Monitored Natural Attenuation for Inorganic Contaminant Remediation in Ground Water

Robert Ford , Richard Wilkin , Robert Puls
EPA/ORD, Ada, OK 74820

Kenneth Lovelace, Stuart Walker
EPA/OSWER/OSRTI, Washington, DC 20460

Ronald Wilhelm
EPA/OAR/ORIA, Washington, DC 20460

Environmental Remediation Sciences Program Workshop
12 June 2006

Nothing in this presentation changes Agency policy regarding remedial selection criteria, remedial expectations, or the selection and implementation of MNA. The information presented does not supercede any guidance. Its intended purpose is to provide a technical perspective for evaluation of MNA as a potential ground-water cleanup remedy as described in OSWER Directive 9200.4-17P, “Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites”

Natural Attenuation Definition

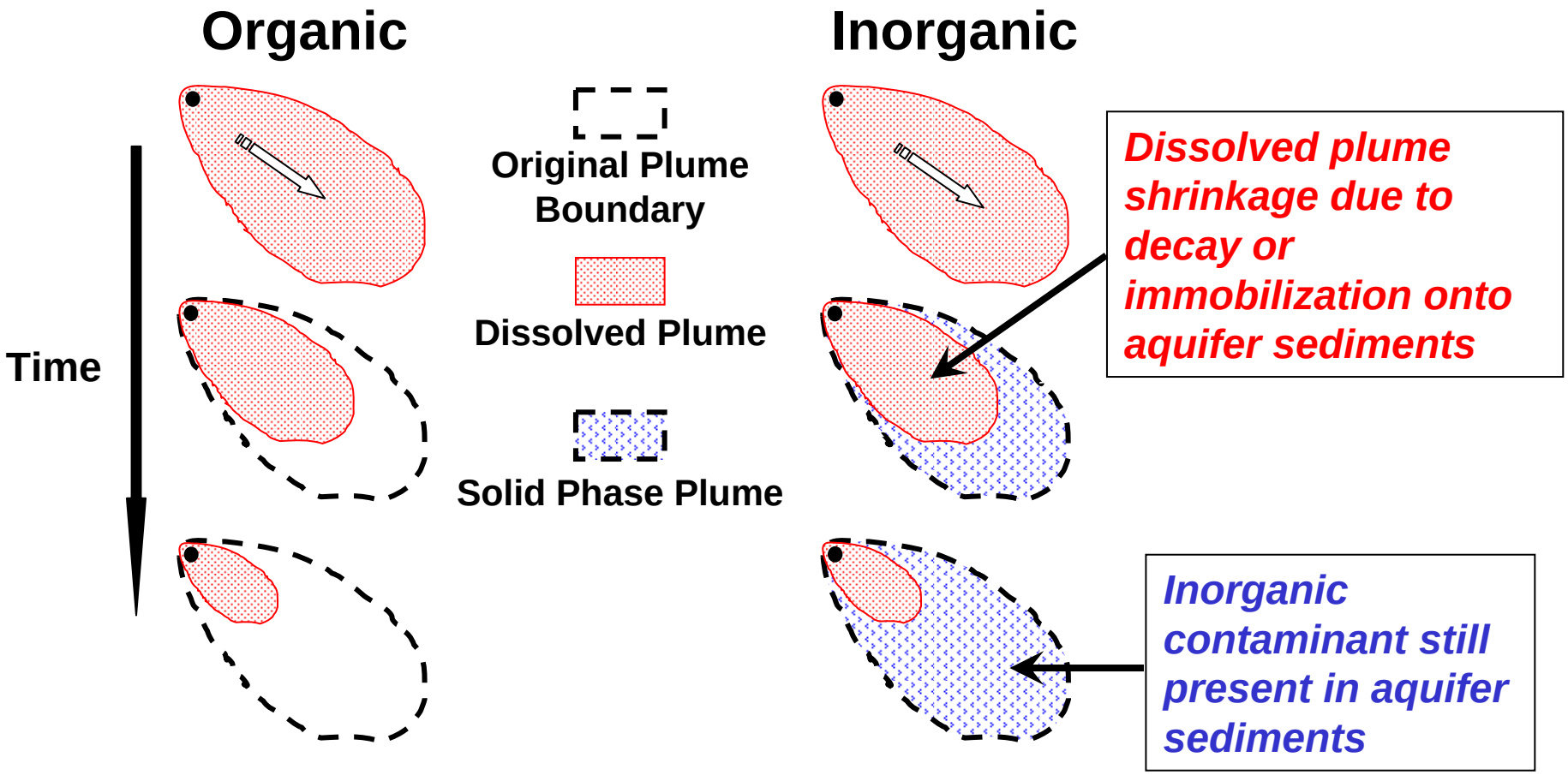
OSWER Directive 9200.4-17P

"The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the ***mass****, toxicity, ***mobility****, volume, or concentration of contaminants in soil or groundwater."

* Immobilization & radioactive decay identified as primary processes operative for contaminant metals and metalloids
* Knowledge-based technology

Monitored Natural Attenuation: USEPA Research Program – An EPA Science Advisory Board Review
EPA-SAB-EEC-01-004
http://www.epa.gov/sab/pdf/eec01004.pdf

Conceptual Distinction for MNA Applied to Inorganic vs. Organic Contaminants



Technical Issues

Scientific foundation for assessment and acceptance:

- Timescale of attenuation process consistent with regulatory needs for site remediation
- Stability of immobilized contaminant sufficient to resist re-mobilization due to changes in site geochemistry
- Assessment of immobilization process employing technically feasible and scientifically defensible analytical methods
- Reactive-transport models properly supported through data collection to evaluate feasibility or sensitivity of decay and/or immobilization process

Scientific and Technical Needs

Evaluation of candidate sites and assessing the technical requirements to demonstrate viability.

- Identification of contaminant- and site-specific immobilization or decay processes
- Determination of site-specific rate and capacity of immobilization process
- Evaluation and codification of test methods to assess stability of immobilized contaminant
- Development and application recommendations for use of reactive-transport models as a tool to assist site characterization

Focus of MNA Technical Resource Document

- Inorganic contaminants in ***GW***
- Tiered approach to streamline evaluation of use of MNA
- Focus on GW; unsaturated (vadose) zone addressed only as potential source term
- Addresses both ‘rad’ and ‘non-rad’ contaminants

Evaluation of MNA
Tiered Approach

I. Actively demonstrate removal from ground water & dissolved plume stability (site-specific data and theoretical basis)

II. Determine rate and mechanism of attenuation

III. Determine long-term capacity for attenuation and stability

IV. Design monitoring program, define triggers for MNA failure, and establish contingency plan

Elements Addressed in Inorganics MNA Technical Resource Document

Non - 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	

Arsenic
Cadmium
Chromium
Copper
Lead
Nickel
Nitrate
Perchlorate
Selenium

Elements Addressed in Inorganics MNA Technical Resource 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

Inorganics MNA Background Document Structure

- Two major components:
  - Scientific basis and approaches for technical assessment of inorganics MNA
  - Element-specific assessment of feasibility based on current state of knowledge
- Strong emphasis placed on site characterization:
  - Hydrogeology (Where? & How fast?)
  - Biogeochemistry (*solid* and aqueous phases; rate and capacity)

Inorganics MNA Technical Resource Document Structure
Volume 1 – Basis for Assessment

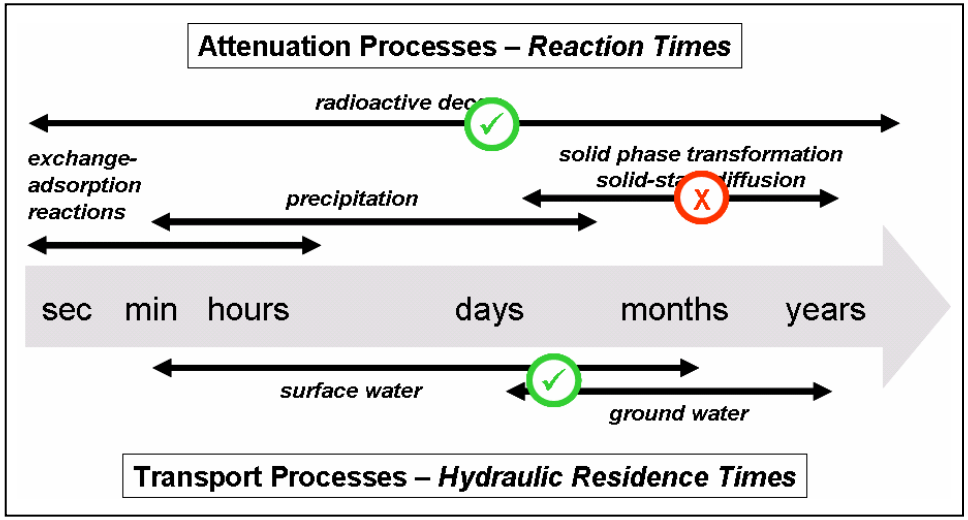
- *Section I* – Regulatory and Conceptual Background for Natural Attenuation
- *Section II* - Scientific Basis for Natural Attenuation
- *Section III* - Modeling and the Tiered Approach
- *Section IV* - Site Characterization

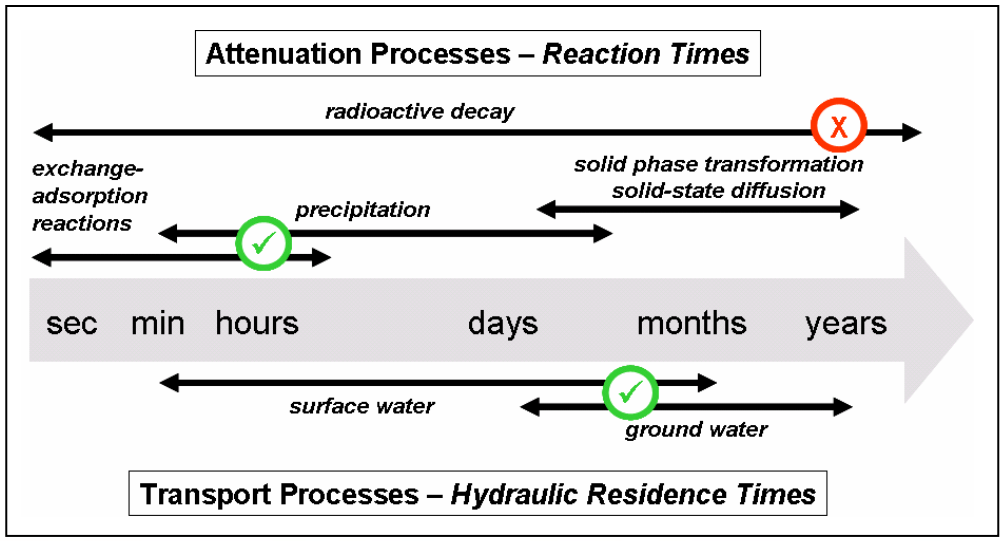
Evaluating NA Processes - Timescale Comparison

Reaction Time **versus** *Transport Time*

Attenuation by Decay

- Radioactive decay sufficiently fast relative to transport
- Immobilization mechanism too slow relative to transport



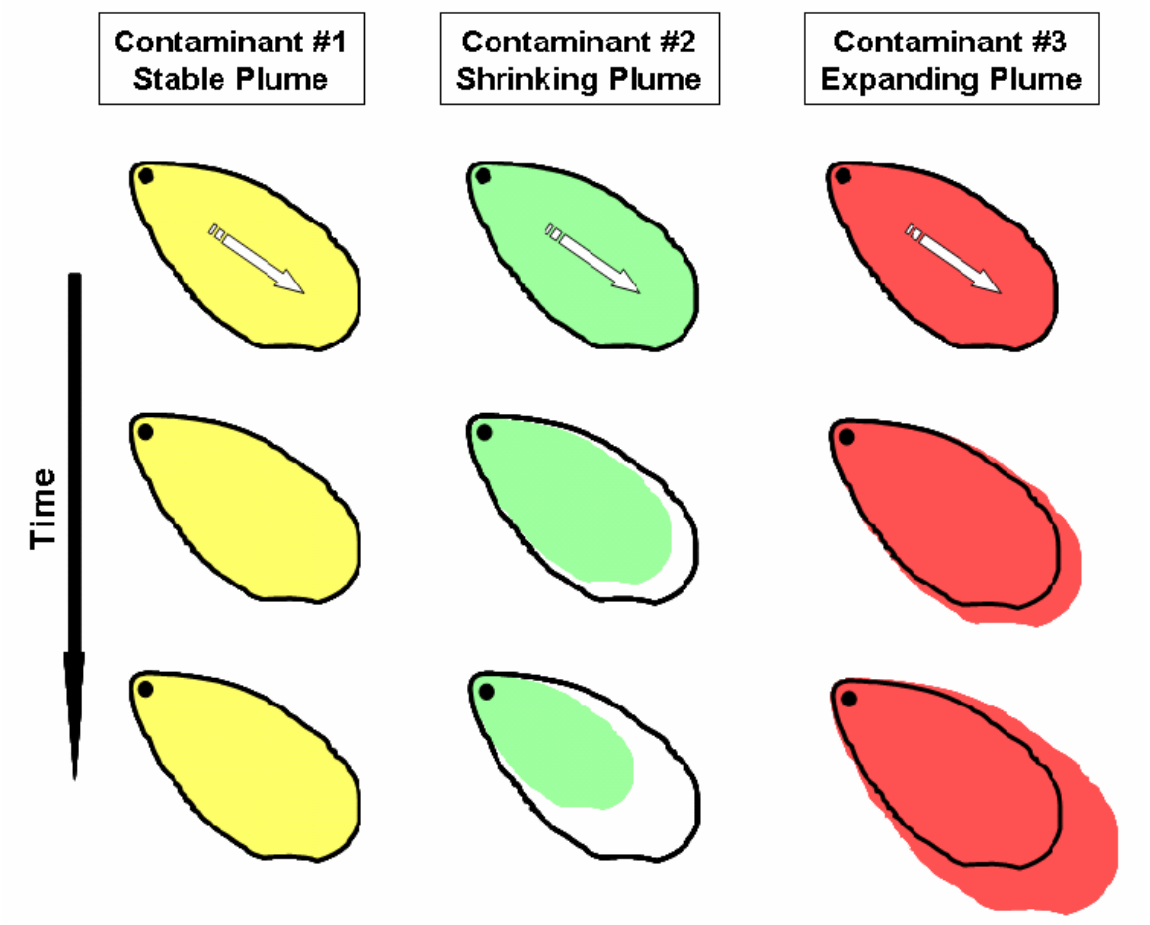


Attenuation by Immobilization

- Immobilization mechanism sufficiently fast relative to transport
- Radioactive decay too slow relative to transport

Evaluating NA Processes – Interaction Between Radioactive Decay & Immobilization

Independent Evaluation of Each Contaminant for Complex Plumes



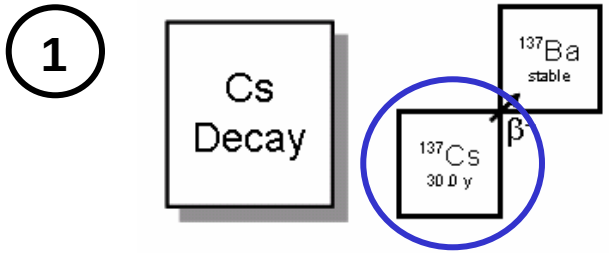
- MNA may not be suitable for all contaminants
- May limit feasibility of site-wide implementation of MNA as a remedy

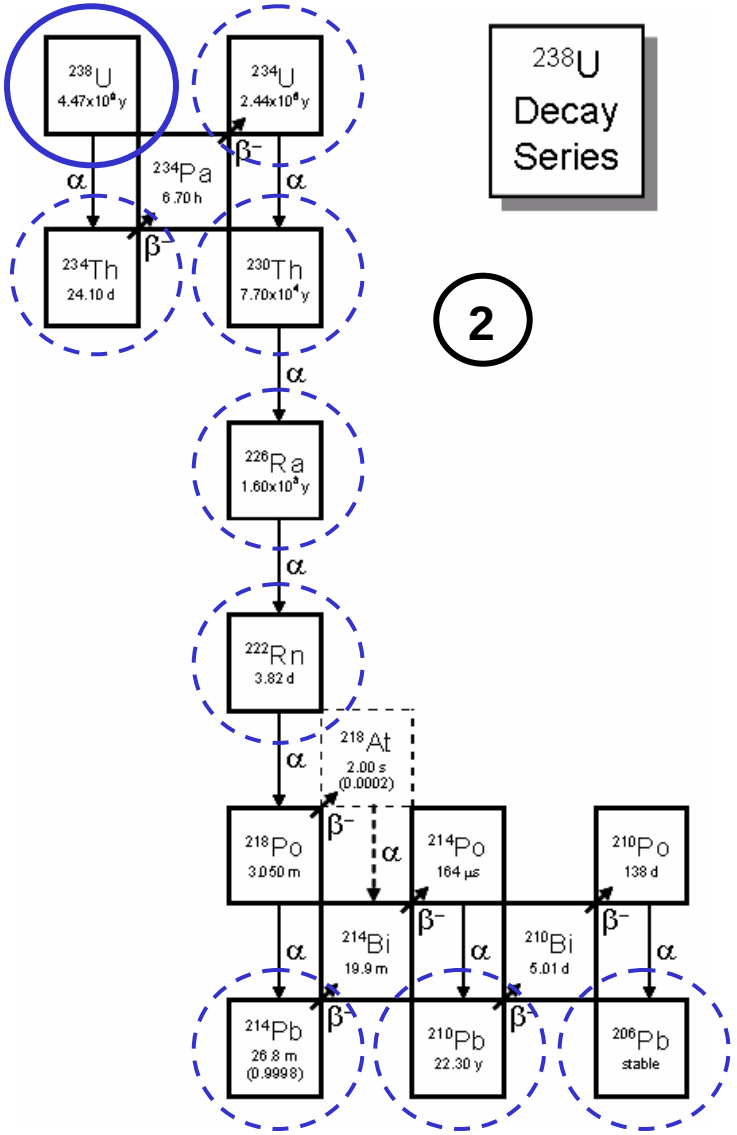
Evaluating NA Processes

Radioactive Decay & Daughter Products

1) Single-step Decay
   - Daughter product may posses its own risk characteristics due to radioactivity or chemical toxicity
   - Daughter products may also possess different transport characteristics

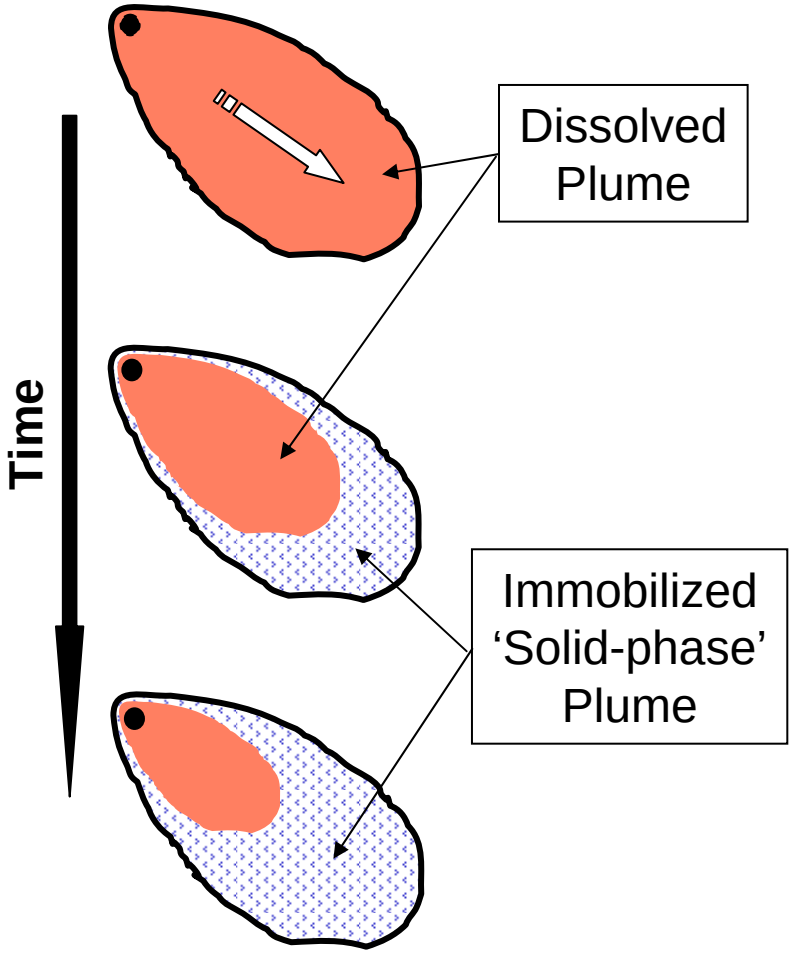
2) Decay Chain
   - A series of daughter products will be produced that may possess radiation/chemical risk characteristics
   - Daughter products may also possess different transport characteristics
   - Decay rates may vary significantly





'Dissolved' & 'Solid Phase' Plume Behavior

Balancing Investments in Characterization of Radioactive Decay and Immobilization Issues



- Significant mass of non-conservative radionuclide may be accumulated onto aquifer solids
- Emphasis of MNA analysis may shift to evaluating stability of immobilized contaminant if radionuclide (or immobilized daughter products) has a relatively long half-life or inherent chemical toxicity
- Accumulation of contaminant on aquifer solids would not necessarily preclude consideration of MNA, but it may expand/increase the level of site characterization

Questions to be Addressed through Site Characterization & Analysis

- What are the transport pathways within the aquifer?
- What is the rate of fluid flow along critical transport pathways?
- What processes control attenuation of the contaminant along transport pathways?
- What are the rates of attenuation & capacity of aquifer to sustain contaminant attenuation?

The data collected to address these questions also serve as the input into reactive transport models that may be employed as one of the tools to assess 1) the accuracy of the Conceptual Site Model and 2) the capacity and longevity of attenuation.

Characterizing Site Hydrogeology

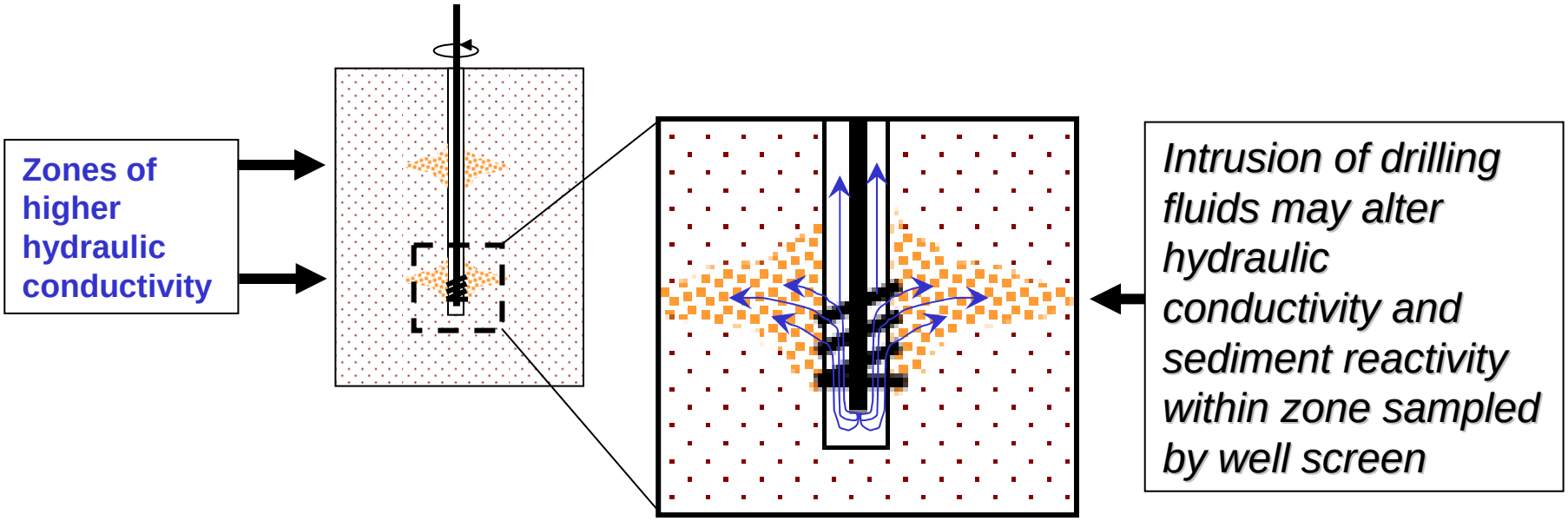
Characterization Goals

- Identify pathways of contaminant transport relative to compliance boundaries and risk receptors
- Establish GW monitoring network that allows collection of data to identify spatial heterogeneity and temporal variability of hydrologic and biogeochemical characteristics of aquifer
- Establish GW monitoring network that supports collection of samples that are representative of aquifer conditions

Characterizing Site Hydrogeology

Example – Well Drilling Methods

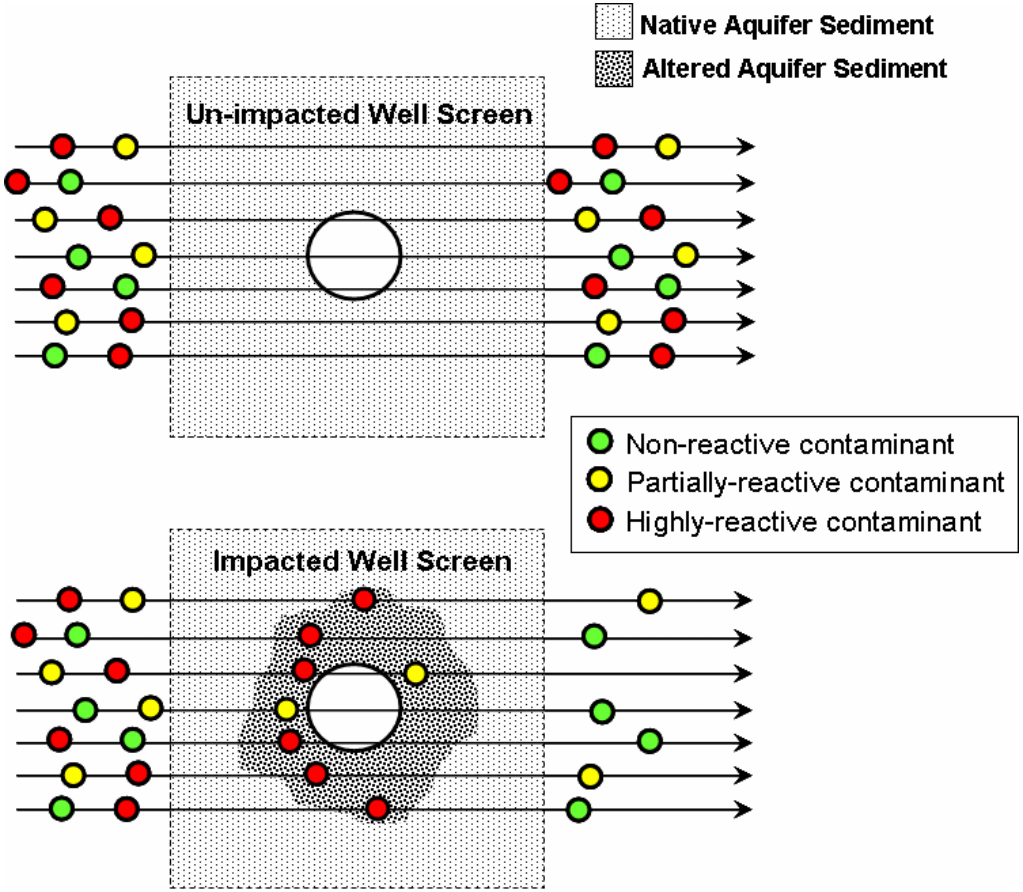
- Drilling fluids introduced into the well screen may ***alter hydraulic conductivity*** and/or reactivity of aquifer sediments along GW flow path
- Introduction of bentonite and/or alteration of sediment mineralogy (from degradation of organic drilling fluids) may ***change the sorption properties*** of the aquifer sediment adjacent to well screen



Characterizing Site Hydrogeology

Well Drilling Methods – Implications for Assessment of Contaminant Transport

- Organic contaminants (also perchlorate/nitrate) may be degraded/transformed concurrent with biotic reactions that degrade organic-based drilling fluids or via abiotic reactions with Fe(II)-bearing minerals
- Differential transport behavior of inorganic contaminants that possess varying sorption affinity to bentonite or newly precipitated minerals



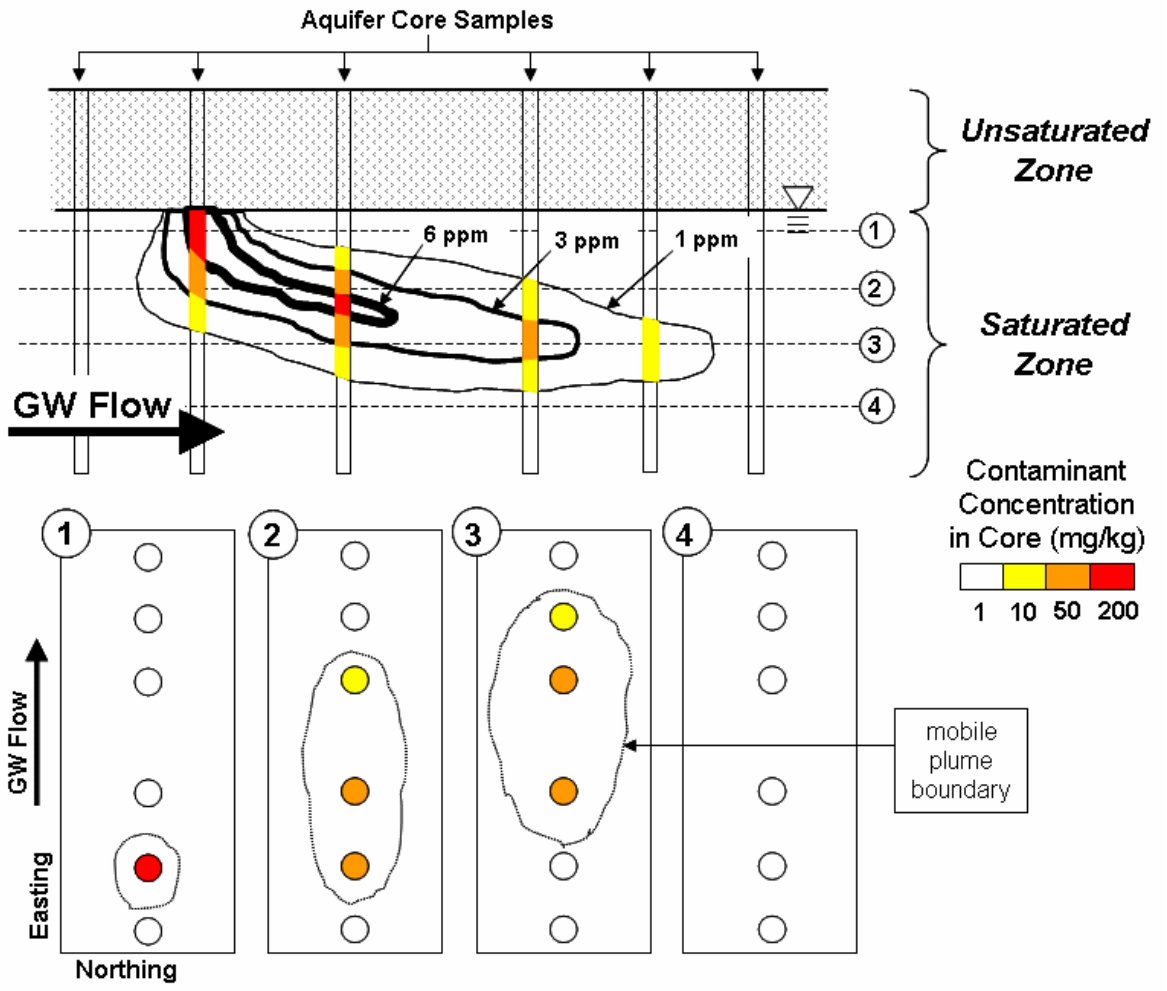
Characterizing Site Biogeochemistry

Characterization Goals

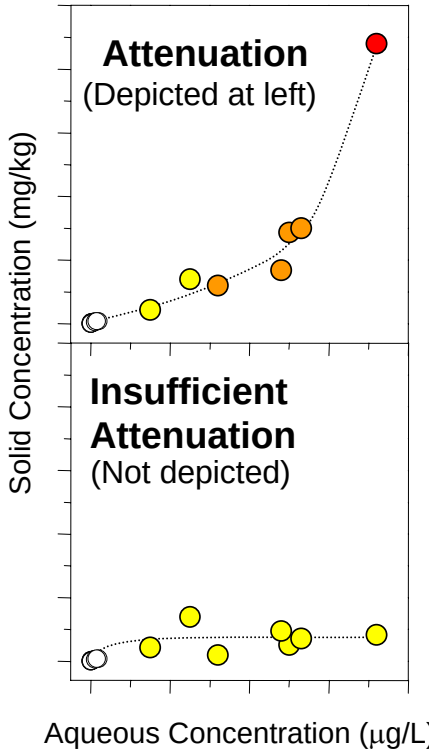
- Identify reaction mechanisms/processes that control contaminant transport
- Collect data that 1) support evaluation of Conceptual Site Model and 2) verify performance of identified attenuation process(es)
- Employ sample collection and analysis procedures that 1) maintain sample integrity and 2) characterize the factors that control contaminant partitioning between aqueous and solid matrices

Characterizing Site Biogeochemistry

Issue: Determining Attenuation by Immobilization

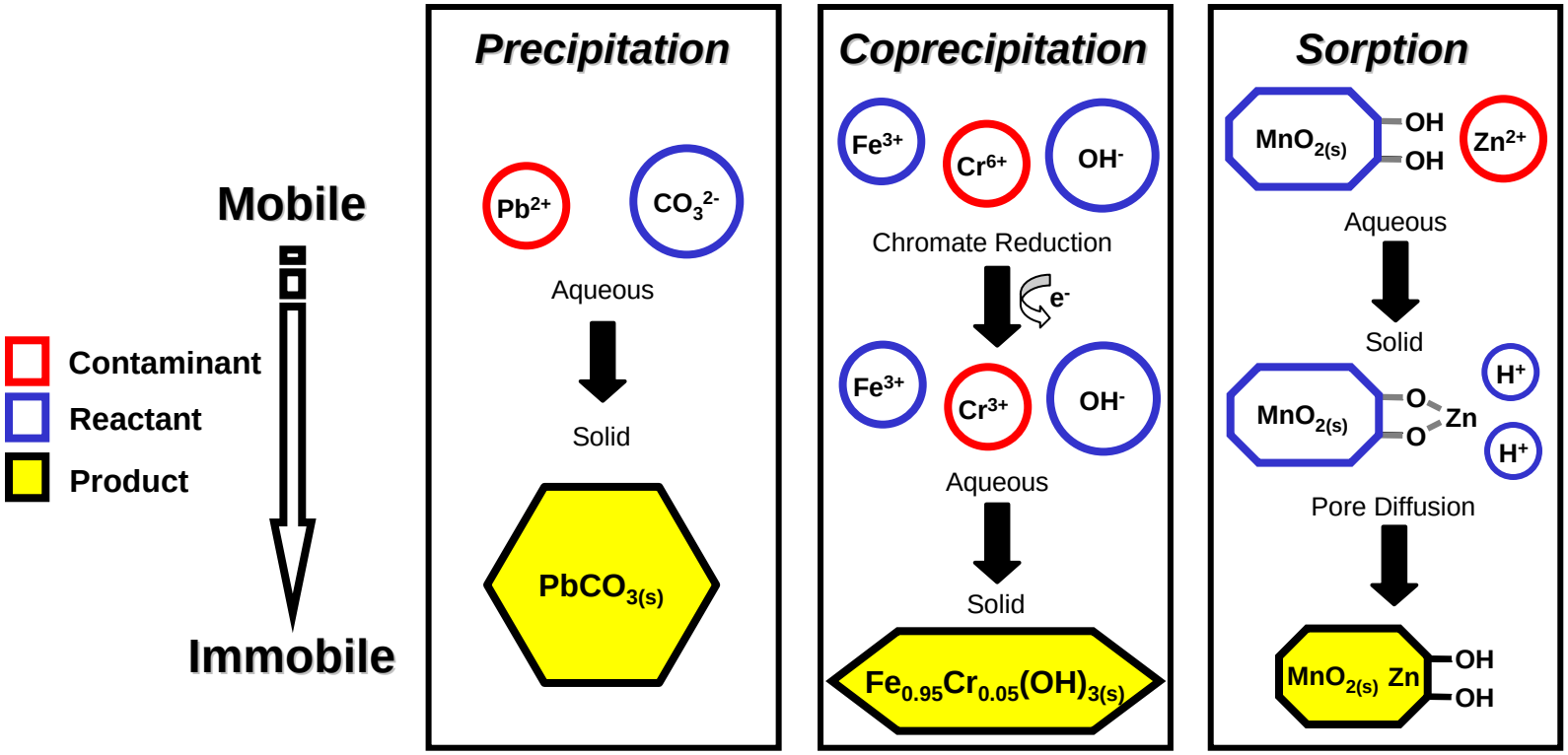


Site-Specific Sorption Isotherm



Characterizing Site Biogeochemistry

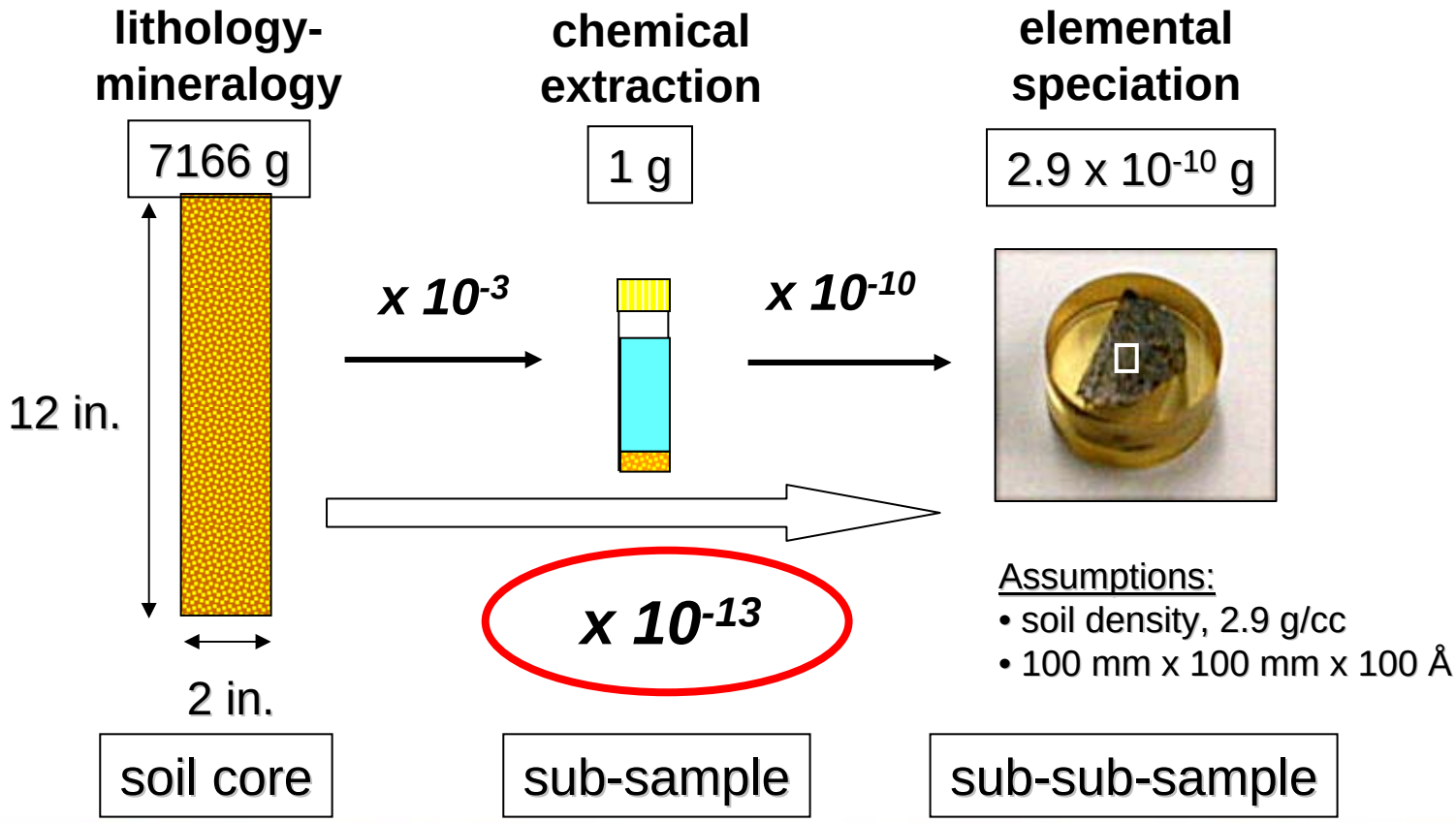
Issue: Immobilization Mechanism



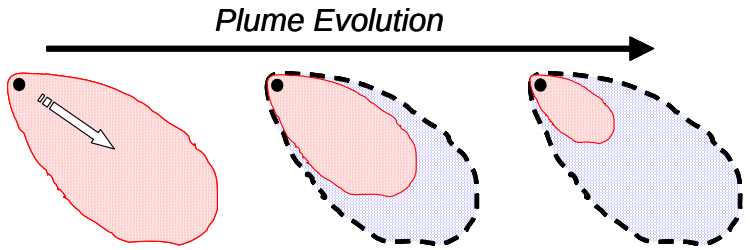
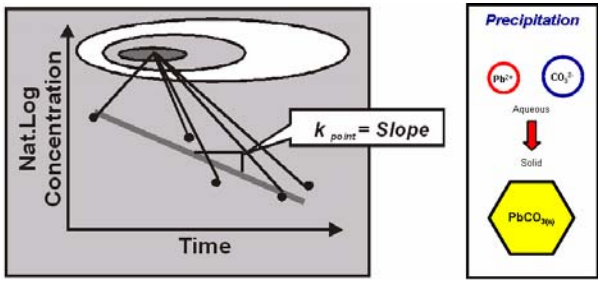
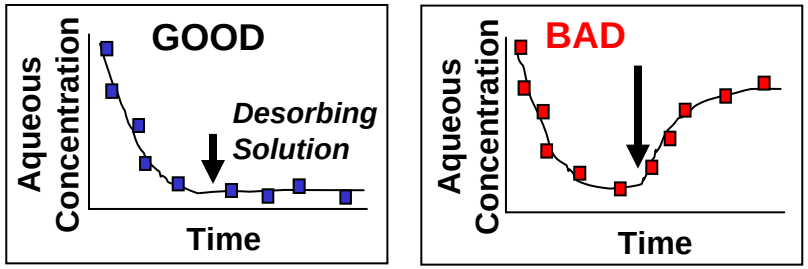
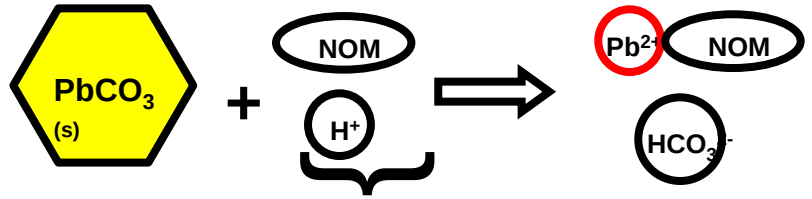
Identification of reaction mechanism(s) and participating reactants (biotic/abiotic) informs data needs for assessment and performance monitoring

Characterizing Site Biogeochemistry

Issue: Contaminant speciation (solid phase) and scaling observations using multiple characterization approaches to address site heterogeneity



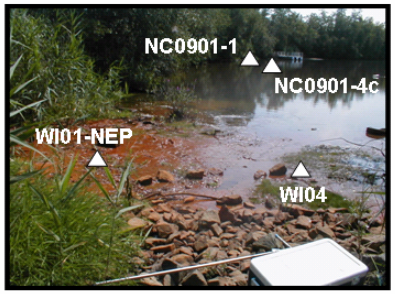
Tiered Analysis Concept

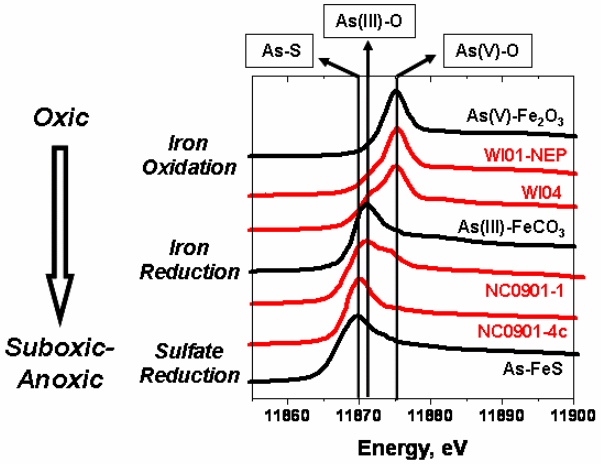
Tier 1 Actively demonstrate removal from ground water (site-specific data and geochemical basis) and/or adequate decay to prevent plume expansion	
Tier 2 Identify rate and mechanism(s) of attenuation	
Tier 3 Demonstrate long-term capacity and stability	
Tier 4 Design monitoring program, define triggers for MNA failure, and establish contingency plan(s)	 ***Performance Monitoring Parameters***

Principles in Practice

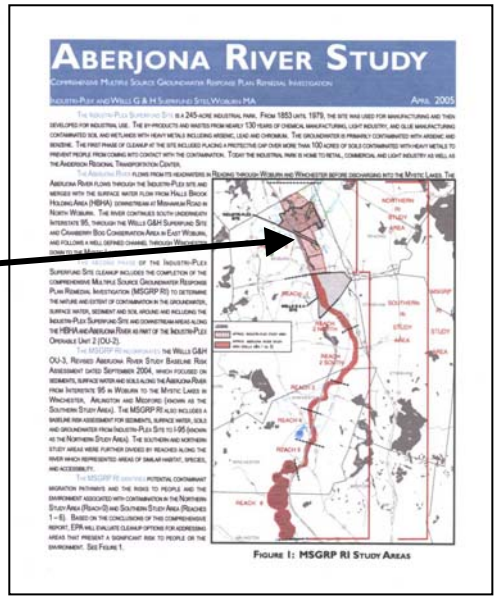
Industri-Plex Superfund Site

- ***'Enhanced' MNA*** chosen as part of site remedy for GW restoration





EPA Region 1 – OU2



http://www.epa.gov/region01/superfund/sites/industriplex/237453.pdf

Supporting Documentation

- EPA/ORD Final Report to Region 1
  http://www.epa.gov/ne/superfund/sites/industriplex/230912.pdf
- EPA/ORD Research Brief
  http://www.epa.gov/ada/download/briefs/epa_600_s05_002.pdf
- EPA/ORD Research Report
  http://www.epa.gov/ada/download/reports/600R05161/600R05161.pdf

Thanks - Questions?

EPA Documentation Relevant to Inorganics MNA

- Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, OSWER Directive 9200.4-17P - The purpose of this Directive is to clarify EPA's policy regarding the use of monitored natural attenuation (MNA) for the cleanup of contaminated soil and groundwater in the Superfund, RCRA Corrective Action, and Underground Storage Tank programs. (http://www.epa.gov/swerust1/directiv/d9200417.pdf)
- Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration, EPA/600/R-02/002 – This document provides a current survey of the scientific basis for understanding redox behavior in subsurface systems within the framework of site characterization, selection of remedial technologies, performance monitoring of remediation efforts, and site closure. (http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf)
- Performance Monitoring of MNA Remedies for VOCs in Ground Water, EPA/600/R-04/027 - This document provides technical recommendations regarding the types of monitoring parameters and analyses useful for evaluating the effectiveness of the natural attenuation component of ground-water remedial actions. (http://www.epa.gov/ada/download/reports/600R04027/600R04027.pdf)