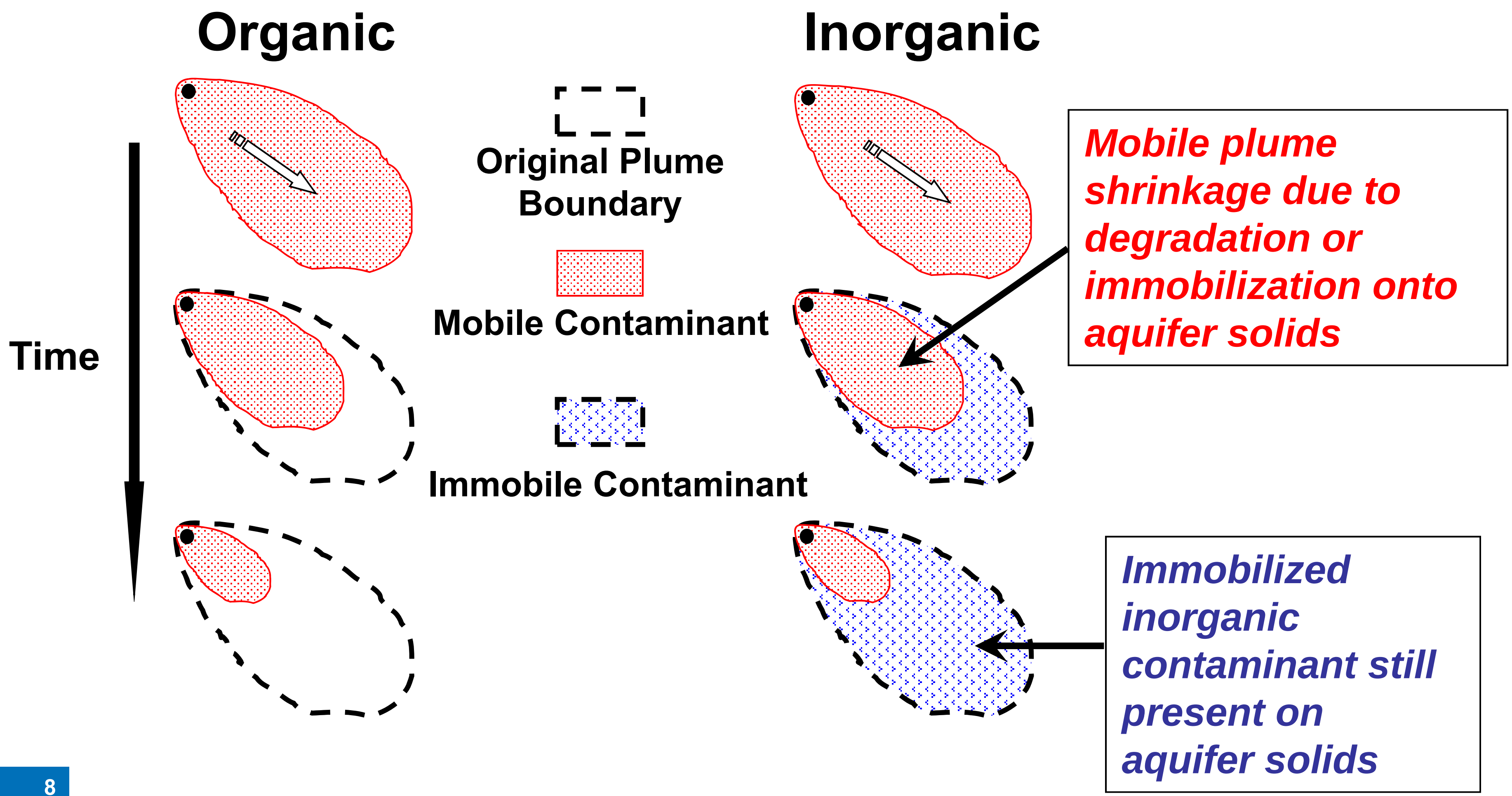


1 Reduce contaminant flux in subsurface…

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

Attenuation Concepts

- Attenuation due to some biogeochemical reaction

Contaminant + Reactant = Product

"Reactants"

"Attenuated"

Immobilization

$Pb_{(GW)} + CO_{3\,(GW)} \rightarrow PbCO_{3\,(Sed)}$

$Cu_{(GW)} + goethite_{(Sed)} \rightarrow Cu\text{-}goethite_{(Sed)}$

Degradation

$6NO_3^-{}_{(GW)} + benzene_{(GW)} + 6H^+{}_{(GW)} + microbe_{(Sed)} \rightarrow 3N_2 + 6CO_2 + 6H_2O$

Or nonhazardous synthetic/natural organic carbon…

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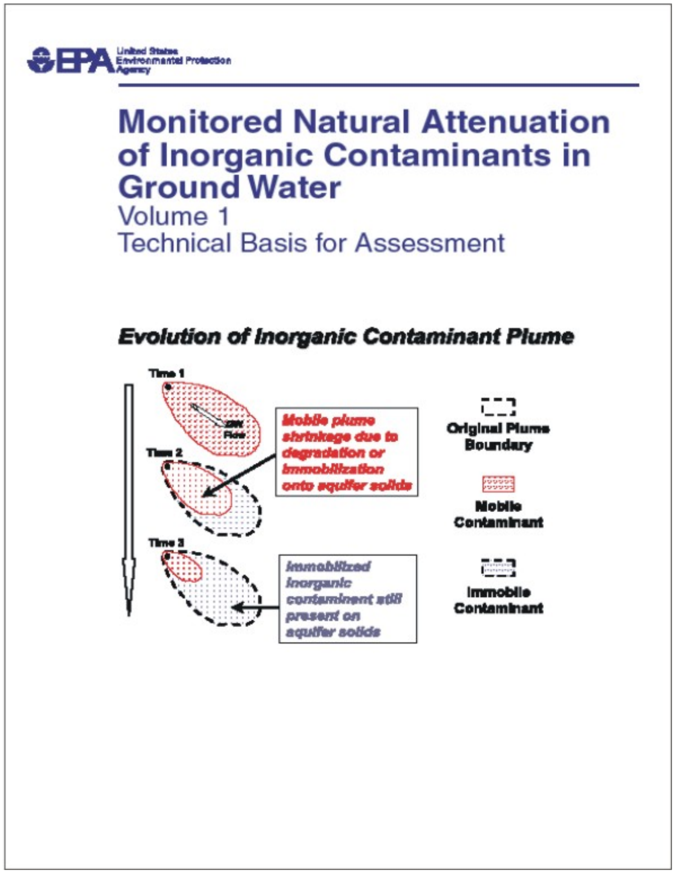
Volume I – Technical Basis



- 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

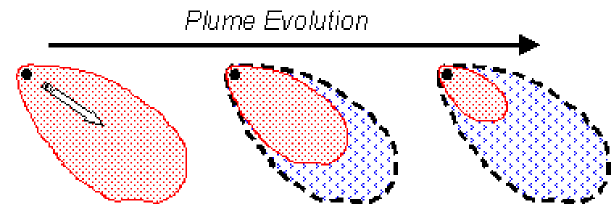
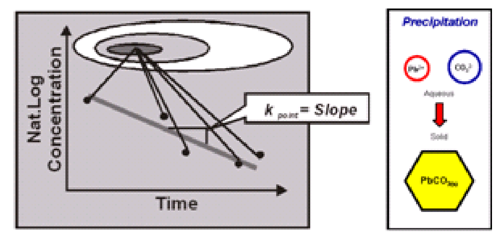
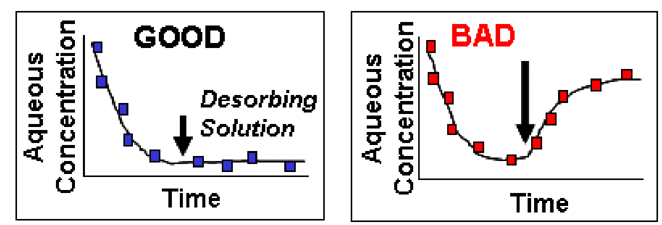
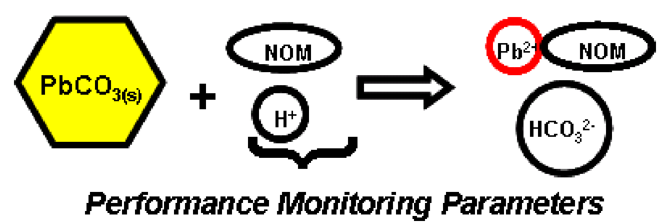
Tiered Analysis Approach

Tier 1: Evaluation of plume stability

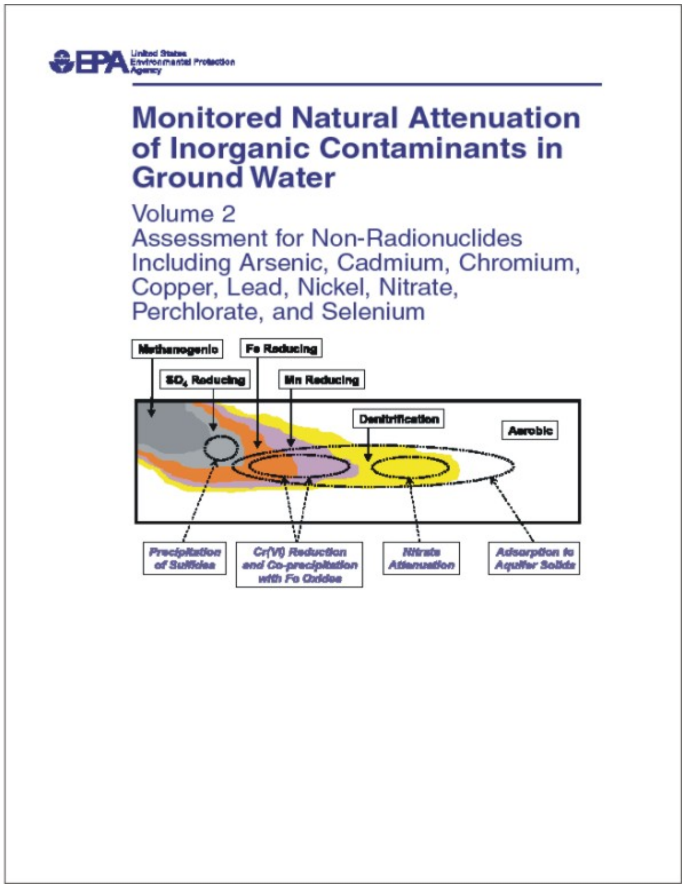
Tier 2: Evaluation of rate and mechanism(s) of attenuation

Tier 3: Demonstrate capacity & stability

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

Tier 1	
Tier 2	
Tier 3	
Tier 4	

Volume II – NA of Non-Rads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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

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Elements Addressed in Inorganics MNA Reference Document

Radionuclides

H																	He
Li	Be											B	C	**N**	O	F	Ne
Na	Mg											Al	Si	P	S	**Cl**	Ar
K	Ca	Sc	Ti	V	**Cr**	Mn	Fe	Co	**Ni**	**Cu**	Zn	Ga	Ge	**As**	**Se**	Br	Kr
Rb	**Sr**	Y	Zr	Nb	Mo	**Tc**	Ru	Rh	Pd	Ag	**Cd**	In	Sn	Sb	Te	**I**	Xe
Cs	Ba	La[1]	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	**Pb**	Bi	Po	At	**Rn**
Fr	**Ra**	Ac[2]	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		Uuo
Lanthanides[1]			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides[2]			**Th**	Pa	**U**	Np	**Pu**	**Am**	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

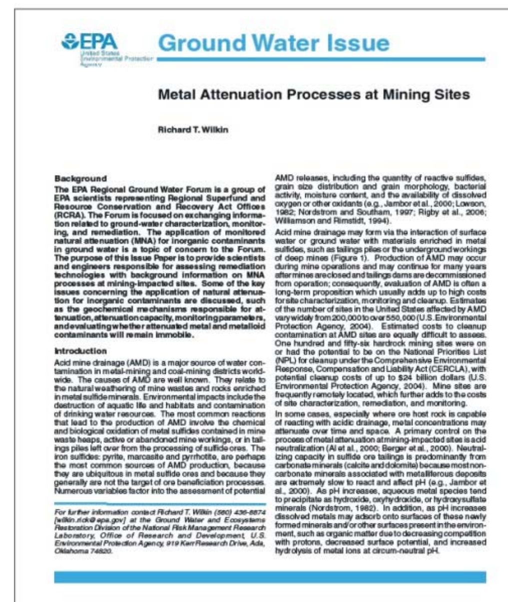
Americium
Cesium
Iodine
Plutonium
Radium
Radon
Strontium
Technetium
Thorium
Tritium
Uranium

MNA at Mining Sites

- Attenuation processes occur and impact the long-term distribution and behavior of contaminants

- Natural processes are not sustainable in most cases

- EPA Ground Water Issue Paper
(EPA/600/R-07/092)
Metal Attenuation Processes at Mining Sites
http://www.epa.gov/nrmrl/pubs/



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Ground Water Issue

Metal Attenuation Processes at Mining Sites

Richard T. Wilkin

Background

The EPA Regional Ground Water Forum is a group of EPA scientists representing Regional Superfund and Resource Conservation and Recovery Act Offices (RCRA). The Forum is focused on exchanging information related to ground-water characterization, monitoring, and remediation. The application of monitored natural attenuation (MNA) for inorganic contaminants in ground water is a topic of concern to the Forum. The purpose of this Issue Paper is to provide scientists and engineers responsible for assessing remediation technologies with background information on MNA processes at mining-impacted sites. Some of the key issues concerning the application of natural attenuation for inorganic contaminants are discussed, such as the geochemical mechanisms responsible for attenuation, attenuation capacity, monitoring parameters, and evaluating whether attenuated metal and metalloid contaminants will remain immobile.

Introduction

Acid mine drainage (AMD) is a major source of water contamination in metal-mining and coal-mining districts worldwide. The causes of AMD are well known. They relate to the natural weathering of mine wastes and rocks enriched in metal sulfide minerals. Environmental impacts include the destruction of aquatic life and habitats and contamination of drinking water resources. The most common reactions that lead to the production of AMD involve the chemical and biological oxidation of metal sulfides contained in mine waste heaps, active or abandoned mine workings, or in tailings piles left over from the processing of sulfide ores. The iron sulfides: pyrite, marcasite and pyrrhotite, are perhaps the most common sources of AMD production, because they are ubiquitous in metal sulfide ores and because they generally are not the target of ore beneficiation processes. Numerous variables factor into the assessment of potential AMD releases, including the quantity of reactive sulfides, grain size distribution and grain morphology, bacterial activity, moisture content, and the availability of dissolved oxygen or other oxidants (e.g., Jambor et al., 2000; Lowson, 1982; Nordstrom and Southam, 1997; Rigby et al., 2006; Williamson and Rimstidt, 1994).

Acid mine drainage may form via the interaction of surface water or ground water with materials enriched in metal sulfides, such as tailings piles or the underground workings of deep mines (Figure 1). Production of AMD may occur during mine operations and may continue for many years after mines are closed and tailings dams are decommissioned from operation; consequently, evaluation of AMD is often a long-term proposition which usually adds up to high costs for site characterization, monitoring and cleanup. Estimates of the number of sites in the United States affected by AMD vary widely from 200,000 to over 550,000 (U.S. Environmental Protection Agency, 2004). Estimated costs to cleanup contamination at AMD sites are equally difficult to assess. One hundred and fifty-six hardrock mining sites were on or had the potential to be on the National Priorities List (NPL) for cleanup under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), with potential cleanup costs of up to $24 billion dollars (U.S. Environmental Protection Agency, 2004). Mine sites are frequently remotely located, which further adds to the costs of site characterization, remediation, and monitoring.

In some cases, especially where ore host rock is capable of reacting with acidic drainage, metal concentrations may attenuate over time and space. A primary control on the process of metal attenuation at mining-impacted sites is acid neutralization (Al et al., 2000; Berger et al., 2000). Neutralizing capacity in sulfide ore tailings is predominantly from carbonate minerals (calcite and dolomite) because most non-carbonate minerals associated with metalliferous deposits are extremely slow to react and affect pH (e.g., Jambor et al., 2000). As pH increases, aqueous metal species tend to precipitate as hydroxide, oxyhydroxide, or hydroxysulfate minerals (Nordstrom, 1982). In addition, as pH increases dissolved metals may adsorb onto surfaces of these newly formed minerals and/or other surfaces present in the environment, such as organic matter due to decreasing competition with protons, decreased surface potential, and increased hydrolysis of metal ions at circum-neutral pH.

For further information contact Richard T. Wilkin (580) 436-8874 [wilkin.rick@epa.gov] at the Ground Water and Ecosystems Restoration Division of the National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 919 Kerr Research Drive, Ada, Oklahoma 74820.

East Helena SF Site, MT

- Former lead smelter
- Arsenic/Selenium in groundwater, offsite migration
- Lead/cadmium/zinc in onsite groundwater

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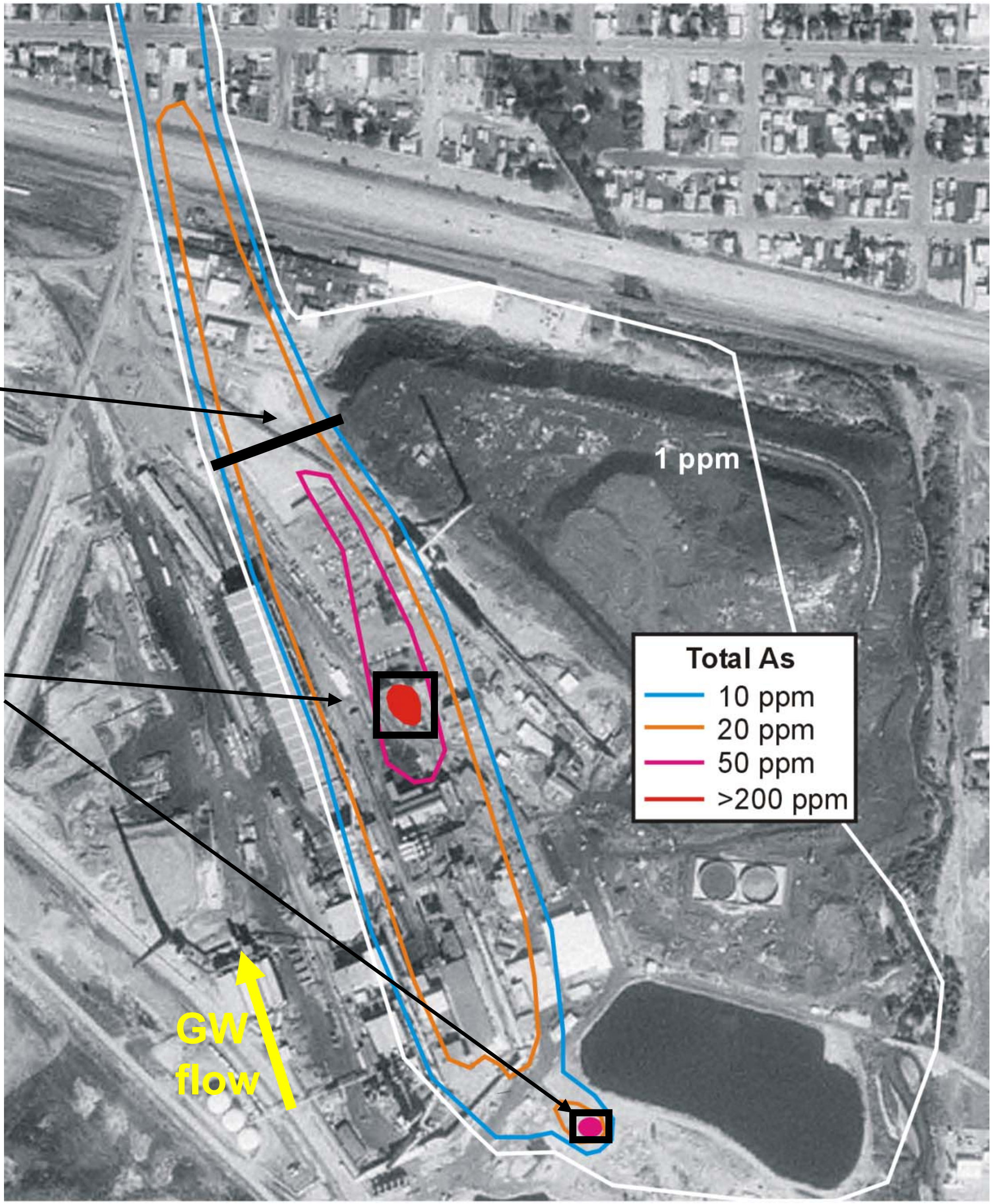
PRB

Source Isolation



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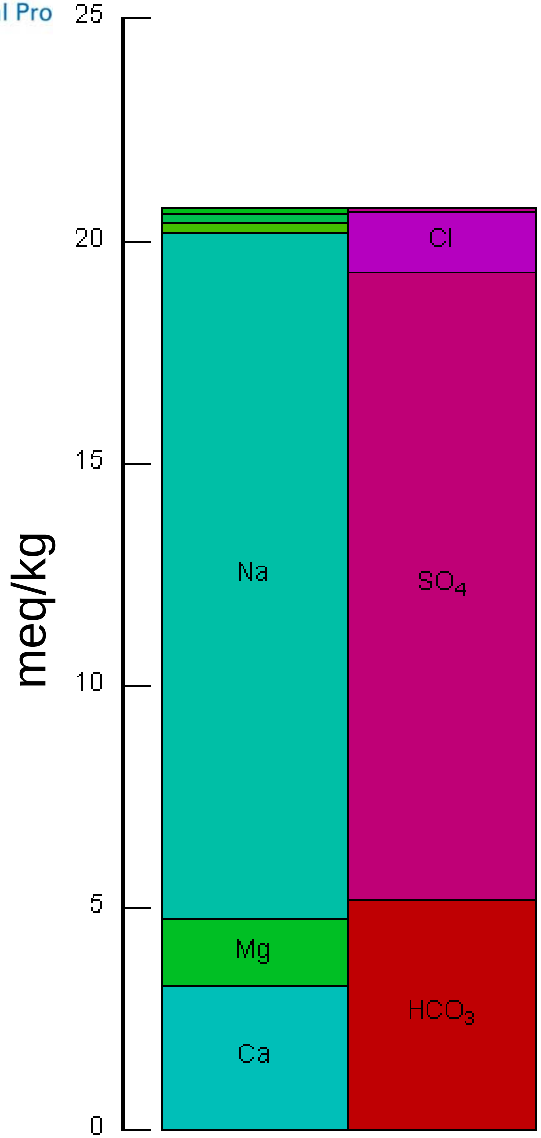
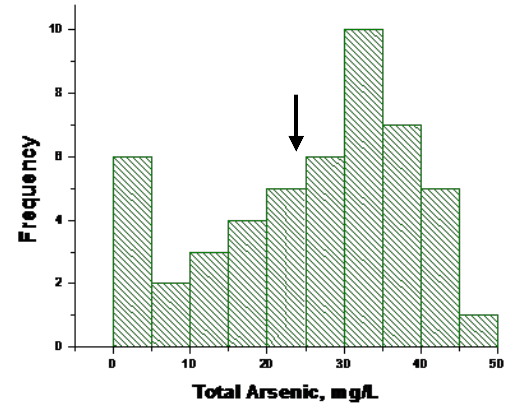
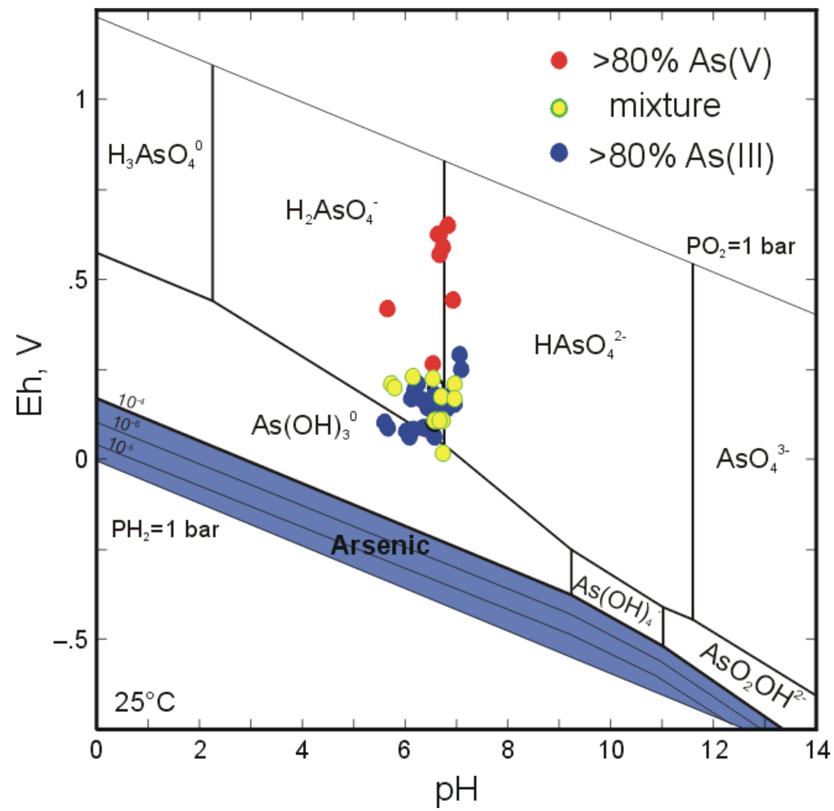
Ground-water chemistry



Well PBTW-1





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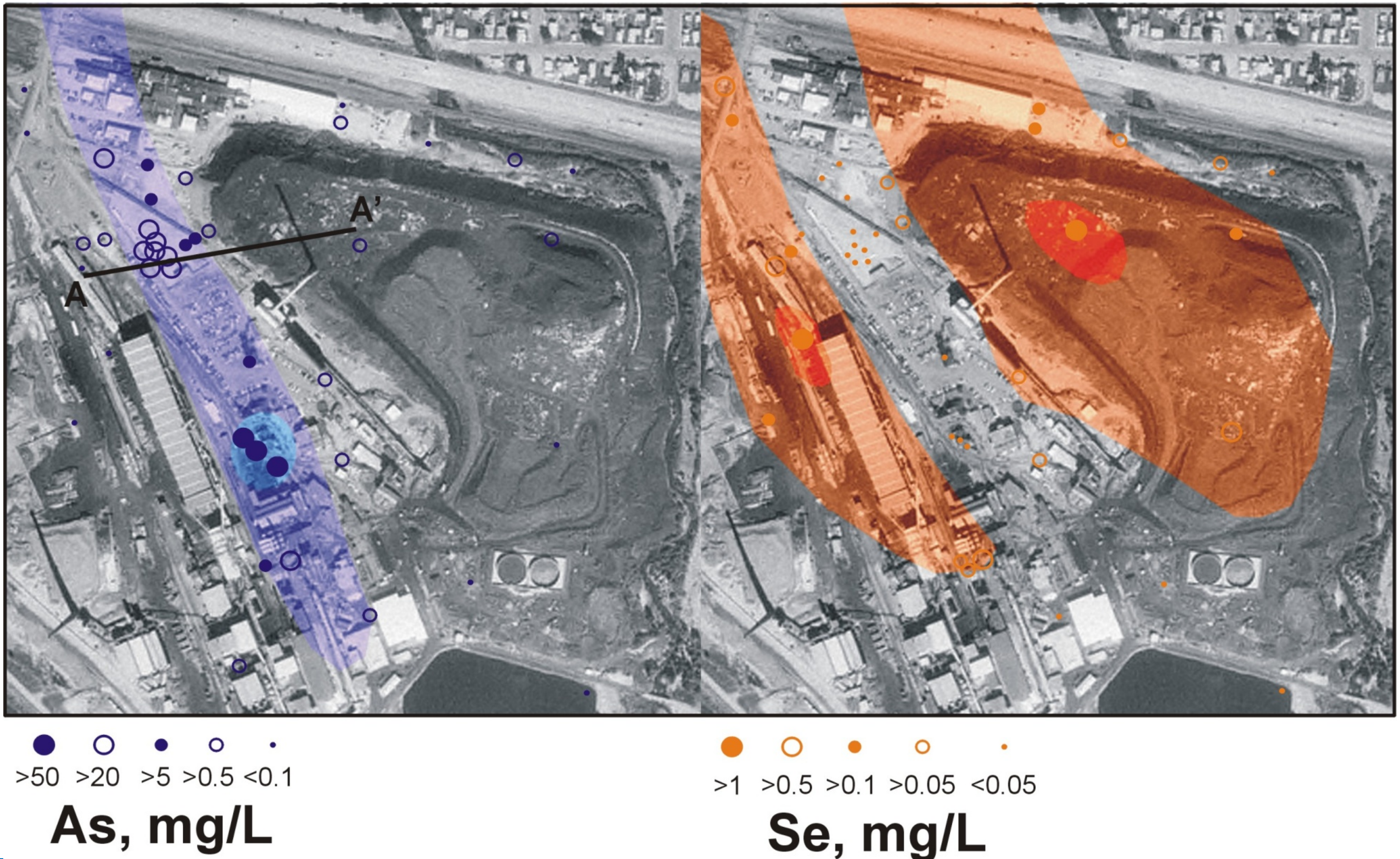
Arsenic and Selenium Plumes

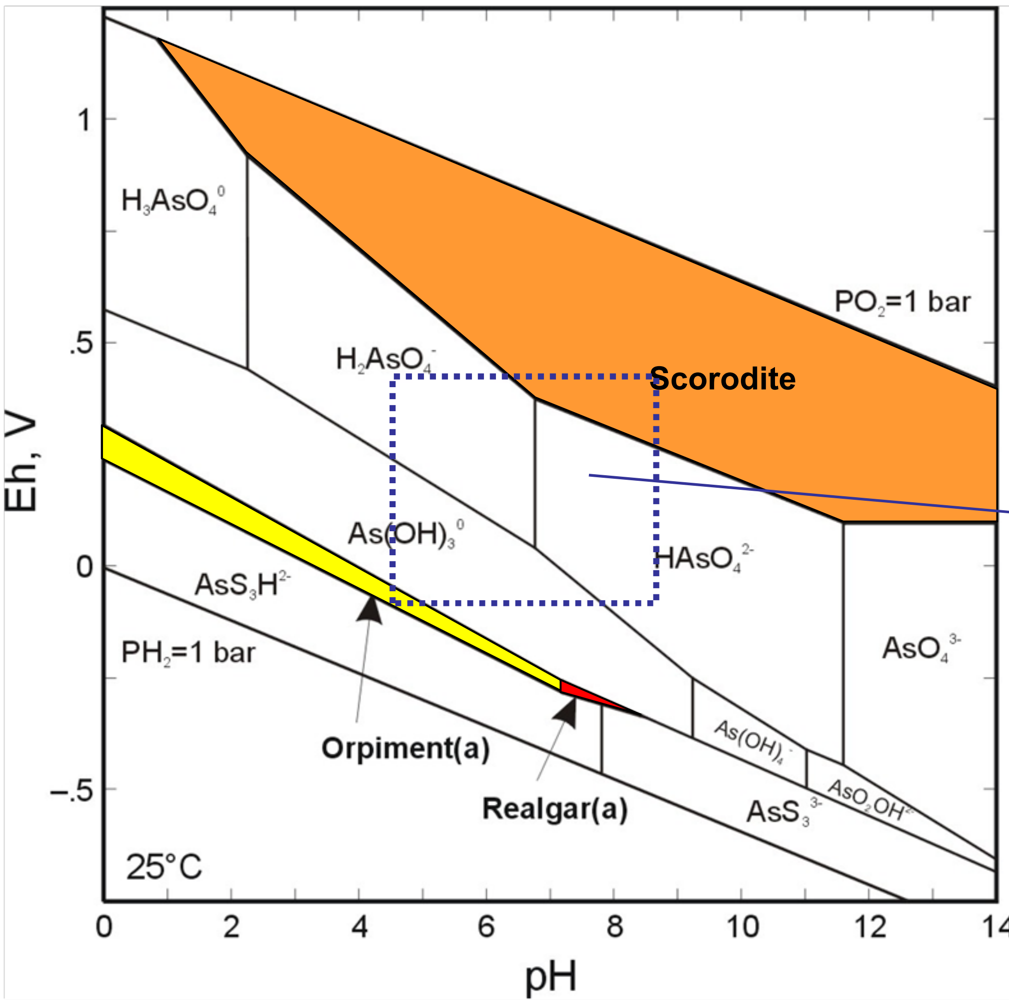


Arsenic Attenuation

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

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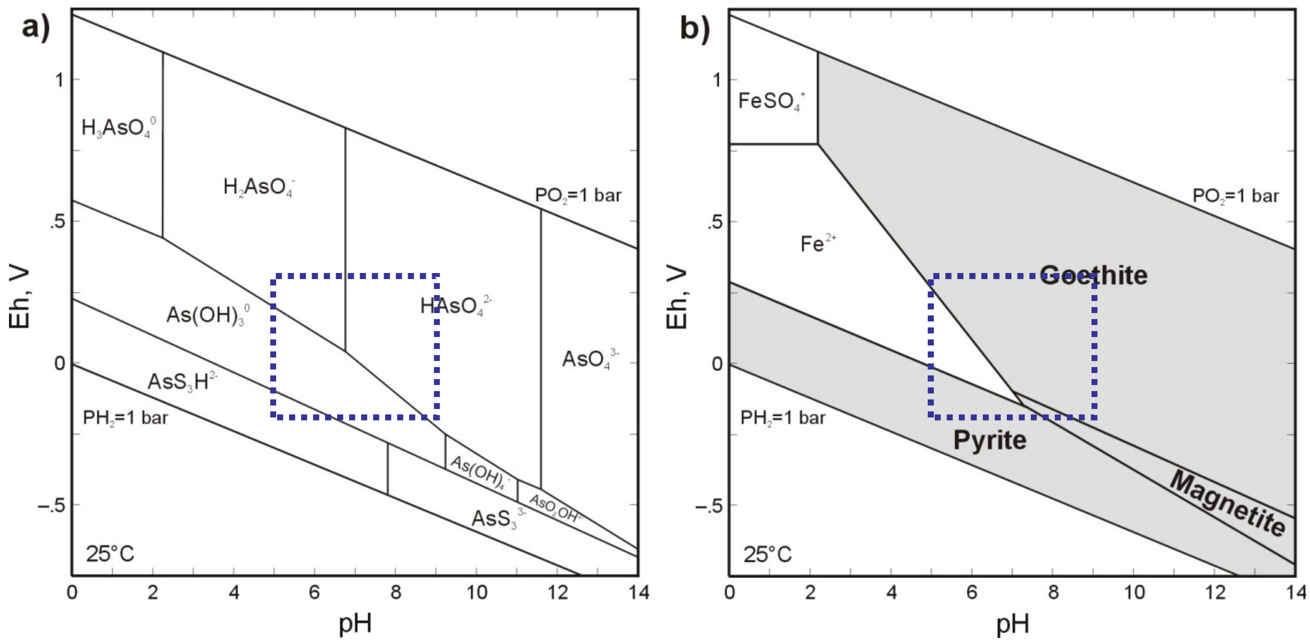
Arsenic - Adsorption

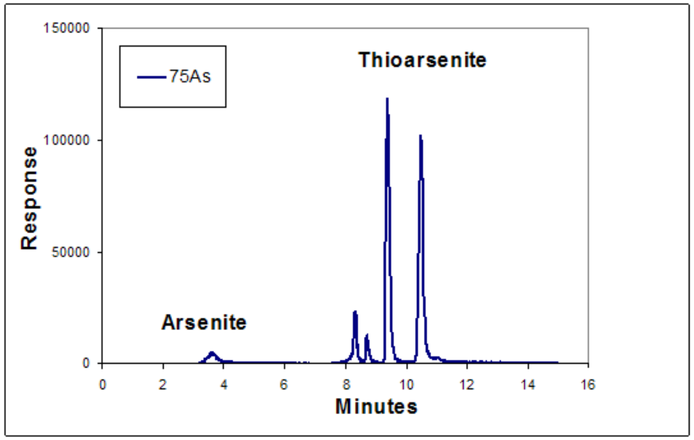
Aqueous As ***Aquifer Fe-bearing Minerals***



- 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

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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

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Klau – Buena Vista: Efflorescent Salt Study

Rick Wilkin and Steve Acree – EPA/ORD, Ada, OK

Update for Region 9/April 20, 2010
revised

Water Solubility of Efflorescent Salts

- Conceptual Site Model – efflorescent salts provide a potential source of inorganic contaminants during precipitation events…
  - Scenario 1 – all elements associated with salts dissolve into solution
  - Scenario 2 – other mineral/water interface processes sequester metals
  - Are all components in the salts soluble?? – key question
- Experimental methodology – column test – No…
  - High solubility of Mg-sulfates, e.g., hexahydrite 428 gm/kg water; starkeyite 604 gm/kg water
- Batch mode dissolution w/variable water/solid ratio
  - Compare water soluble fraction w/expectation from totals analysis

Water Soluble Contents - Nickel

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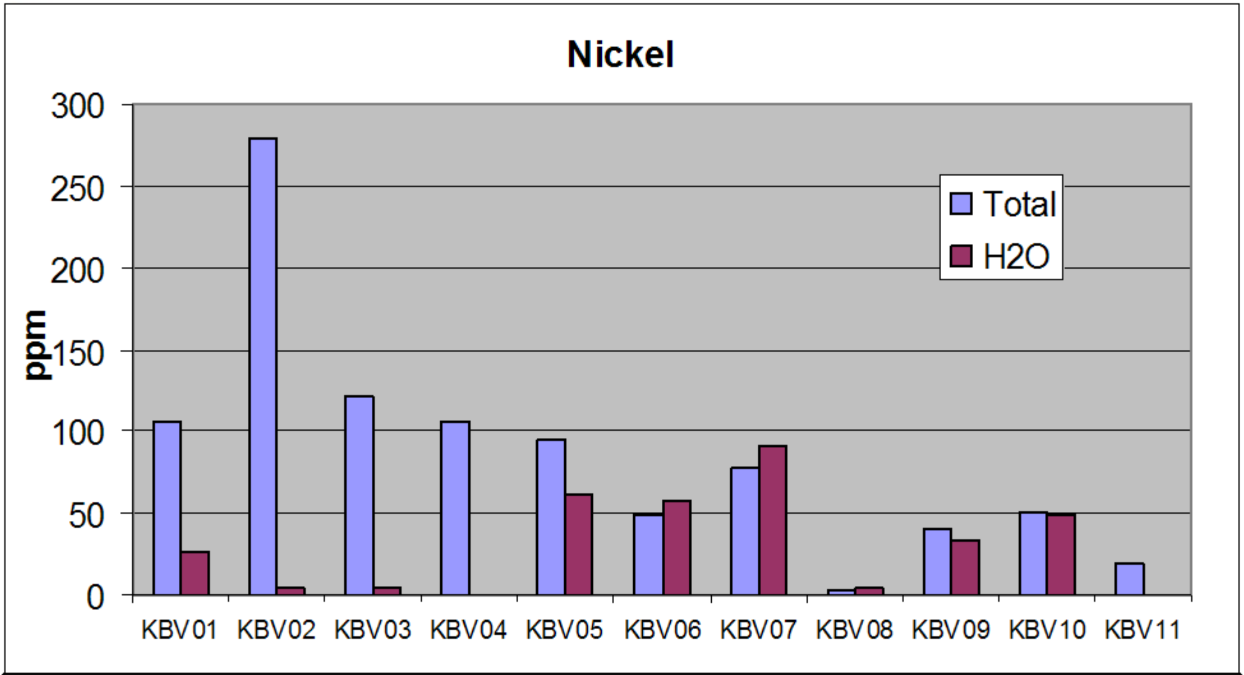
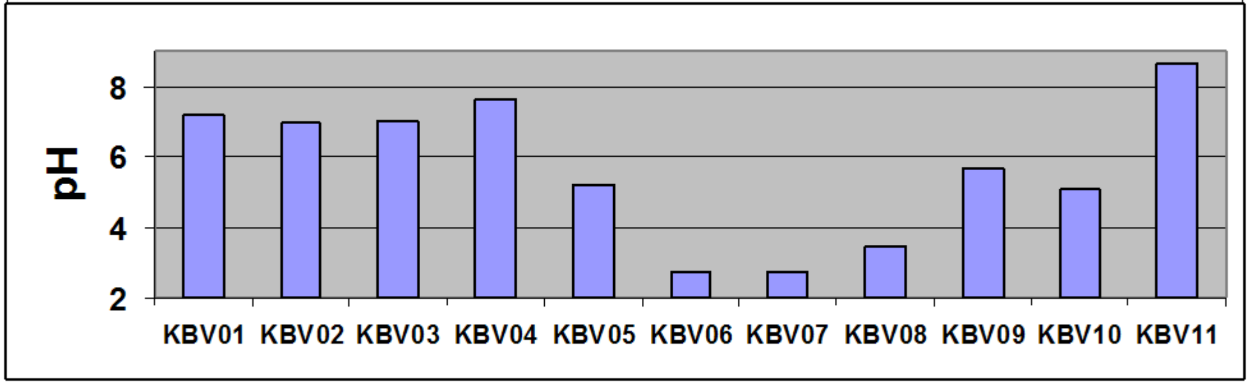
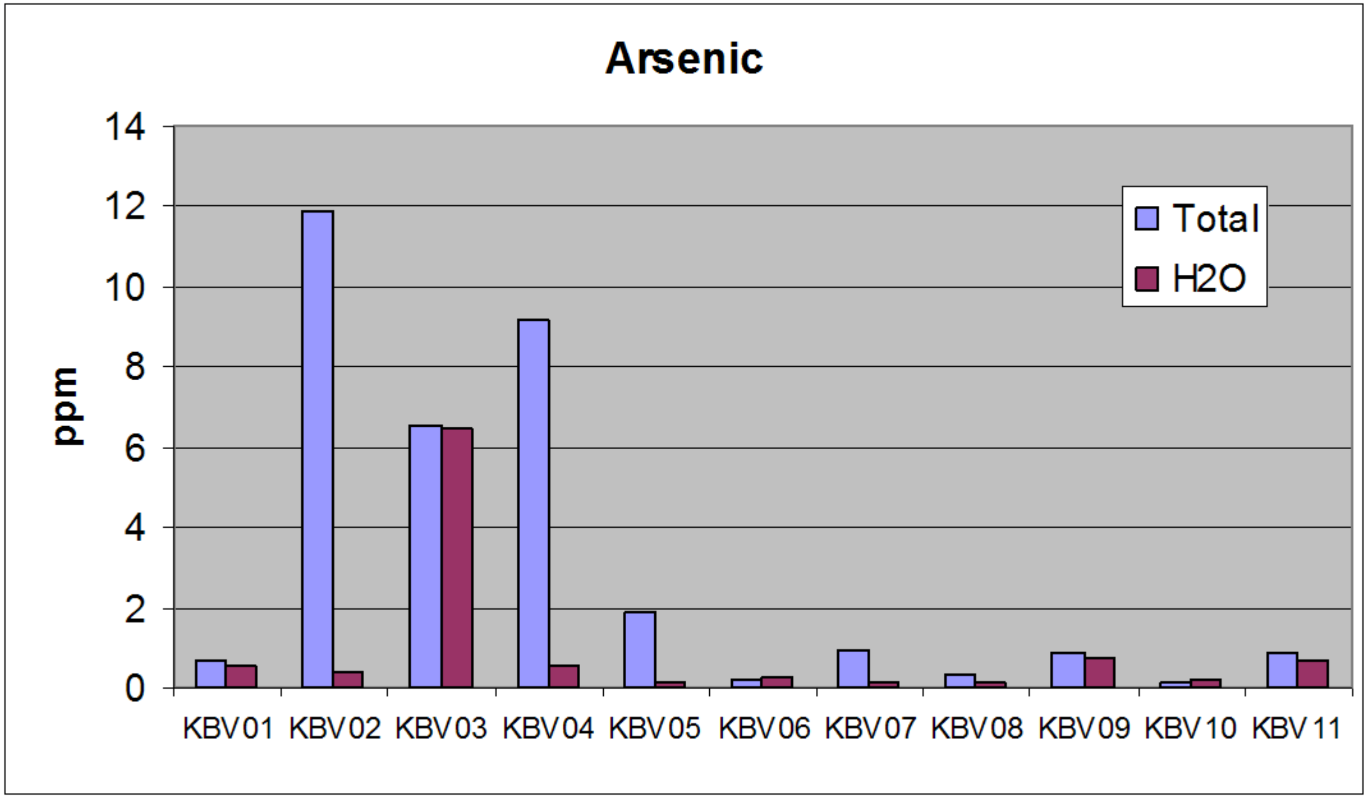
0.2 g to 100 mL Solid:H_2O [2 g/L]

Water-soluble content in solid, ppm



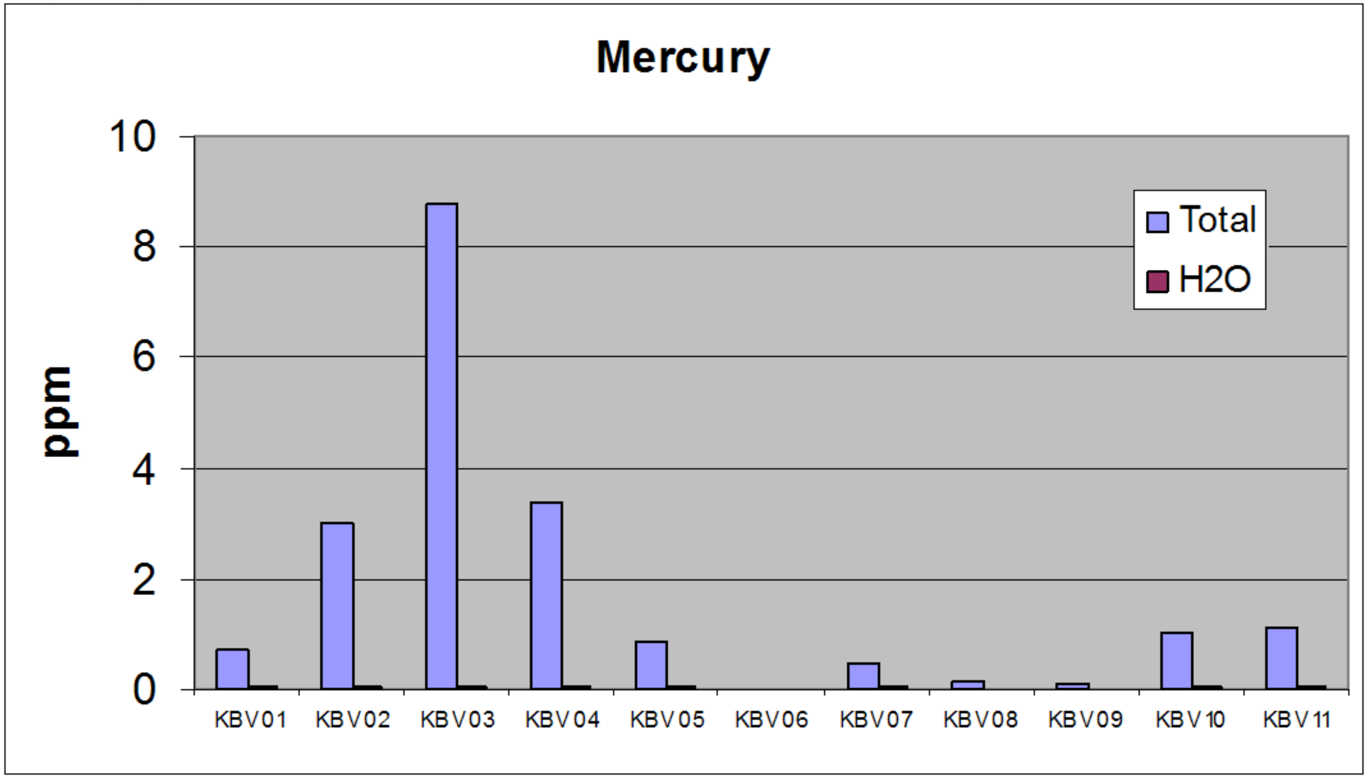


Water Soluble Contents - Arsenic



Results more complicated for As, because both pH and iron content have on impact on arsenic solubilization/sequestration

Water Soluble Contents - Mercury



Hg mainly insoluble (not completely though)

Behaviors, water solubility: Refractory [Cr, Hg, Pb, Tl]
pH-dependent response [Ni, Zn, Mn]
other [As, Cu, Co]

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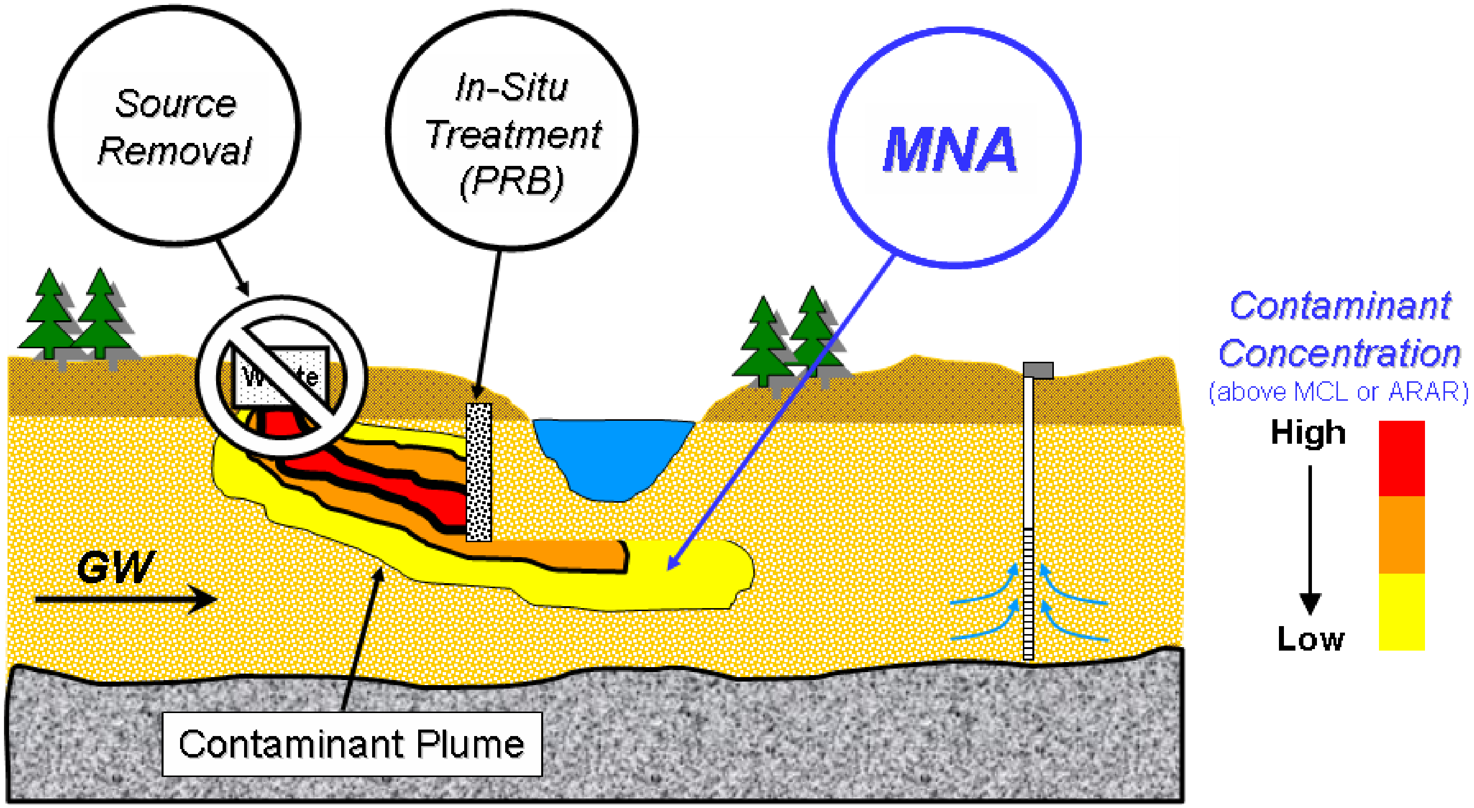
Discussion Points & Future Directions

- Field-scale attenuation processes – “red” mineralogy, interaction with surface and groundwater
- Total Hg and MeHg values in salts
  - Temporal variability
  - Spatial variability
- Salt formation
  - How & where, can metal/mobilization content be controlled??
- MeHg in Water
  - Dissolution of salts, other sources

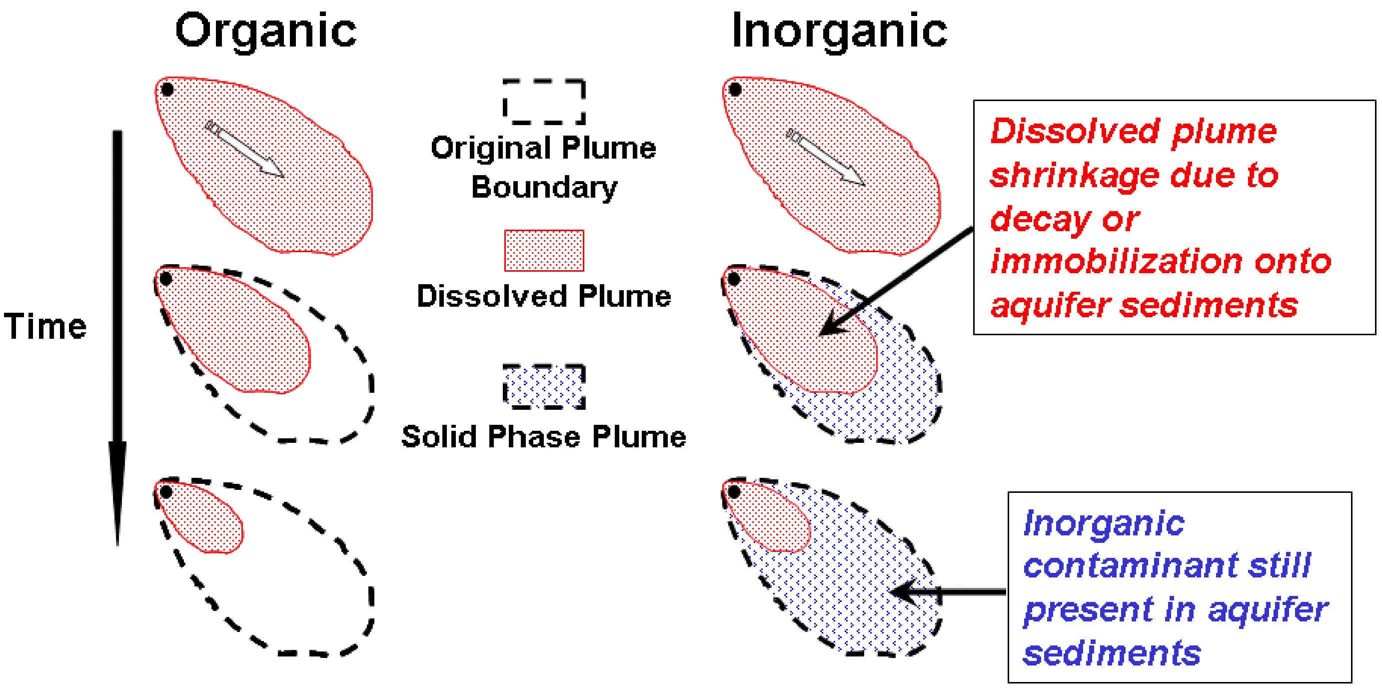
Role of MNA in Site Cleanup

Most likely used in combination with other remediation technologies & institutional controls



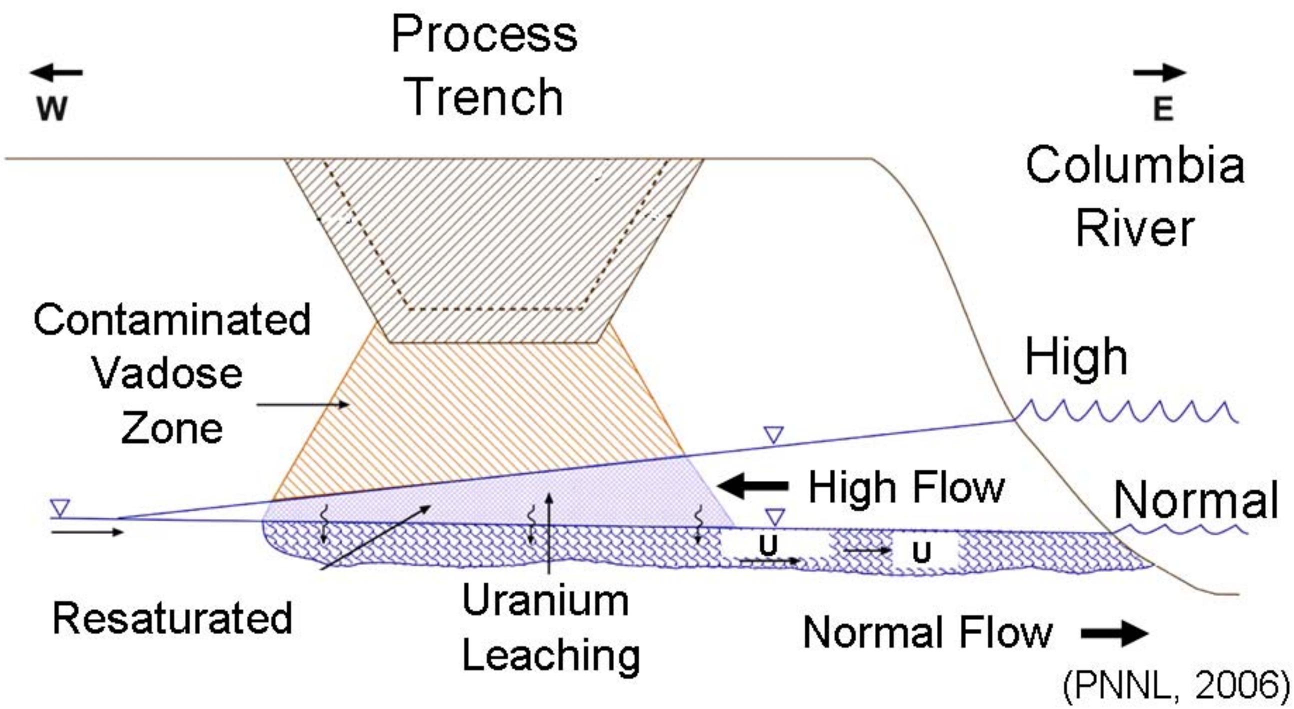
Take Home Message

- "Plume" composed of contaminant in GW ***and*** on aquifer sediments
  - Need to account for reversibility of attenuation



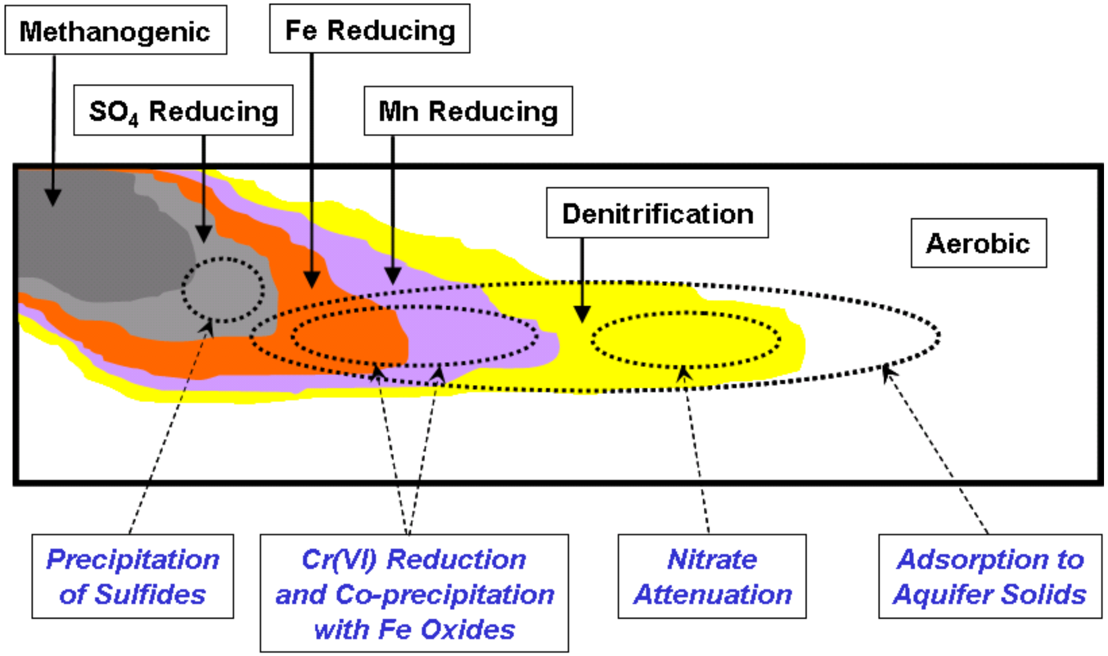
Take Home Message

- Adequate understanding of hydrology
  - Need to know where the GW is moving to understand where the contaminant is being attenuated



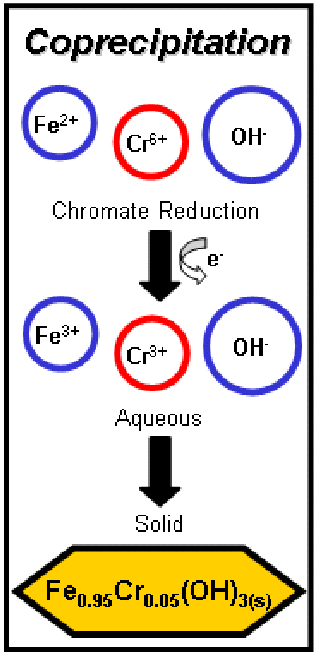
Take Home Message

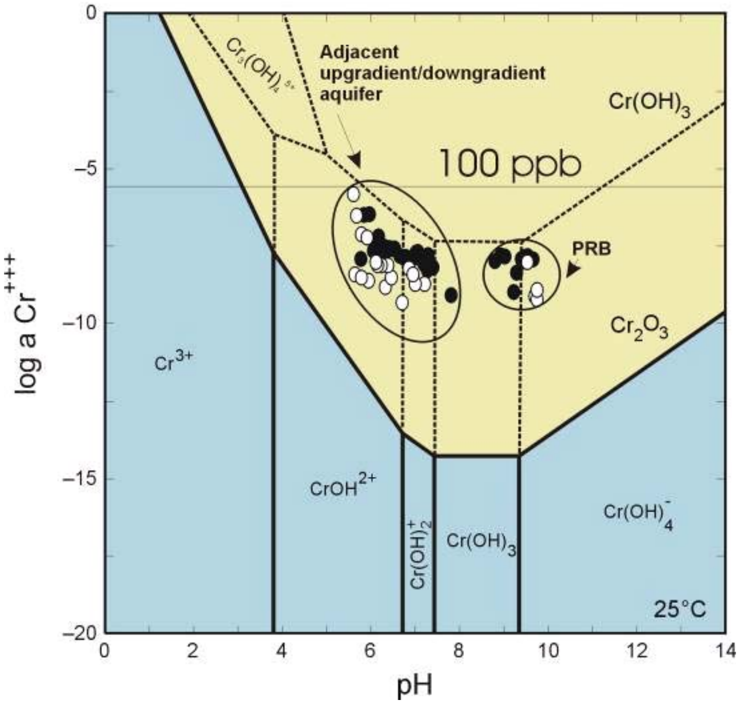
- Different inorganic contaminants have different chemical properties
  - Mobility will depend on the “interaction” between contaminant properties & GW chemistry



Take Home Message

- Models – need to be quantitative, i.e., move beyond CSM
  - Quantitative ≠ 3D Reactive Transport Model





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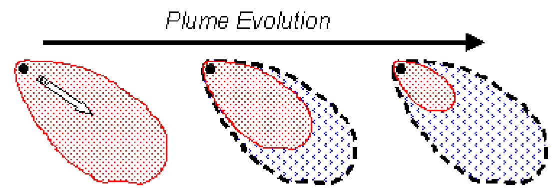
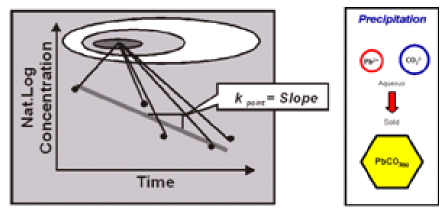
Take Home Message

- Tiered analysis process is a means of organizing site characterization tasks

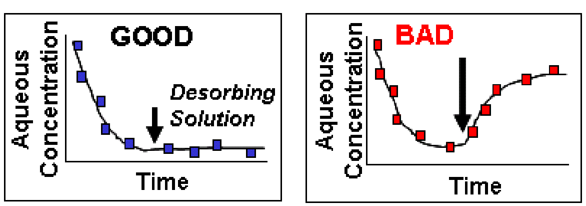
Tier 1



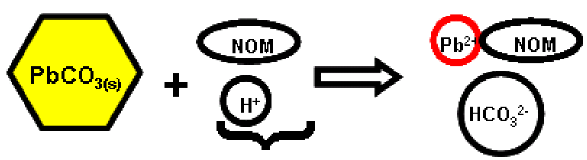
Tier 2



Tier 3



Tier 4



Performance Monitoring Parameters