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Site Characterization for MNA of Radionuclides in Ground Water

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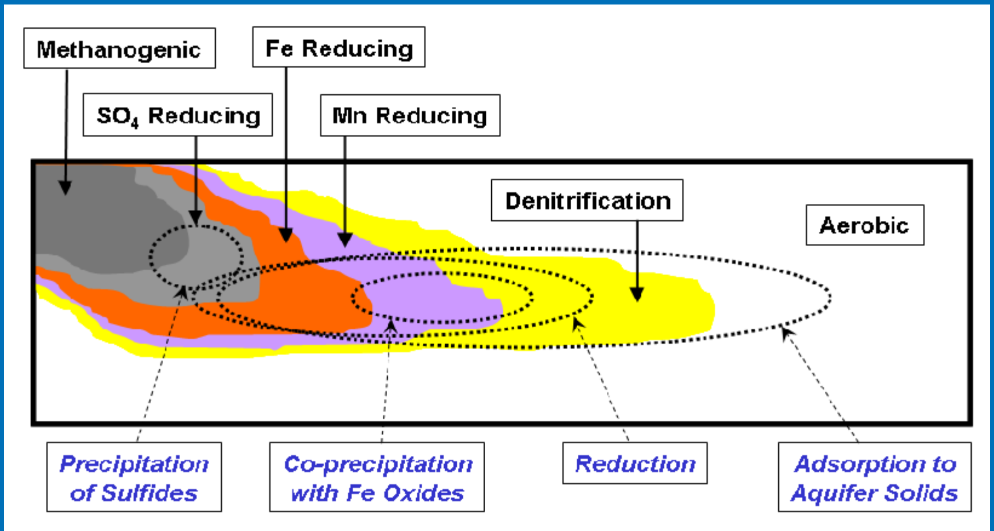

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Presentation Outline

- Attenuation Concepts
- Site Characterization Goals
- Potential Pitfalls
- Select Examples of Challenges
- Final Remarks

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What Controls Contaminant Transport?

- **Physical constraints:**
  - Contaminant source mass and distribution
  - Subsurface flow velocities
  - Spatial distribution of flow paths
  - Temporal variability of flow velocity & direction
- **Chemical constraints:**
  - Contaminant properties (decay rate, transformation rate, *sorption affinity*)
  - Aquifer sediment properties (mass distribution, *sorption affinity, chemical stability*)
  - Ground-water chemistry – as it affects 1) *contaminant chemical speciation* and 2) *aquifer solids stability & sorption characteristics*

This information determines accuracy of conceptual or predictive site model, which is the basis for projecting contaminant transport.

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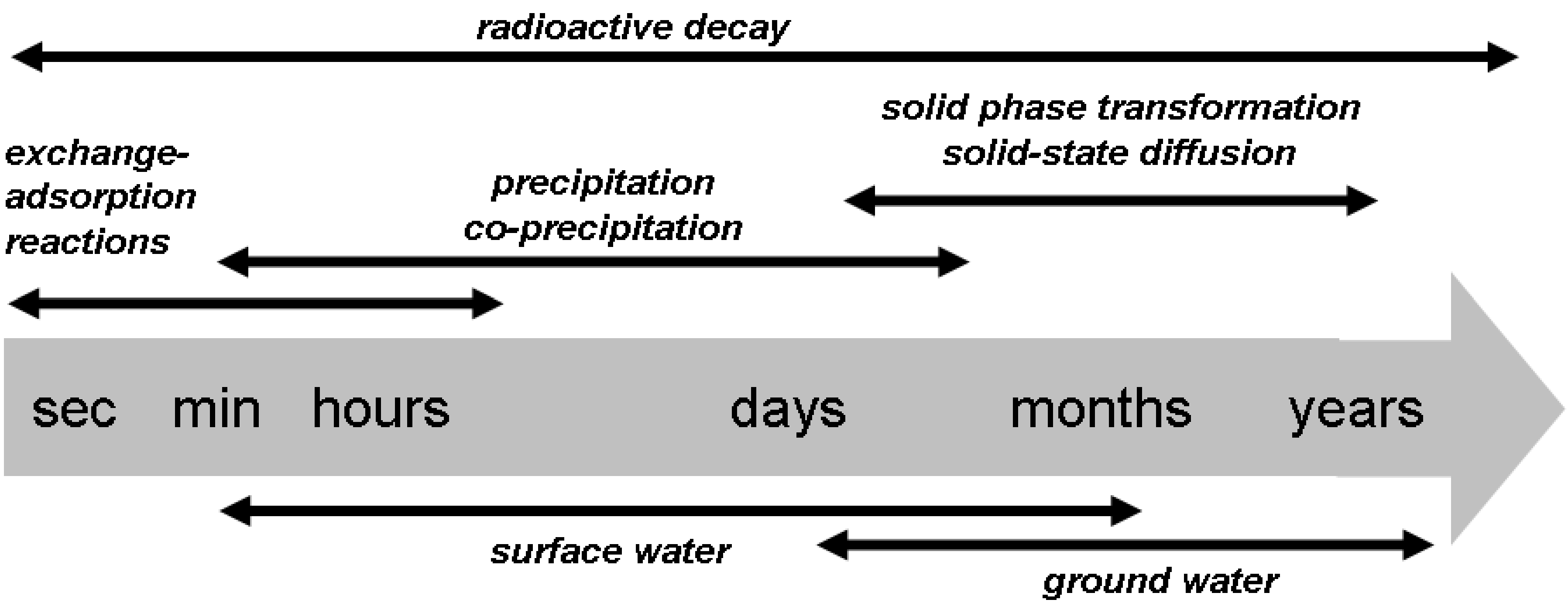
Questions to be Addressed through Site Characterization & Analysis

- 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? Reactants?
- What are the rates of attenuation & capacity of aquifer to sustain contaminant attenuation?
- Is the stability of the immobilized contaminant sufficient to resist re-mobilization?

Relative Process Timescales

Reaction Rate vs. GW Velocity

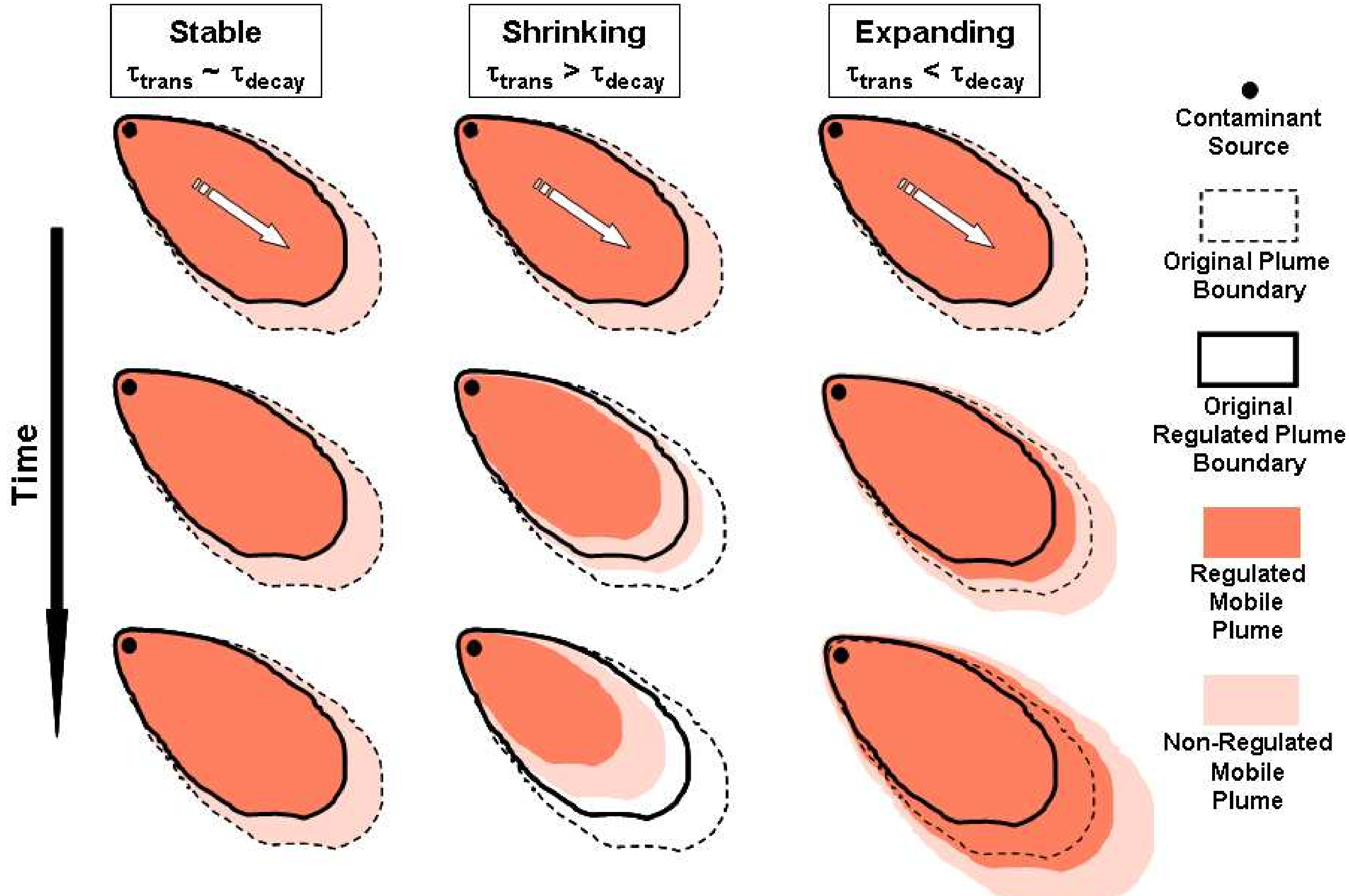
Attenuation Processes – *Reaction Times (τ_{rxn})*



Transport Processes – *Hydraulic Residence Times (τ_{trans})*

Subsurface Mobile Plume Behavior

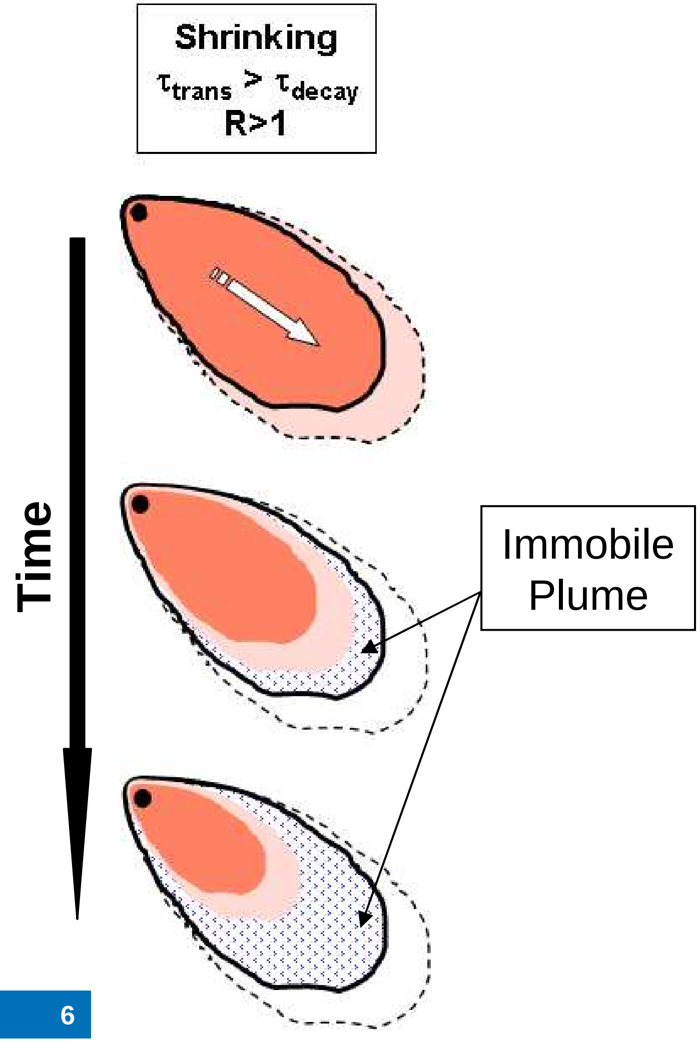
Decaying Radionuclide - Conservative Physical Transport, Uncontrolled Source
(Regulated = exceeds Risk-based or ARAR criterion; τ = characteristic time)



Radioactive Decay → *Starting mass/activity is important!*

Subsurface Plume Behavior

Decaying Radionuclide – Non-conservative Physical Transport, Uncontrolled Source



- **Significant mass of non-conservative radionuclide may be accumulated onto aquifer solids**
- **'*Immobile*' plume represents contaminant mass attenuated at any point in time**
- **Future scenarios for evolution of '*immobile*' plume**
  1) **Declines in mass & spatial distribution due to decay**
  2) **Remains invariant in mass & spatial distribution**
  3) ***Evolves to new state that serves as source for development of new dissolved plume***
     - ***Radioactive decay produces more mobile daughter product(s)***
     - ***Changes in ground-water chemistry cause re-mobilization***

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 (*drilling methods & materials important!*)
  - Avoid alteration of hydraulic conductivity
  - Avoid alteration of geochemistry adjacent to well screen

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Characterizing Site Biogeochemistry

Characterization Goals

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

Potential Pitfalls in Site Characterization

- **Hydrology – internal & external variability**
  - Spatial variation in hydraulic conductivity
  - Water exchange across GW-SW transition zone
  - Surface recharge variation that accompanies land-use change
  - Transport model calibration & validation (use of proprietary codes)
- **Well installation and construction**
  - Drilling methods & development procedure
  - Well materials (e.g., Cr, Ni, Mn from S/S corrosion)
  - Screen characteristics (length, opening size)
  - Horizontal & vertical resolution relative to plume dimensions

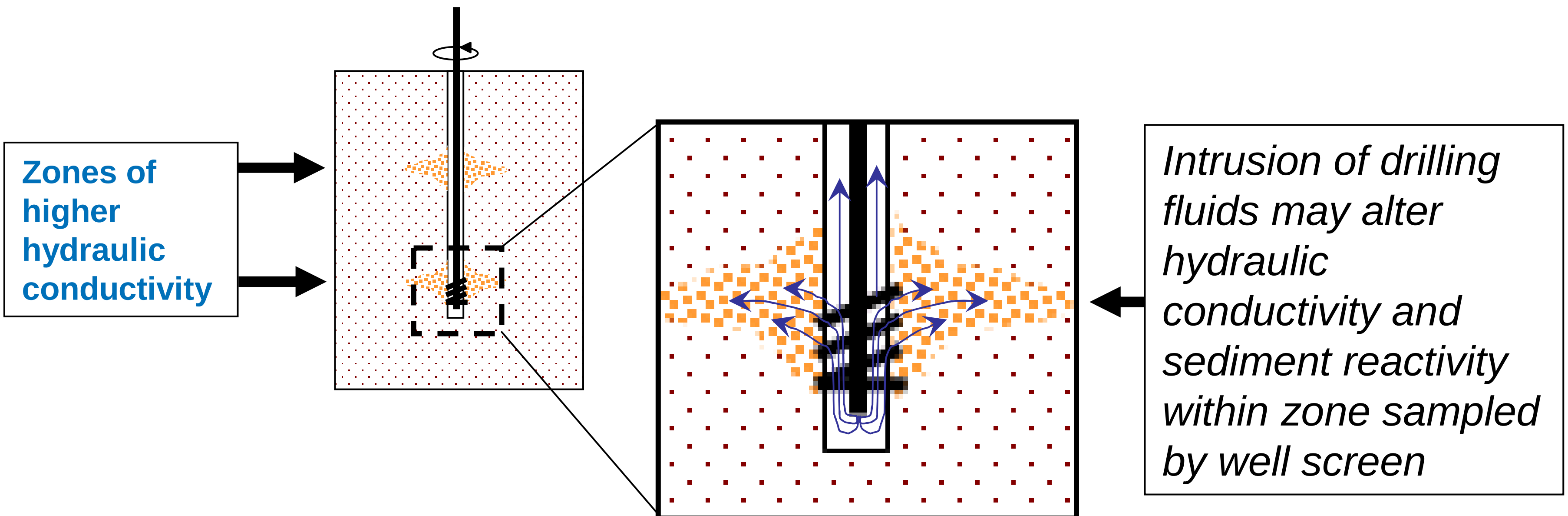
Potential Pitfalls in Site Characterization

- **Acquisition of subsurface samples**
  - Representative samples (e.g., well purging)
  - Preservation of in-situ geochemistry
    - Sample handling
  - Collection of mobile colloids
- **Characterization of subsurface samples**
  - Field vs. laboratory procedures
  - Scaling and heterogeneity (e.g., solid phase)
  - Methods for solid phase characterization
    - Extraction-based approaches

Well Installation and Construction

Drilling Methods & Development Procedure

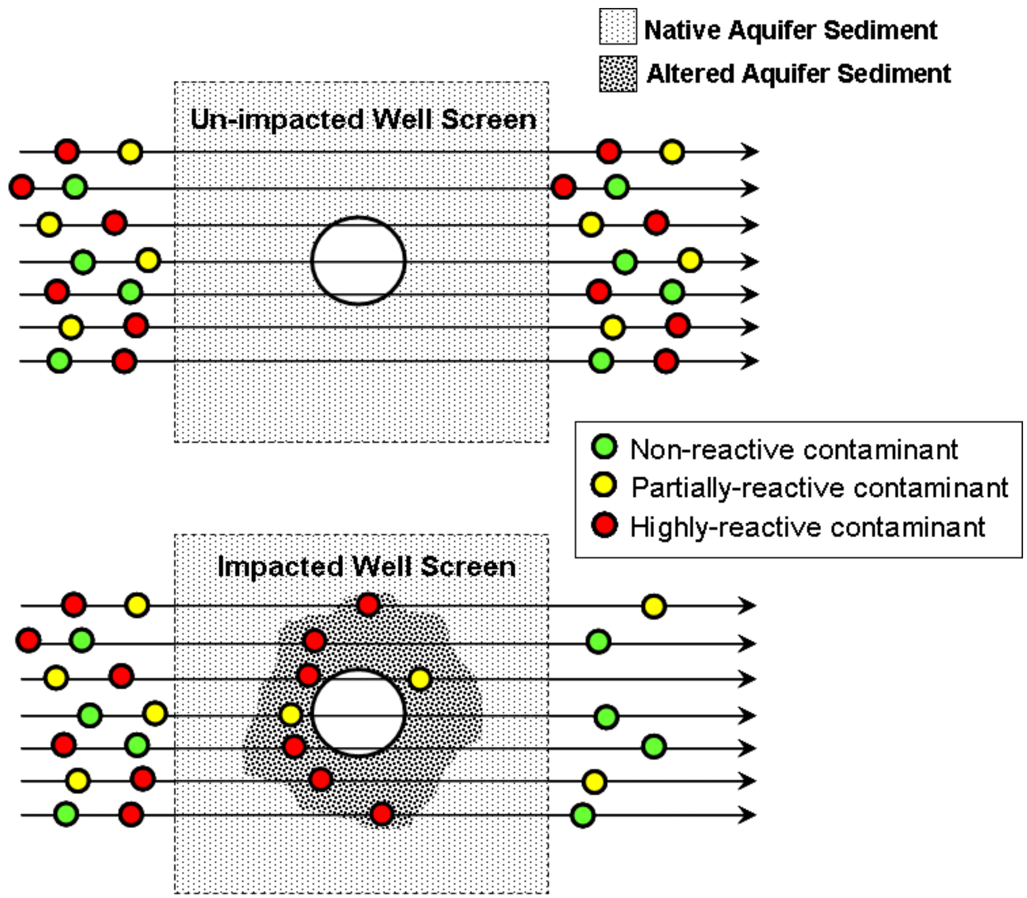
- Drilling fluids introduced into the well screen may ***alter hydraulic conductivity*** and/or reactivity of aquifer sediments along GW flow path
- Introduction of bentonite and/or alteration of sediment mineralogy (from degradation of organic drilling fluids) may ***change the sorption properties***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



Well Installation and Construction

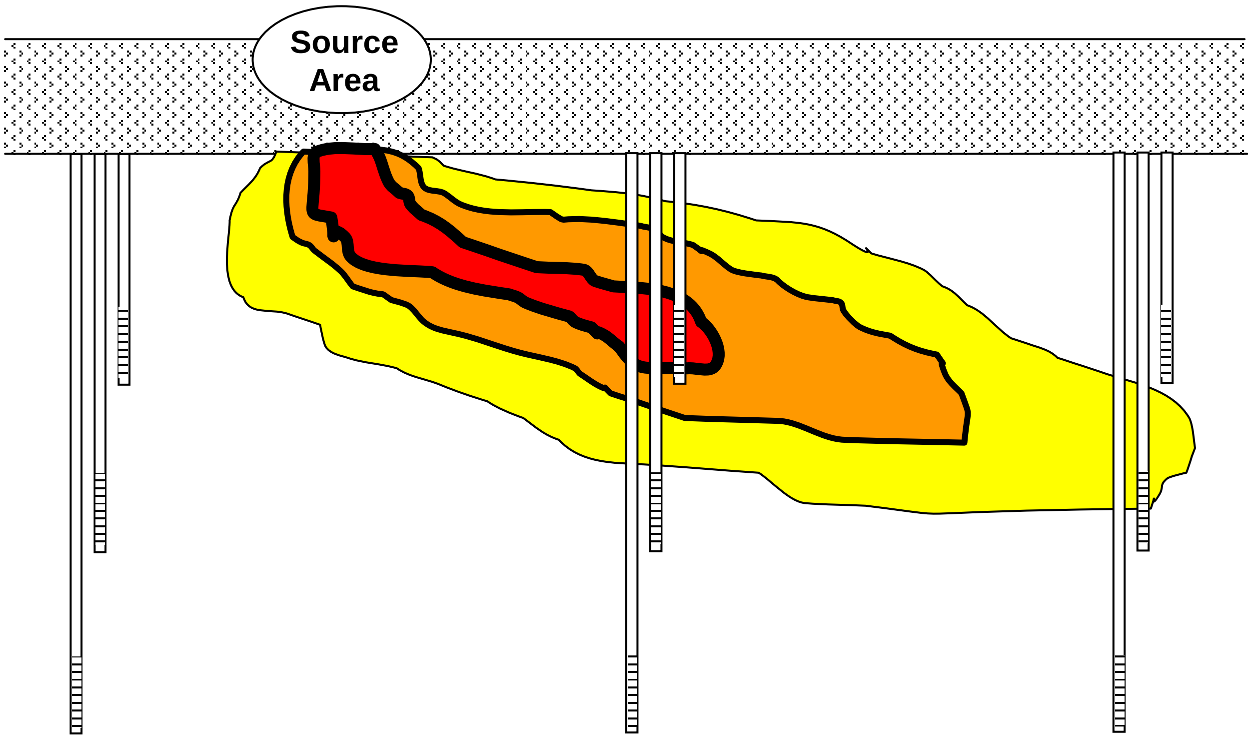
Well Drilling Methods – Implications for Assessment of Contaminant Transport

- 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



Acquisition of Subsurface Samples

Preservation of In-situ Geochemistry



1 *Reduced*

High Fe^{2+}
$HS^{-} >> SO_4^{2-}$
No DO

2 *Mildly Reduced*

Low Fe^{2+}
$HS^{-} \sim SO_4^{2-}$
Low DO

3 *Oxidized*

No Fe^{2+}
SO_4^{2-}, No HS^{-}
High DO

Acquisition of Subsurface Samples

Impact of Improper Sampling/Preservation

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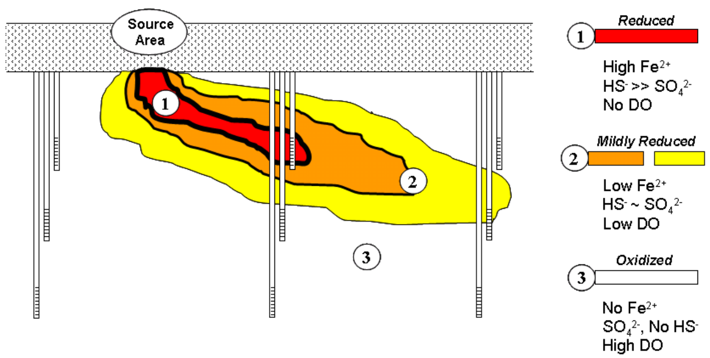
1. Loss of contaminant due to sorption to precipitating Fe^{2+}; HS^- oxidation; change in contaminant oxidation state; change in distribution of dissolved contaminants due to different affinities to precipitated Fe
2. Same as above, but less dramatic
3. Little or no impact due to similarity in surface & subsurface conditions

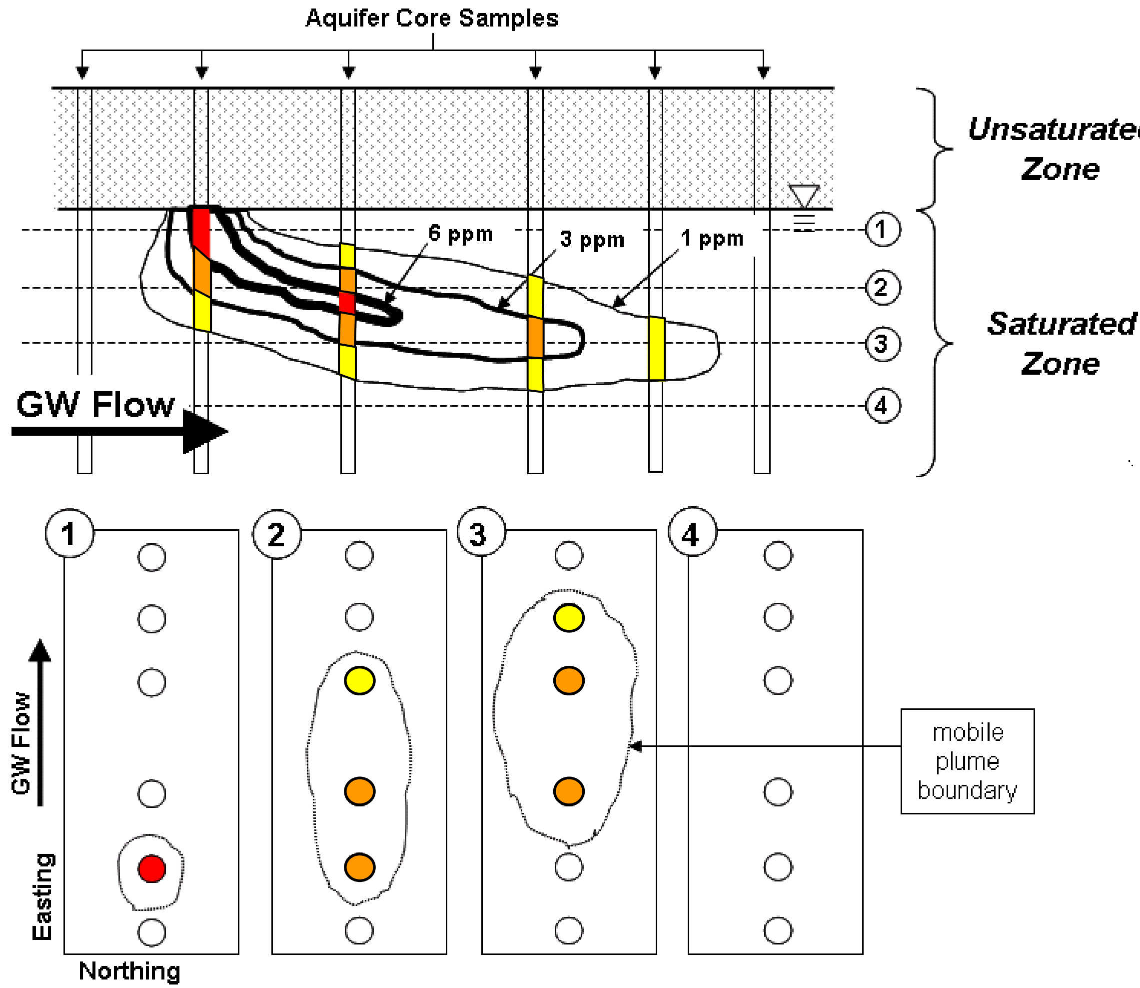


Increasing Severity of Impact

High DO, Negative ORP, H_2S detected → ***Sample collection or preservation is suspect!***

Acquisition of Subsurface Samples

Preservation of In-situ Geochemistry



1 ***Reduced***

Reduced Fe Minerals
Sulfides
Anaerobic Microorganisms

2 ***Mildly Reduced***

Mixed Fe(II)-Fe(III) Minerals
Carbonates-Sulfides?
Mixed Populations

3 ***Oxidized***

Fe Oxides
No sulfides (unless native)
Aerobic Microorganisms

Acquisition of Subsurface Samples

Impact of Improper Sampling/Preservation

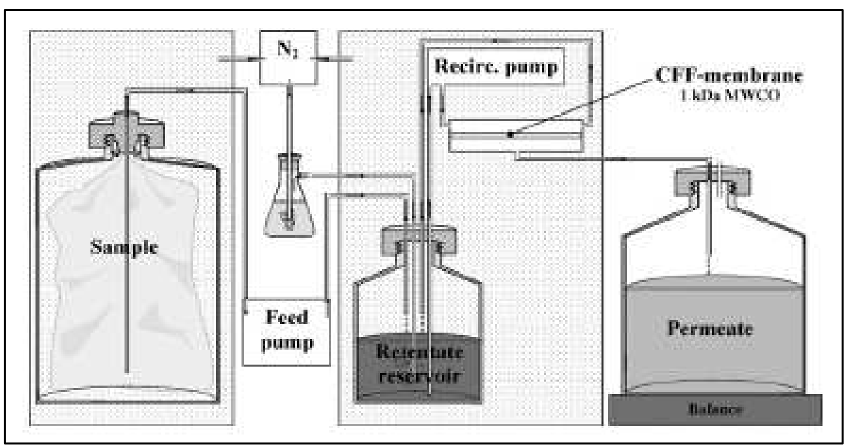
- **Transformations in aquifer solids mineralogy (Wilkin, EPA/600/R-06/112)**
  - Misleading identification of mineral(s) controlling contaminant immobilization
  - Changes in sorption characteristics for laboratory tests
  - Changes in chemical speciation of contaminant(s) leading to misidentification of attenuation process(es)
- **Loss of viable organisms that can be cultured to determine microcosm transformation rates (EPA/600/R-02/002)**

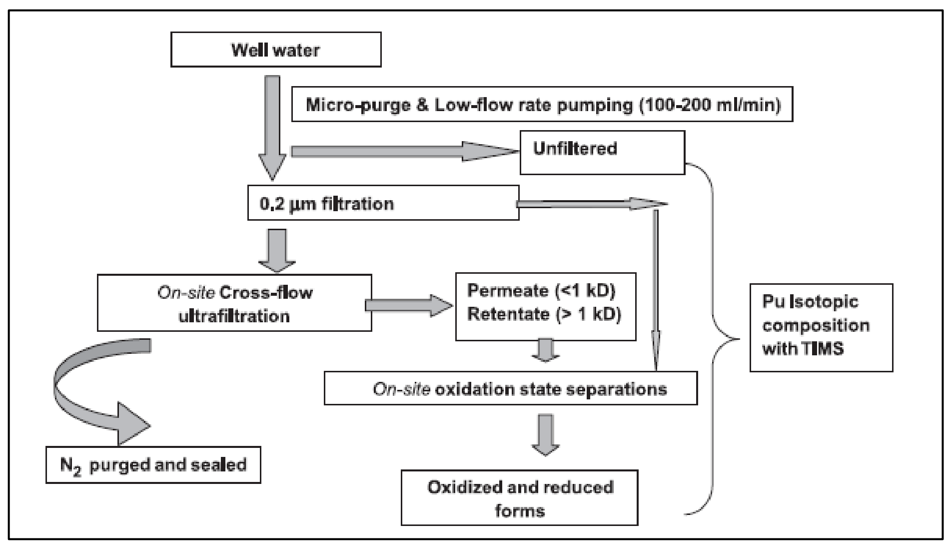
http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

Acquisition of Subsurface Samples

Collection of Mobile Colloids

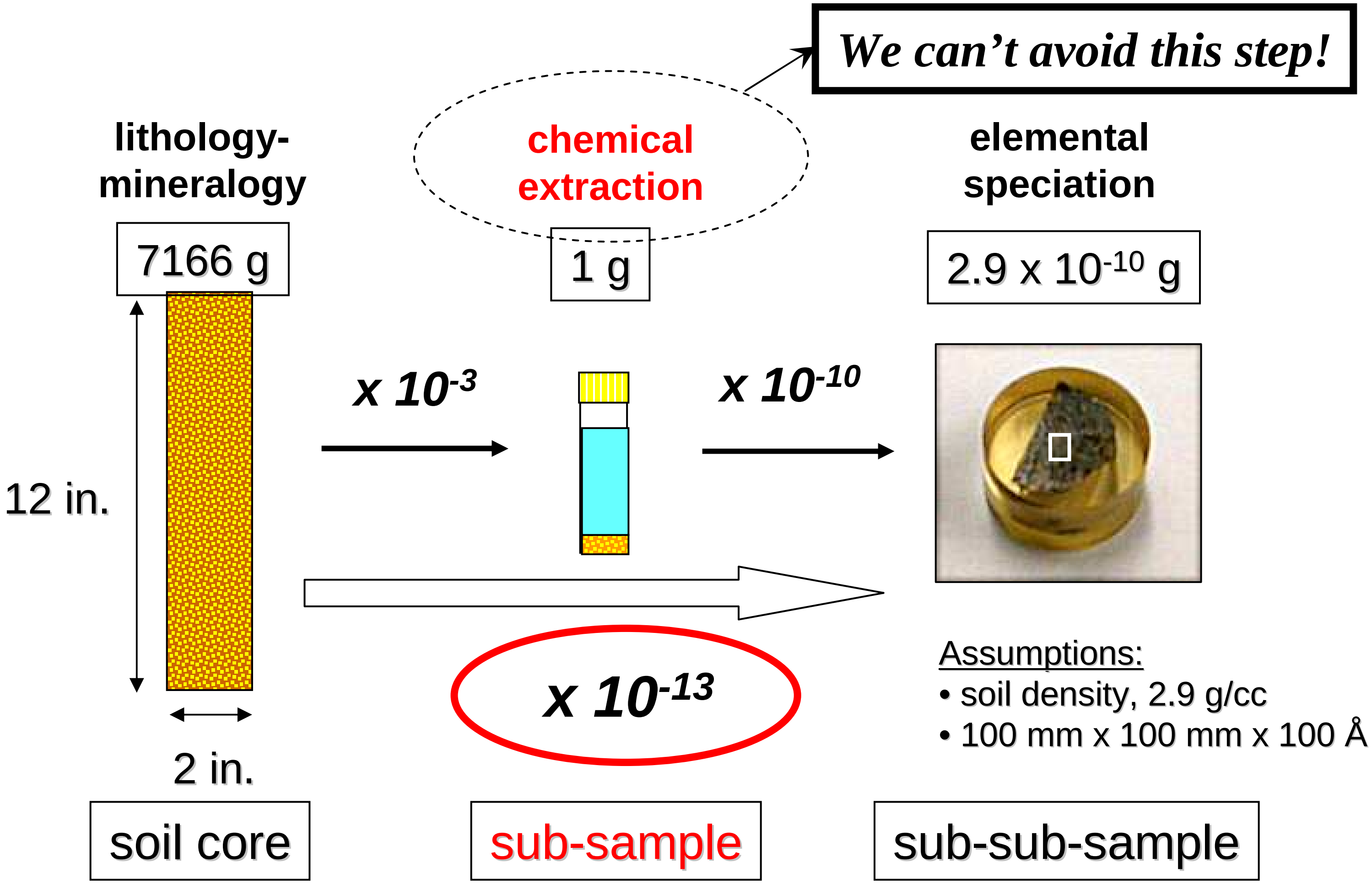
- Adequacy of well screen development?
- Verified lack of sampling artifacts?
- Characterization of colloidal material?
  - mineralogy, isotopic composition
- Use of sampling protocol capable of distinguishing colloidal transport?





Characterization of Subsurface Samples

Scaling and Heterogeneity



Characterization of Subsurface Samples

Extraction-based Approaches to Speciation

Pros:
- General applicability
- Good sensitivity for trace components
- High throughput
- May be used to define chemical speciation of contaminant in aquifer sediment

Cons:
- Chemical fractions are, in part, operationally defined
- Potential analytical artifacts due to contaminant carryover between extraction steps
- Selectivity may be poor for certain sediment types or contaminants

Characterization of Subsurface Samples

Chemical Extraction Protocols

Q: Why has there been limited improvement in these methods and their application?

A: Methods are not applied using the same level of analytical rigor commonly applied to water analyses.

Improvements:

- Verify *presence of target mineral* prior to method design and application (e.g., FeS via AVS w/ Fe conc.)
- *Matrix spiking* with synthetic references (e.g., Ni-FeS coprecipitate) to demonstrate recovery
- *Certified Reference Materials* – real matrices
- Employ chemical speciation model to evaluate potential for *carryover* based on knowledge of total sediment & extractant solution composition (e.g., $NiCO_3$ precipitation in bicarbonate-buffered solution)

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Characterization of Subsurface Samples

Alternative Approach to Protocol Design

1) Use knowledge of GW chemistry to guide aquifer solids sampling and preservation approach
2) Characterize mineralogy of aquifer solids
   a) GW chemistry – saturation state
   b) Total Sulfide, Acid Volatile Sulfide, Total Inorganic Carbon, Total Carbon (TOC by difference), Elemental Composition
   c) Mineral identification in physical fractions (size- or magnetic-fractionation, “differential” analyses before/after extraction)
3) Select extractant solutions based on mineralogy & contaminant characteristics
4) Evaluate potential for carryover
   a) Chemical speciation model (oversaturation, re-adsorption)
   b) Influence of solid matrix on final aqueous chemistry, e.g., pH
5) Include matrix spikes (i.e., known contaminant-mineral association) to assess recovery
6) Evaluate reference material(s) – assess laboratory performance

Characterization of Subsurface Samples

Standard Reference Materials & Protocols

NIST Ionizing Radiation Division
Environmental Radioactivity Section
Kenneth Inn (kenneth.inn@nist.gov) and Iisa Outola
http://physics.nist.gov/Divisions/Div846/Gp4/environ.html

- Optimize sequential extraction protocol to determine speciation of radionuclides in lake sediment SRM
- Organize intercomparison where labs use this sequential extraction protocol to analyze sediment
- Certify sediments for U, Pu, and stable elements by using the optimized method

NIST Speciation Workshop, 1995
(http://nvl.nist.gov/pub/nistpubs/jres/101/5/j5schu.pdf)

Final Remarks

- Adequate knowledge of site *hydrology and chemistry*
- Subsurface monitoring network that captures *spatial and temporal variability*
- Sample collection procedures that *minimize alterations* to in-situ geochemistry
- *Solid phase characterization* to support determination of immobilization mechanism, attenuation rates, attenuation capacity, and stability of immobilized contaminants
- *Documentation* of calibration and validation of contaminant transport model

Thanks - Questions?

Documentation Relevant to Subsurface Characterization and Analysis

- Guidelines and Standard Procedures for Studies of Ground-Water Quality: Selection and Installation of Wells, and Supporting Documentation, USGS Water-Resources Investigations Report 96-4233 (http://water.usgs.gov/owq/pubs/wri/wri964233/)
- Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures, EPA/540/S-95/504 - This document is intended to provide background information on the development of low-flow sampling procedures and its application under a variety of hydrogeologic settings. (http://www.epa.gov/ada/download/issue/lwflw2a.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)
- Documenting Ground-Water Modeling at Sites Contaminated with Radioactive Substances, EPA/540/R-96/003 - (http:// www.epa.gov/radiation/docs/cleanup/540-r-96-003.pdf)