Welcome – Thanks for joining this ITRC Training Class



A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater



ITRC Technical and Regulatory Guidance: A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater (APMR-1, 2010)

Sponsored by: Interstate Technology and Regulatory Council (www.itrcweb.org)
Hosted by: US EPA Clean Up Information Network (www.cluin.org)

Sites contaminated with metals and radionuclides present unique challenges to the development of effective remedial alternatives that also provide long-term protection to human health and the environment. The high costs of ongoing conventional treatment, total removal, and/or management combined with the scale of potential health and environmental risks make it important to evaluate attenuation-based remedial alternatives. Sites that have been identified as having metal and/or radionuclide contamination include federal facilities, industrial (e.g., mines) sites, disposal sites, and transportation corridors. Common metals include arsenic, cadmium, chromium, lead, nickel, copper, and selenium. For radioactive hazardous substances, uranium, radium, strontium, technetium, tritium, and thorium are the most common contaminants of concern. The attenuation processes affect most metals and radionuclides by changing their valence state, which in turn affects their solubility and therefore mobility. When properly employed, Monitored Natural Attenuation (MNA) is an effective knowledge-based remedy where a thorough engineering analysis informs the understanding, monitoring, predicting, and documenting of natural processes. In order to properly employ this remedy, there needs to be a strong scientific basis supported by appropriate research and site-specific monitoring implemented in accordance with quality systems.

This training and the associated ITRC Technical and Regulatory Guidance document, A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater (APMR-1, 2010), is intended for anyone involved with evaluating, investigating, remediating or managing a site that involves metal and radionuclide contaminants in groundwater. This training and document provides:

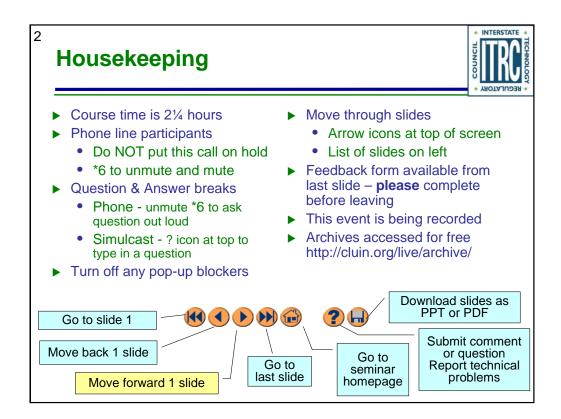
- -- Introduction to key attenuation processes for metals and radionuclides
- -- Information on incorporating MNA into remedial alternatives for metals/rads
- -- Overview of the decision framework on MNA for metals and radionuclides in groundwater within the larger evaluation framework of a contaminated site

For reference during the training class, participants should have a copy of the decision framework, Figure 3-1 on page 48 of the ITRC Technical and Regulatory Guidance document, A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater (APMR-1, 2010) and available as a 1-page PDF at http://www.cluin.org/conf/itrc/apmr/ITRC-APMR-DecisionFramework.pdf.

ITRC (Interstate Technology and Regulatory Council) www.itrcweb.org

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ITRC Training Program: training@itrcweb.org; Phone: 402-201-2419



Although I'm sure that some of you are familiar with these rules from previous CLU-IN events, let's run through them quickly for our new participants.

We have started the seminar with all phone lines muted to prevent background noise. Please keep your phone lines muted during the seminar to minimize disruption and background noise. During the question and answer break, press *6 to unmute your lines to ask a question (note: *6 to mute again). Also, please do NOT put this call on hold as this may bring unwanted background music over the lines and interrupt the seminar.

You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments using the? icon. To submit comments/questions and report technical problems, please use the? icon at the top of your screen. You can move forward/backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our presentation overview, instructor bios, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation slides.

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ITRC (<u>www.itrcweb.org</u>) – Shaping the Future of Regulatory Acceptance



- ▶ Host organization
 - Network <u>E C</u>
 - State regulators
 - All 50 states, PR, DC
 - Federal partners







 ITRC Industry Affiliates Program



- Academia
- Community stakeholders

- Wide variety of topics
 - Technologies
 - Approaches
 - Contaminants
 - Sites
- Products
 - Technical and regulatory guidance documents
 - Internet-based and classroom training

The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition of regulators, industry experts, citizen stakeholders, academia and federal partners that work to achieve regulatory acceptance of environmental technologies and innovative approaches. ITRC consists of all 50 states (and Puerto Rico and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and advance the regulatory acceptance of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision making while protecting human health and the environment. With our network of organizations and individuals throughout the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

For a state to be a member of ITRC their environmental agency must designate a State Point of Contact. To find out who your State POC is check out the "contacts" section at www.itrcweb.org. Also, click on "membership" to learn how you can become a member of an ITRC Technical Team.

ITRC Course Topics Planned for 2011 – More information at www.itrcweb.org



Popular courses from 2010

- Enhanced Attenuation of Chlorinated Organics: A Site Management Tool
- ► In Situ Bioremediation of Chlorinated Ethene - DNAPL Source Zones
- LNAPL 1: An Improved Understanding of LNAPL Behavior in the Subsurface
- LNAPL 2: LNAPL Characterization and Recoverability - Improved Analysis
- LNAPL 3: Evaluating LNAPL Remedial Technologies for Achieving Project Goals
- ► Mine Waste Treatment Technology Selection
- Phytotechnologies
- Quality Considerations for Munitions Response Projects
- Use and Measurement of Mass Flux and Mass Discharge
- ► Use of Risk Assessment in Management of Contaminated Sites

New in 2011

- ► Decision Framework for Applying Attenuation Processes to Metals and Radionuclides
- Biofuels: Release Prevention, Environmental Behavior, and Remediation
- Development of Performance Specifications for Solidification/Stabilization
- Bioavailability Considerations for Contaminated Sediment Sites
- PRB: Technology Update
- Project Risk Management for Site Remediation

2-day Classroom Training:

- ► Vapor Intrusion Pathway
- LNAPLs

More details and schedules are available from www.itrcweb.org under "Internet-based Training" and "Classroom Training."

Meet the ITRC Instructors





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Ann Charles is a Research Scientist with the New Jersey Department of Environmental Protection's (NJDEP) Site Remediation Management and Response Program in Trenton, New Jersey. Since 1988, Ann has been working for the NJDEP in the Bureau of Environmental Evaluation and Risk Assessment, overseeing publicly funded investigations and remediations that include radionuclide contaminated sites in the Site Remediation Program. Program and policy initiatives have involved the current development of soil remediation standards for the State of New Jersey, Technical Requirements for Site Remediation, New Jersey remedial process optimization team, and biennial certification and cap value teams. Ann has been a member of the ITRC Radionuclides team since 2004. She earned a bachelor's degree from Franklin and Marshall College in Lancaster, Pennsylvania in 1982 and a master's degree from Miami University in Oxford, Ohio in 1990.

Jennifer Nyman is a Senior Project Engineer in the Emeryville, CA office of ARCADIS. Since 2006, Jennifer has worked at ARCADIS/Malcolm Pirnie on applied research projects and as technical lead for field projects with metal/radionuclide or bioremediation components. She specializes in the characterization and remediation of groundwater and sediment, and is a recognized expert on the topics of bioremediation and metal/radionuclide contamination. Jennifer has authored numerous scientific and professional papers on these topics, including manuscripts published in the journals Environmental Science & Technology and Applied and Environmental Microbiology. While at Stanford University, Jennifer assisted in the design and implementation of bioremediation for a uranium-impacted aquifer in Oak Ridge, Tennessee, that for several decades had received radioactive waste from nuclear weapons production. She joined the Attenuation Processes for Metals and Radionuclides Team of ITRC in 2008. Jennifer earned a bachelor's degree in chemical engineering from Montana State University in Bozeman, Montana in 2000 and master's degree in 2002 and doctoral degree in 2006, both in Environmental Engineering and Science from Stanford University in Palo Alto, California.

Ryan Fimmen is a research scientist at Geosyntec Consultants in Columbus, Ohio. Ryan started with Geosyntec Consultants in March 2011. Previously, he worked for 3 years at Battelle where he managed and worked on several projects with metals impacted sediments, soils and groundwater. Ryan's primary job responsibilities include development and execution of bench-scale and field-scale research studies in the area of soil/groundwater remediation. His most recent project experience involves development of a suite of bench-scale experiments to determine the most effective strategy for remediation of mercury impacted lake and river (freshwater) sediments. Ryan has also worked with the EPA to develop a technical resource document on the topic of monitored natural recovery of sediments impacted with metal and/or organic contaminants. Ryan joined the *Attenuation Processes of Metals and Radionuclides* ITRC team in January 2009 and has worked closely with the team in integrating basic geochemical processes and principals into the technical regulatory guidance document. Ryan earned a bachelor's degree in chemistry from Carleton College in Northfield, Minnesota in 1995, a master's degree in chemistry from the University of Wisconsin-Madison in Madison, Wisconsin in 1998, and completed his doctoral studies in geochemistry from Duke University in Durham, North Carolina in 2004.

Karen Vangelas is a fellow engineer at the Savannah River National Laboratory (SRNL) in Aiken, South Carolina. She has been employed at the Savannah River Site since 1989. Karen worked one year at SRNL before transferring to the newly formed Environmental Restoration organization in 1990. In that role she led site characterization and remedial assessment work at both metal/radionuclide contaminated sites as well as organic contaminated sites. In 1996, Karen returned to SRNL where she participated in applied research projects, gaining increasing levels of responsibility through the years. Her early work was focused on field efforts associated with organic contaminants. Karen's latest and ongoing work involves managing two applied research efforts, one developing enhanced attenuation approaches for chlorinated solvents and the other a broad research initiative developing an approach, as well as, tools and treatment technologies for groundwater contaminated with metals and radionuclides. Karen has been a member of the ITRC beginning in 2004 as a member of the Enhanced Attenuation: Chlorinated Organics Team. With the formation of the Attenuation Processes for Metals and Radionuclides Team in 2007 she became a team member. Karen earned a master degree in Environmental Engineering from The Pennsylvania State University in State College, Pennsylvania in 1990.

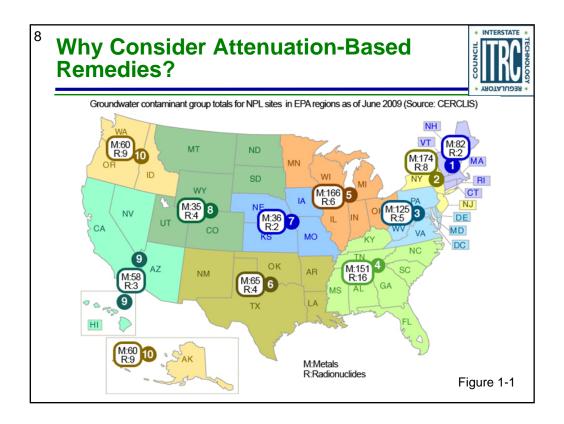
ITRC Attenuation Processes for Metals and Radionuclides (APMR) Team



- ▶ Develop consistent approach to evaluate attenuation-based remedies
- ▶ Pool technical and regulatory knowledge
- ▶ Issue guidance documents and offer training



The ITRC APMR Team has a widespread membership base that includes regulators from EPA headquarters, regional EPA offices, Dept of Energy, State regulators from nearly 10 states, tribes, public stakeholders, contractors, and representatives from National laboratories



Thousands of sites contaminated with metals and / or radionuclides

These are long-lived contaminants that cannot be physically destroyed

Intractable site closure

How Will You Evaluate Attenuation-Based Remedies?



- ➤ You will be submitting or reviewing proposals for attenuation-based remedies
- ➤ You will be deciding if an attenuation-based remedy is appropriate



Why We're Here Today



- Provide framework to evaluate Monitored Natural Attenuation (MNA) for groundwater contaminated with metals or radionuclides
- ► Strong scientific basis
- Governing policies and guidelines

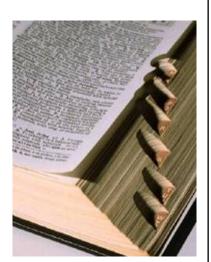


Photo is from Weldon Springs DOE Superfund Site, near St. Louis, Missouri

Definitions



- ▶ Monitored Natural Attenuation (MNA) includes processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants
- ► Enhanced Attenuation (EA) uses engineered technologies to augment the natural attenuation processes



Monitored Natural Attenuation (MNA) includes processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater.

Enhanced Attenuation (EA) is the use of low-energy, long-acting (sustainable) technologies to augment the natural attenuation processes, essentially bridging the gap between high-energy, short-term remedial alternatives and MNA.

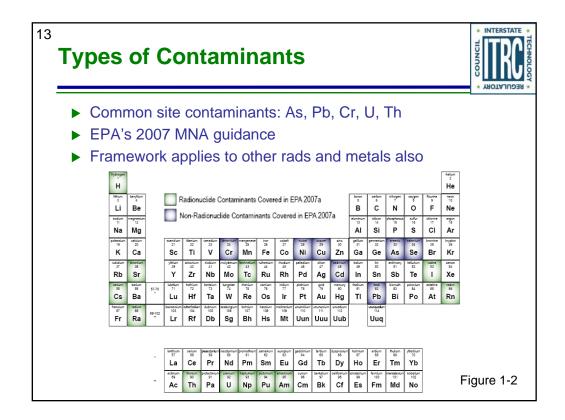
Types of Sites



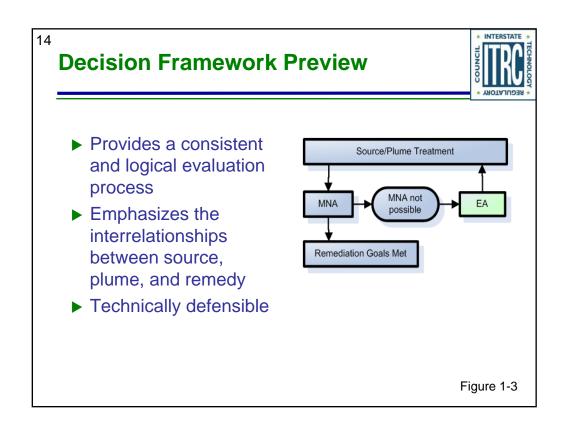
- ► Nuclear production sites
- ▶ Disposal sites
- ▶ Mining operations
- ► Agricultural applications
- ► Federal facilities
- ► Industrial facilities



There are many sites with potential for metals or rad contamination, and there are many types of waste release scenarios.

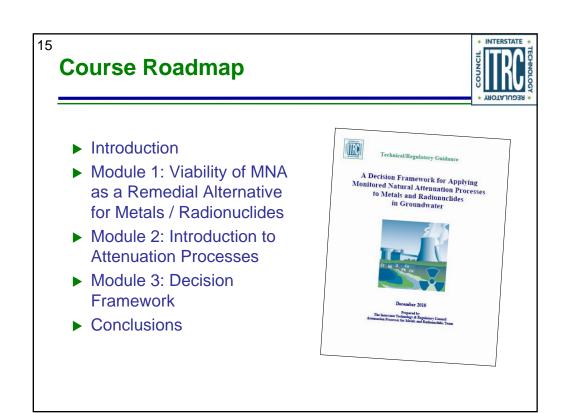


For more details, see Figure 1-2 and Section 1.1.2 of our companion document.



This graphic is a simplified version of the MNA Decision Framework.

The full Decision Framework is discussed in detail in Module 3 and in Chapter 3 of the companion document, Figure 3-1.



This is our roadmap for today's presentation



A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater

MODULE 1:

Viability of MNA as a Remedial Alternative for Metals / Radionuclides

Module 1: Viability of MNA as a Remedial Alternative **Barriers to Acceptance**



- ▶ Controversial as a remedy
- ▶ Need for consistent policies, training
- ▶ Factors affecting acceptance
- ► Advantages, challenges

Some perceptions may result from a lack of experience with metals and radionuclides.

One example challenge is the potentially long timeframes associated with attenuation processes.

In order to properly employ this remedy, there needs to be a strong scientific basis supported by appropriate research and site-specific monitoring implemented in accordance with quality controls.

Most of the topics of this module are covered in Section 4 of the guidance document (Regulatory Overview).

Also refer to the ITRC document Enhanced Attenuation: Chlorinated Organics, from 2008: http://www.itrcweb.org/guidancedocument.asp?TID=50.

Module 1: Viability of MNA as a Remedial Alternative Regulatory Systems: Federal



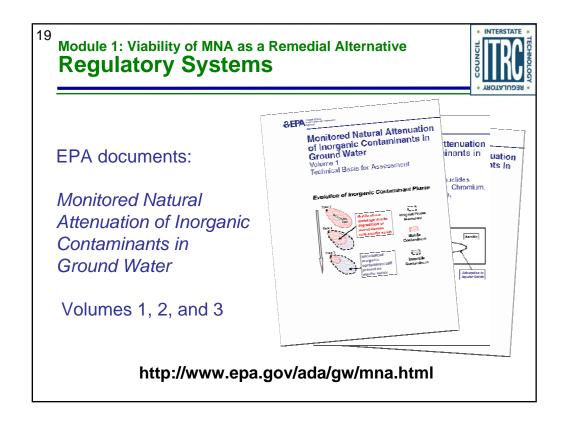
- ▶ 1999 EPA Office of Solid Waste and Emergency Response (OSWER) Directive
- ► Policies for site remediation (e.g., CERCLA)
- ► EPA policy on MNA forthcoming

USE OF MONITORED NATURAL ATTENUATION AT SUPERFUND, RCRA CORRECTIVE ACTION, AND UNDERGROUND STORAGE TANK SITES

U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response Directive 9200.4-17P

April 1999

Federal regulations are covered in Section 4.1 of the guidance document.



Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 1: Technical Basis for Assessment EPA 600-R-07-139, 2007

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 EPA 600-R-07-140, 2007

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water Volume 3: Assessment for Radionuclides Including Tritium, Radon, Strontium, Technetium, Uranium, Iodine, Radium, Thorium, Cesium, and Plutonium-Americium EPA 600/R-10/093, 2010

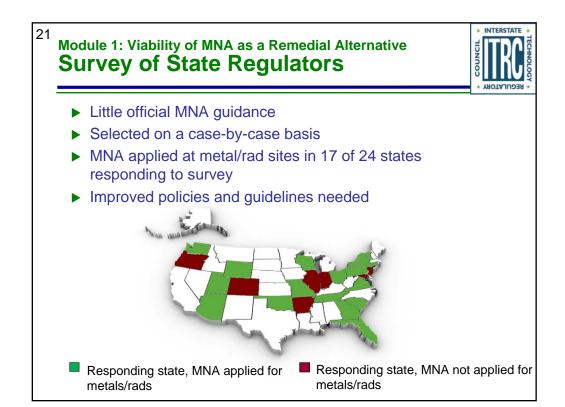
Module 1: Viability of MNA as a Remedial Alternative Regulatory Systems: State



- ▶ Not an available remedy historically
- ▶ MNA can fit intent of the existing regulations
- ► Variable policy between states

Section 4.2 of the ITRC guidance document

State regulation of MNA is covered in Section 4.2 of the guidance document.

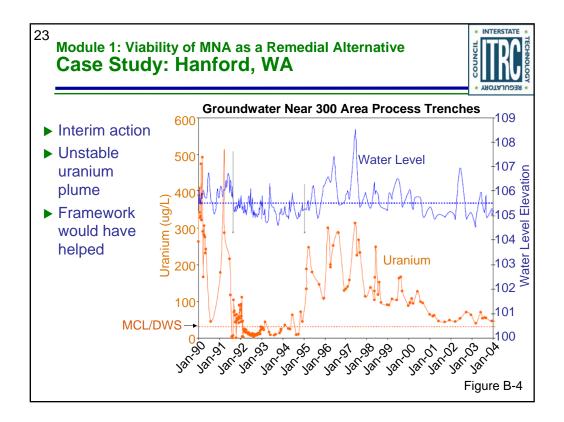


Responses to other questions of the survey are in Table 4-1 of the guidance document, and more details are presented in Appendix C.

Module 1: Viability of MNA as a Remedial Alternative Factors Affecting Regulatory Acceptance*



- ► Removal of source
- ► Site characterization
- ▶ Stable or shrinking plume
- ► Stability of end-products
- ► Availability of other remedies
- ► Timeframe/attenuation capacity
- ► Monitoring program
- ► Contingencies/institutional controls
 - * Not all factors apply in every case and the list is not exhaustive



This case study is described in detail in Appendix A of the guidance document.

Source of Figure: Robert G. Ford, Richard T. Wilkin, and Steven Acree, Site Characterization to Support Use of Monitored Natural Attenuation for Remediation of Inorganic Contaminants in Ground Water. EPA. 2007

Expedited Response Action to remove contaminated soil from process trenches started in 1991. Discharge of uranium-free water to trench continued, however.

All discharges to process trenches are stopped in December 1994.

Note that the decision framework presented in this training was not available during the interim remedy selection for this site. Had the framework been available, the interim remedy likely would not have relied so heavily upon MNA.

Module 1: Viability of MNA as a Remedial Alternative Factors Affecting Regulatory Acceptance*



- ▶ Removal of source
- ► Site characterization
- ► Stable or shrinking plume
- ► Stability of end-products
- ► Availability of other remedies
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- ► Contingencies/institutional controls
 - * Not all factors apply in every case and the list is not exhaustive

Module 1: Viability of MNA as a Remedial Alternative Advantages of MNA for Metals/Rads

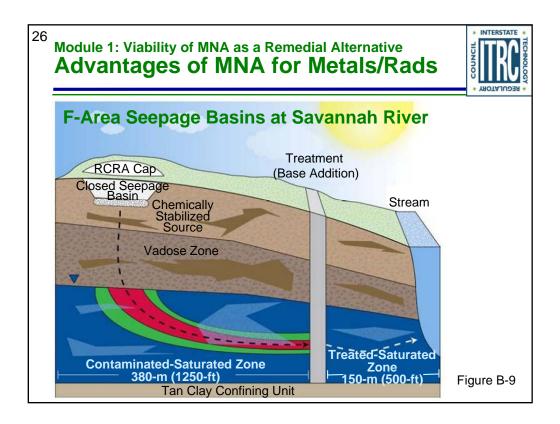


- ▶ Less remediation wastes
- Less cross-media transfer
- ▶ Reduced risk of human exposure
- ► Smaller footprint
- ▶ Used with other remedial measures
- ► Generally lower overall remediation costs



These lists of advantages and challenges of natural attenuation are modified from the 1999 EPA OSWER Directive and guidance from the Alaska Department of Environmental Conservation.

Expanded lists are in Section 4.4 of the guidance document.



Additional details are presented in Appendix A and Section 6 of the guidance document.

Module 1: Viability of MNA as a Remedial Alternative Advantages of MNA for Metals/Rads



- Less remediation wastes
- Less cross-media transfer
- ▶ Reduced risk of human exposure
- ► Smaller footprint
- ▶ Used with other remedial measures
- ► Generally lower overall remediation costs



These lists of advantages and challenges of natural attenuation are modified from the 1999 EPA OSWER Directive and guidance from the Alaska Department of Environmental Conservation.

Expanded lists are in Section 4.4 of the guidance document.

Module 1: Viability of MNA as a Remedial Alternative Challenges of MNA for Metals/Rads



- Significant site characterization
- Persistence in the subsurface
- ► Long-term immobilization
- ► Long-term monitoring
- ▶ Timeframes
- Education and outreach efforts



Photo courtesy of the U.S. Department of Energy

In the photo, a groundwater remediation project crew is conducting a sampling at a Geoprobe borehole near Hanford's U Plant Processing Canyon. The photo was taken in 2005.

Module 1: Viability of MNA as a Remedial Alternative **Tribal and Stakeholder Issues**



- ► Stakeholders want
 - Minimal exposure and acceptable risk
 - Usefulness of the site
 - Long-term monitoring, institutional controls
 - Well-defined contingency plan
- ► Tribal nations as stakeholders

Stakeholder issues are covered in Section 5 of the guidance document.

Module 1: Viability of MNA as a Remedial Alternative **Key Points**



- Usually employed with other remedial technologies
- ► Satisfies regulatory requirements
- ▶ Improved guidelines needed





A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater

MODULE 2:

Introduction to Attenuation Processes

Module 2: Introduction to Attenuation

Processes Learning Objectives



- ► Learn about attenuation processes for metals and radionuclides
- ► Understand the relationship between attenuation processes and aquifer properties
- ► Understand reversibility of metals attenuation and the need for long-term monitoring
- ► Hypothetical case study
 - Co-precipitation of Ni with FeS

Module 2: Introduction to Attenuation Processes

MNA Processes



- ► MNA processes include
 - Precipitation / co-precipitation
 - Sorption
 - Radioactive decay
 - Dilution / dispersion
- At most sites sorption, precipitation, or coprecipitation will be attenuation mechanism
 - Balance between forces that tend to keep contaminant in solution vs. forces that tend to partition contaminant to solid

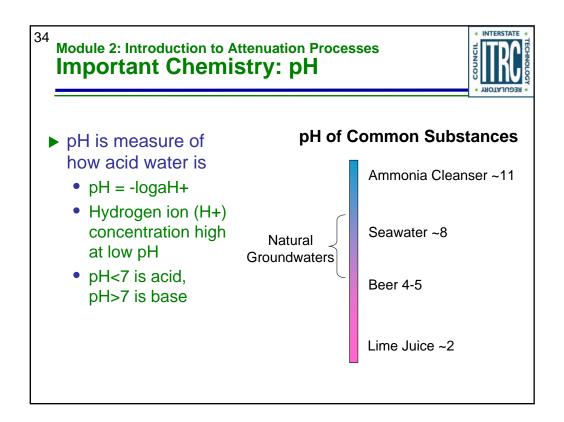
Precipitation binds a contaminant within a mineral that has the contaminant as a major component (Example: cerussite PbCO3)

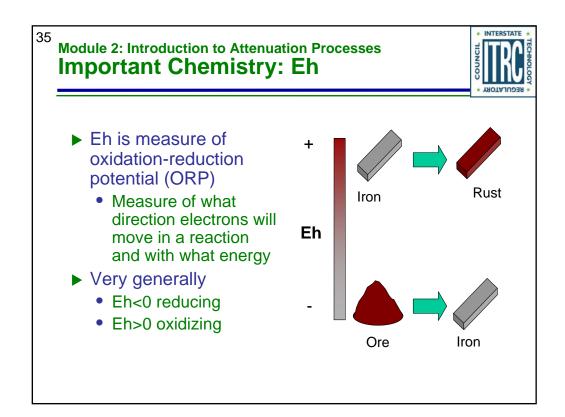
Co-precipitation binds a contaminant within a mineral in which the contaminant is a minor component (Example: hematite containing chromium Fe1.9Cr0.1O3)

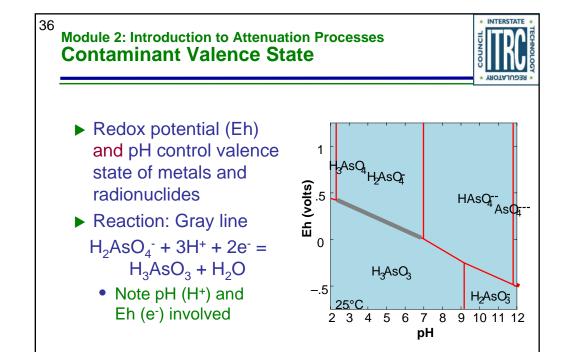
Sorption binds a contaminant at the surface of a mineral - the term sorption often includes adsorption, ion exchange, and in some cases absorption; adsorption is the electrostatic attraction of an ion to the surface of a mineral; cation exchange is the electrostatic attraction of an ion to the surface of a mineral followed by that ion replacing an ion from the mineral; absorption is typically diffusion of an ion into a microporous surface of a mineral or organic matter.

Radioactive decay is an intrinsic property of the contaminant

Dilution/dispersion is a hydrodynamic process rather than a chemical process - USEPA strongly discourages acceptance of dilution/dispersion as a primary attenuation mechanism in applications of MNA







Overall: Eh-pH diagrams valuable to assess attenuation because they show effects of both master variables

Eh is a measure of oxidation-reduction potential – a major control on the species of contaminants that have multiple valence states

Eh-pH diagrams are equilibrium diagrams and thus only show what is thermodynamically favored, not what actually exists

Bullet 1: Common misconception is that Eh is the only control on valence states of contaminants, but pH is also a major control for many contaminants

if H⁺ appears in the reaction between species, then pH is a major control

Example: $H_2AsO_4^- + 3H^+ + 2e^- = H_3AsO_3^0 + H_2O$

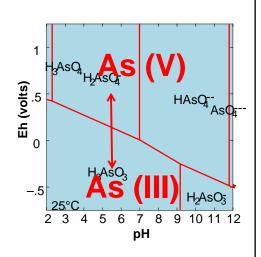
Bullet 2: Example: As(III) is generally less mobile than As(V)

U(IV) forms less soluble minerals than U(VI)





- ► Eh and pH often combined to show dominance of dissolved species and stability of solid phases
- This can help predict how mobile a contaminant might be
 - As (V) strongly adsorbed to iron oxides, As (III) is more mobile
 - Under reducing conditions
 - As (V) is reduced
 - Iron oxides dissolve
 - As (III) is mobilized



Overall: Eh-pH diagrams valuable to assess attenuation because they show effects of both master variables

Eh is a measure of oxidation-reduction potential – a major control on the species of contaminants that have multiple valence states

Eh-pH diagrams are equilibrium diagrams and thus only show what is thermodynamically favored, not what actually exists

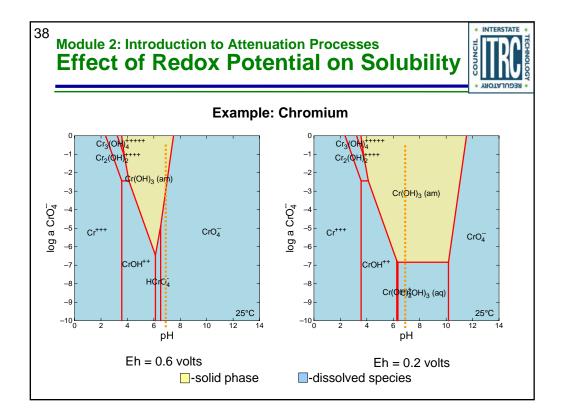
Bullet 1: Common misconception is that Eh is the only control on valence states of contaminants, but pH is also a major control for many contaminants

if H⁺ appears in the reaction between species, then pH is a major control

Example: $H_2AsO_4^- + 3H^+ + 2e^- = H_3AsO_3^0 + H_2O$

Bullet 2: Example: As(III) is generally less mobile than As(V)

U(IV) forms less soluble minerals than U(VI)



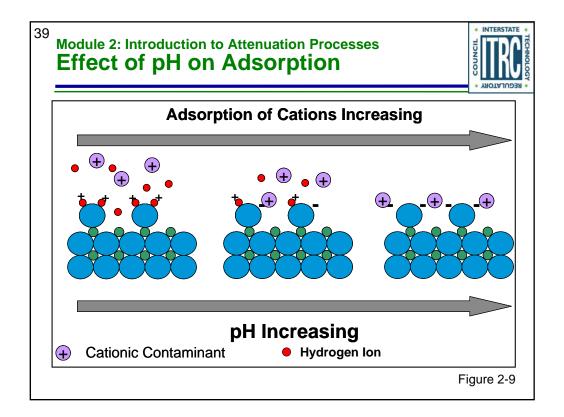
The solid Cr(OH)3(am) is much more soluble at Eh=0.6 volts and pH=7 (orange dotted line) than at Eh=0.2 volts and pH=7

Approximately 10-3 moles/liter at Eh=0.6 volts compared to 10-7 moles/liter at Eh=0.2 volts

Note that the reaction controlling solubility of Cr(OH)3(am) is:

$$Cr(OH)3(am) + H2O = CrO4-2 + 5H+ + 3e-$$

Where e- are electrons, hence relating the solubility of Cr(OH)3(am) to Eh, while the presence of H+ in the reaction relates the solubility to pH



Waters adsorbed to surface of minerals exchange hydrogen ions with pore water as pH changes

leads to change in surface charge on mineral

The change in charge depends on mineral type one reason mineralogy is so important

Positively charged contaminants (cations) attracted to negatively charged mineral surface Adsorb more strongly as pH increases

Negatively charged contaminants behave in the opposite way

40 Module 2: Introduction to Attenuation Processes Variability of Sorption, Precipitation, and Coprecipitation



- Sorption, precipitation, and co-precipitation are chemical reactions
- ▶ Like other chemical reactions, the rate and extent of reaction depends strongly on chemical composition of system
- Evolving chemical compositions can change attenuation of metals and radionuclides



Sorption, precipitation, and co-precipitation are chemical reactions

Like other chemical reactions, the rate and extent of reaction depends strongly on chemical composition of system

Evolving chemical compositions can change attenuation of metals and radionuclides

Module 2: Introduction to Attenuation Processes **Sorption**



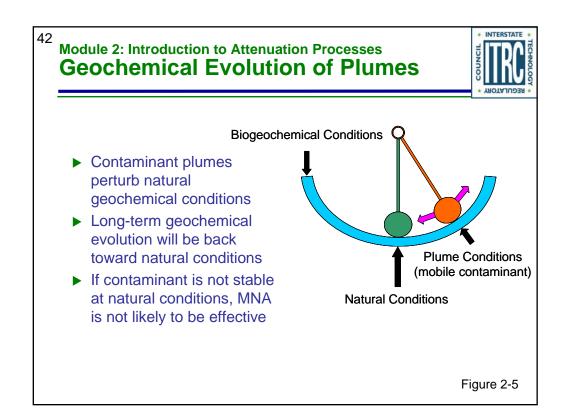
- ► The partitioning of a contaminant from the groundwater onto the surface of a mineral or organic matter in the aquifer
- Common minerals with reactive surfaces
 - Phyllosilicates
 - Oxyhydroxides
 - Sulfides
 - Carbonates
 - Natural organic matter
- Clays
- Fe/Mn
- Fe
- · Ca, Fe
- Humics

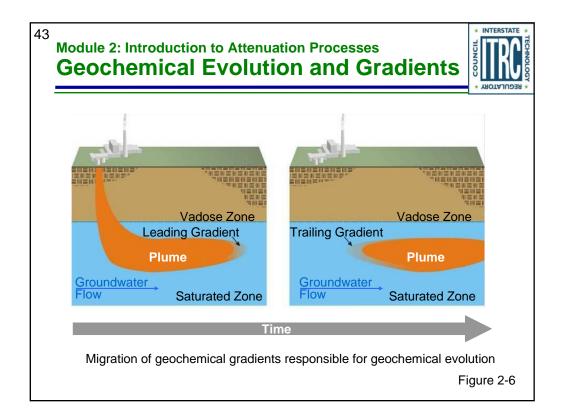
Partitioning often quantified by a coefficient (Kd) where:

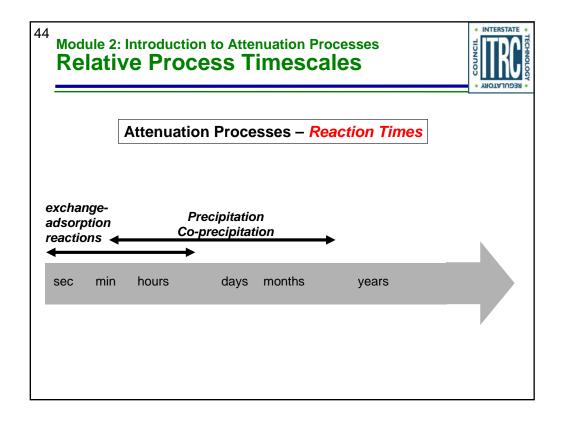
$$Kd = \frac{Concentration(soil)}{Concentration(water)}$$

The higher the Kd, the larger the mass of contaminant partitioned to the solid. In a simple system, the Kd value is related to rate of contaminant movement or retardation factor

Use of Kd values is common, but controversial because they do not capture the complexity of most contaminant plume systems. For example, within a given plume at any one time, multiple Kd values may be measured for a contaminant because of differences in mineralogy and/or chemistry. More complex treatments of sorption require more characterization data. Must balance level of complexity and data needs with level of acceptable uncertainty.

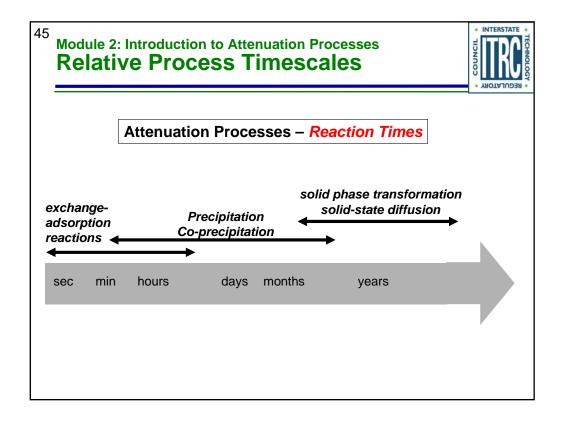






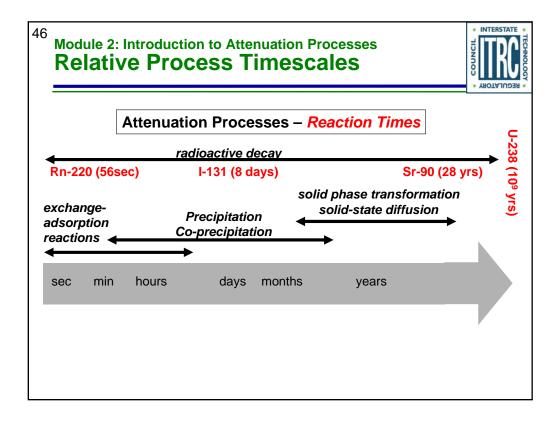
surface reactions (sorption) potentially important precipitation/co-precipitation potentially important

processes that occur at rates on the order of decades less likely to be important on a waste site scale



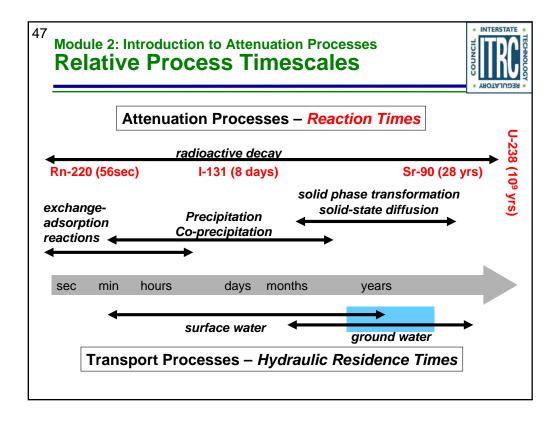
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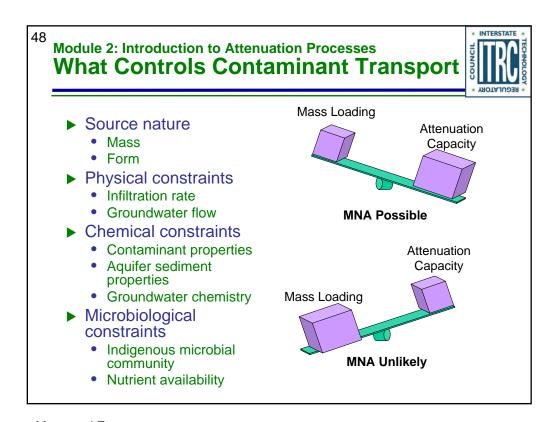
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surface reactions (sorption) potentially important precipitation/co-precipitation potentially important

processes that occur at rates on the order of decades less likely to be important on a waste site scale



Source nature: Mass and Form

Physical constraints: (forces that drive contaminant movement)

Infiltration rate and subsurface flow velocities and flow paths

Chemical constraints: (forces that drive attenuation/mobilization reactions)

Contaminant properties (electronic structure, decay rate)

Aguifer sediment properties (mineralogy, texture)

Groundwater chemistry (dissolved constituents, pH, redox potential)

Microbiological constraints: (forces that affect rates of chemical reactions)

Indigenous microbial community and Nutrient availability

Overall: Physical, chemical, and microbiological constraints are interrelated

Bullet 1: Form of contaminant disposal very important to transport – cadmium released in an acidic solution is likely to reach groundwater faster than cadmium in a solid form in a landfill

Bullet 3: Contaminant properties: electronic structure of contaminant determines its chemical behavior

- Aquifer/sediment properties: mineralogy important to sorption, may provide ions that promote precipitation, may provide ions that keep contaminant in solution, may control pH and/or redox potential; texture includes grain size distribution and spatial distribution of fine grained minerals important to sorption and groundwater flow
- Groundwater chemistry: dissolved constituents can keep contaminant in solution or promote precipitation, pH and redox potential are so important to contaminant transport that they are often referred to as master variables

Bullet 4: For microbial processes to be important to natural attenuation the appropriate microbial community must exist in the subsurface

- -To sustain community activity at a level that will affect contaminant transport requires sufficient nutrient availability
- -Rates of microbial processes are sensitive to pH and redox potential, with different processes operating optimally under different Eh-pH regimes

Module 2: Introduction to Attenuation Processes Microbial Interactions



- ▶ Microbes use redox reactions to gain energy
 - Only affect reactions that are thermodynamically favorable
- ► Microbes can either directly or indirectly change the valence state of the contaminant
 - Result is often a large change in solubility and/or adsorption
 - Change in mobility

Bullet 1: Oxidation-reduction reactions tend to be slow in groundwater systems; redox couples often out of equilibrium

Microbes catalyze reactions of couples such as NO3-/N2, Fe+3/Fe+2, SO4-2/S-2

Bullet 2: Directly -- microbes can catalyze a contaminant redox couple reaction to change the valence state

Indirectly -- microbes can catalyze more abundant redox couple reactions and change overall geochemical conditions, which changes the contaminant valence state

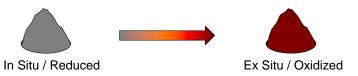
⁵⁰ Site Characterization and Sampling Considerations



- Reliability of understanding is dependent upon preservation of subsurface condition while sampling
- ► Geochemical changes during sampling may dramatically alter our understanding of the natural attenuation processes
 - **Directly:** by altering the contaminant

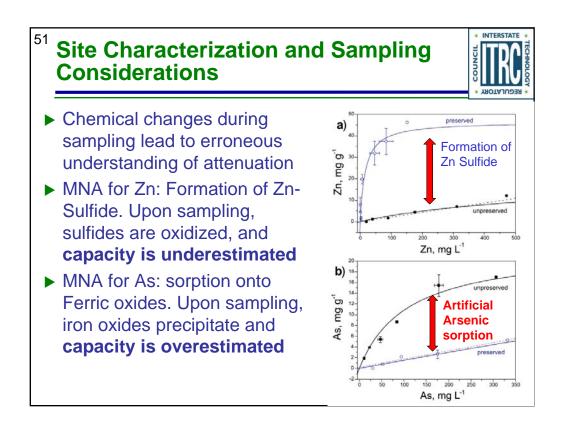
e.g.: As(III) As(V)

• Indirectly: by altering the mineralogy (e.g. Iron)



Note the significance of the distribution of arsenic between the +3 and +5 oxidations states limits and skews the use of predictive modeling of arsenic fate and transport.

Precipitation of iron oxides during sampling can significantly alter attenuation mechanisms and attenuation capacity, leading to erroneous understanding of aquifer properties and MNA potential.



Inadequate sample preservation alters the chemistry of the subsurface material, and may lead to either over- or under-estimation of attenuation capacity.

52 Module 2: Introduction to Attenuation Processes

Investigating a Suspected Attenuation Process



- ► Example → Coprecipitation of Ni with FeS
 - $0.95 \text{Fe}^{2+} + 0.05 \text{Ni}^{2+} + \text{HS-} \rightarrow \text{Fe}_{0.95} \text{Ni}_{0.05} \text{S}_{(s)} + \text{H}^{+}$
- "Mechanism & Rate" questions to address through data collection
 - Site characterization
 - Hydrology, plume mapping, aquifer geochemistry, and background conditions
 - Sample analysis
 - Modern analytical/spectroscopic techniques for laboratory analysis of soils and groundwater
 - Bench-scale tests
 - Evaluate extent of capacity and process rates

Module 2: Introduction to Attenuation Processes **Site Characterization**



- ► Is ambient GW pH significantly different than plume pH? Could this influence coprecipitation efficiency?
 - Background GW data
 - Laboratory tests with pH variation
- ▶ What is the source of Fe(II) and HS-?
 - Site information on source area waste constituents
 - Information/data on microbial processes
- ▶ If source is from microbial reduction, is there sufficient electron donor supply?
 - Information on microbial activity

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Module 2: Introduction to Attenuation Processes Site Data - Sample Analysis

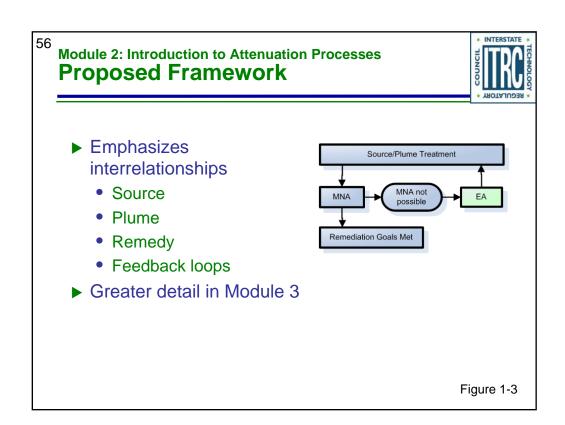


- ▶ Is there sulfate, dissolved sulfide, and Fe(II) in GW?
 - GW analysis
- ▶ Is iron sulfide present in aquifer sediments?
 - Acid volatile sulfide analysis
- ▶ Is Ni associated with iron sulfides in aquifer sediments?
 - Extraction, SEM-EDS
- ▶ Is Ni released from FeS upon exposure to ambient GW oxygen concentration?
 - Laboratory tests using aquifer sediments & ambient GW

Module 2: Introduction to Attenuation Processes Bench Scale Tests – Stability and Reversibility



- ▶ Does Ni coprecipitate with FeS under GW conditions? How fast?
 - Lab studies
- ▶ Is Ni released from FeS upon exposure to ambient GW oxygen concentration?
 - Lab tests using aquifer sediments & ambient GW
- ▶ Is the mass flux of Fe(II) and HS- sufficient to capture Ni given knowledge of process efficiency?
 - Flow data for reactants in combination with lab data on process efficiency



Duestion and Answer Break

Introduction

► Module 1: Viability of MNA as a Remedial Alternative for Metals/ Radionuclides

► Module 2: Introduction to Attenuation Processes

Question and Answer Break

► Module 3: Decision Framework

► Conclusions



A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater

MODULE 3:

Decision Framework

Module 3: Decision Framework Highlighting Module 2 Key Points



- ▶ Metals are not destroyed
- ▶ Attenuation processes tend to be reversible
- ➤ Several controlling factors: pH, oxidationreduction potential, presence/absence of iron
- ▶ Eventually waste sites return to "natural" state
- ▶ Good indicator of potential success of MNA:
 - Contaminants stable when site returns to "natural" state

Module 3: Decision Framework Goal of Flowchart



- ► Roadmap for decision making
- Framework for
 - Transitioning
 - Incorporating EPA tiered process for evaluating MNA
- Decision process for sustainable remedial alternatives
- Defensible protocol
 - Documentation for regulators
 - Flexibility to incorporate innovative solutions

This framework supports transitioning from active remediation to sustainable solutions. This is important because metals are not destroyed. Also, many of the radionuclides of concern have sufficiently long half-lives that for design of treatment systems they can be thought of as not being destroyed. Thus, treatment systems that will maintain the contaminants in an immobile and/or less toxic state for the long-term are desirable.

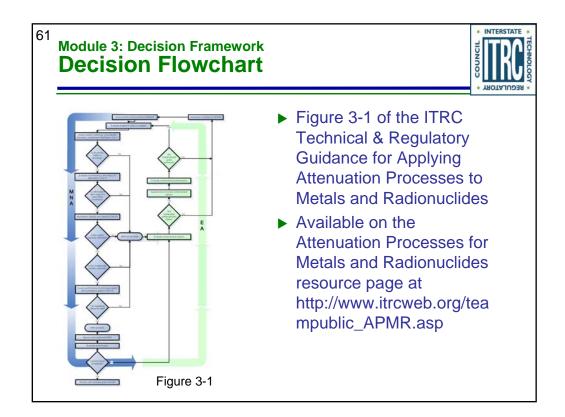
While similar to the ITRC Enhanced Attenuation Chlorinated Organics decision flowchart, this flowchart focused on metals and radionuclides in groundwater incorporates a four tier process developed by the US EPA for MNA of inorganics that is discussed in volume 1 of a 3 volume set of technical reports that were published between 2007 and 2010:

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 1: Technical Basis for Assessment EPA 600-R-07-139, 2007

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 EPA 600-R-07-140, 2007

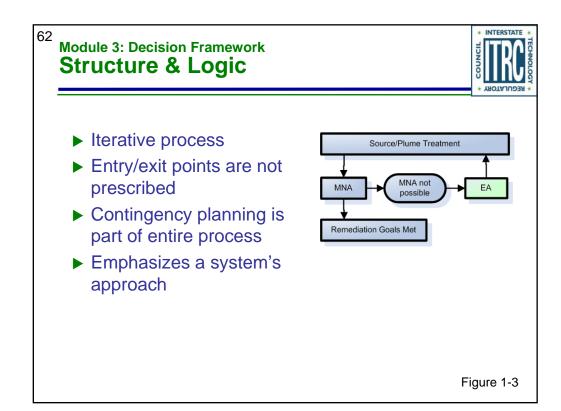
Monitored Natural Attenuation of Inorganic Contaminants in Ground Water Volume 3: Assessment for Radionuclides Including Tritium, Radon, Strontium, Technetium, Uranium, Iodine, Radium, Thorium, Cesium, and Plutonium-Americium EPA 600/R-10/093, 2010

ITRC Enhanced Attenuation: Chlorinated Organics (EACO-1, April 2008) is available from http://www.itrcweb.org/guidancedocument.asp?TID=50

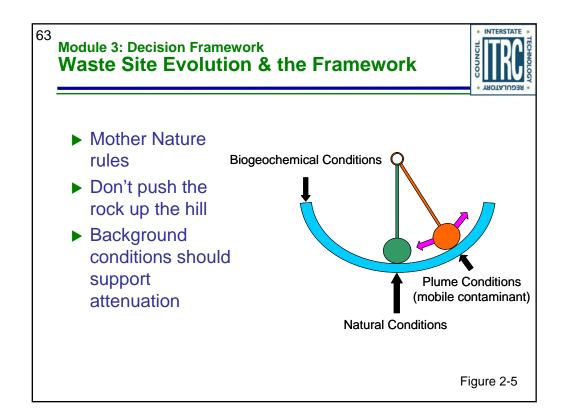


The ITRC Technical & Regulatory Guidance: A Decision-Framework for Applying Attenuation Processes to Metals and Radionuclides is available from the ITRC website (www.itrcweb.org) under "Guidance Documents" and "Attenuation Processes for Metals and Radionuclides".

As discussed in section 2.3.5 of the tech reg document and module 2 of this training, individual metals may behave differently to a single geochemical environment. Thus, movement through the framework and effective treatment technologies may be unique to each contaminant.

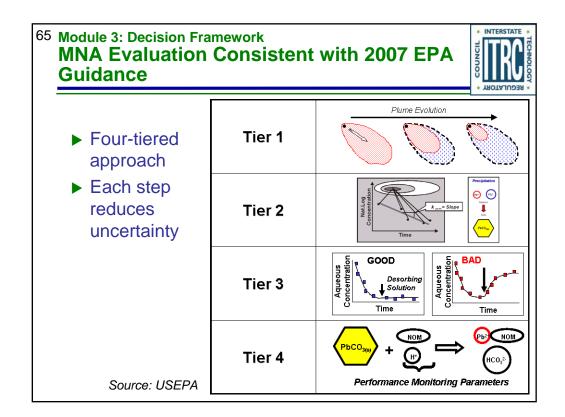


Metals and radionuclides persist in the environment. Treatments, other than removal, are focused on either immobilization or transformation, unlike organics that are focused on destruction or biological degradation. This is true of active treatments in the source or plume or of enhanced attenuation technologies. In section 2.1.6, waste site evolution is discussed. Due to the persistence of metals and radionuclides and the effect of changing subsurface conditions on the stability of these contaminants, understanding how the waste site will evolve and the "final state" of those conditions is a key factor in developing a remediation plan that will foster meeting the remediation goals for the site and maintaining that protective state for the long-term.



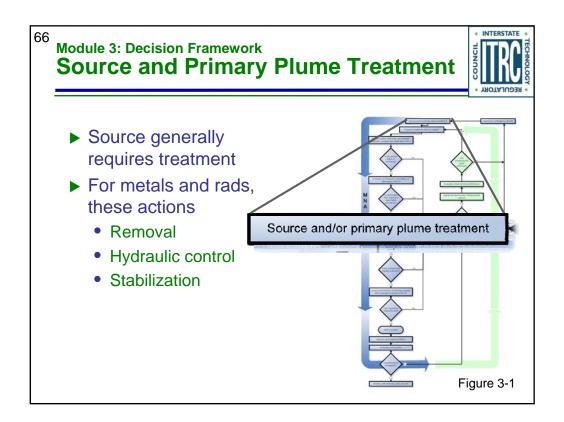
Waste sites are created by introducing "foreign" material into the subsurface over a timeframe that may range from a single short-lived event to a long-term continuous discharge. These events/discharges are typically aqueous in nature. In the case of discharges that result in metals contamination of the subsurface, the process that produces the aqueous waste is typically designed to keep metals in solution. These fluids when introduced will alter the subsurface geochemical environment. After the discharge of waste ceases, up flow (background) groundwater will flow into the system (trailing geochemical gradient) yielding the long-term geochemical conditions. For success, the metal and radionuclide contaminants must be stable at these conditions. Treatments that are based on geochemical conditions that are not consistent with or that cannot be maintained with the up flow groundwater properties will not be effective over the long-term.

Module 3: Decision Framework
Key Features/Factors When Using the
Framework
 Integrates US EPA's tiered
approach for MNA
 Focused approach to data
collection
 Intent is not extensive work or
additional data in each box in
every situation
 e.g., much of Tier I data is
traditional characterization
data for plume delineation



Emphasis of the 4 Tiers:

- Tier 1 Is the plume stable or shrinking
- Tier 2 Identify the attenuation mechanisms that are occurring
- Tier 3 Determine if those mechanisms will be stable and if the attenuation capacity will be sustainable over the long-term
- Tier 4 Design a performance monitoring plan and contingency plans based on those mechanisms that are stable and sustainable



In general, one thinks of the source as the point where the contaminants are found in the subsurface in large volume close to the point of discharge. For metals and radionuclides one may have both primary and secondary sources. Examples include:

- A. As you cross a geochemical gradient, in other words you have moved from one waste compartment to another, a contaminant that was stable becomes mobile and must be addressed, thus a secondary source.
- B. For radionuclides, a secondary source could be a daughter product. This may be spatially located with the primary source or downgradient.

67 Module 3: Decision Framework

Example from Savannah River Site: Strontium, Uranium, and Iodine



► Source was 3 earthen basins that received acidic waste from processing operations

▶ Source treatment

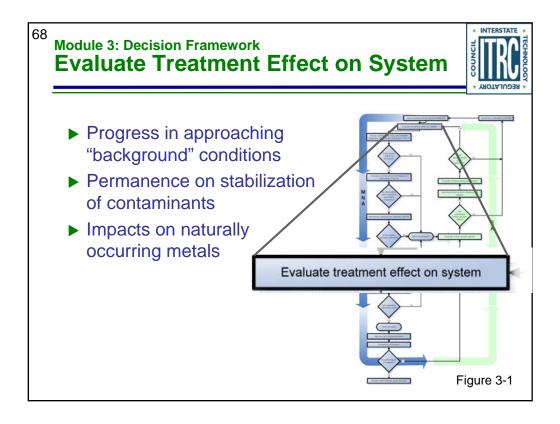


• Groundwater pump-and-treat



Top photo: One of the 3 basins prior to capping.

Bottom photo: Waste site after capping of the basins was completed.



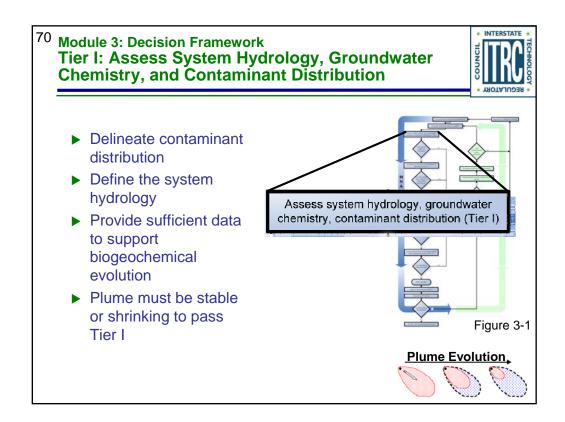
69 Module 3: Decision Framework
Example from Savannah River Site:
Strontium, Uranium, and Iodine



- ▶ Source treatment
 - Capped basins
 - Pump-and-treat system
- Effect of source/primary plume treatment on system
 - All contaminants were reaching compliance points
 - Groundwater pH and geochemical setting fostered contaminants remaining in solution



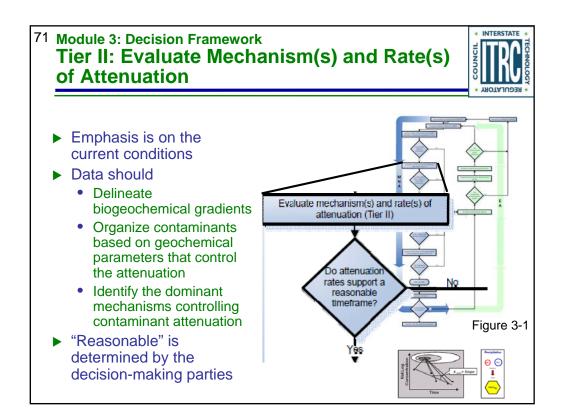
Top Photo: Stream downgradient of the waste site. Middle Photo: Savannah River National Laboratory research collecting field data to support research efforts at the F-Area waste site. Bottom Photo: Aerial photograph of area downgradient of waste site.



The data collected for Tier I may be considered by most, the traditional data set needed to evaluate if a plume is growing, stable, or shrinking. Because the long-term stability of metals and radionuclides will be predicated on the geochemistry of the groundwater upflow from the waste source, a more robust evaluation of the upflow conditions than is typically performed with organic contaminants, may be warranted.

As outlined in Table 2.1 of the Tech Reg document, the data types and analyses include: Groundwater flow direction, aquifer hydrostratigraphy, contaminant concentrations in groundwater and aquifer solids, and general groundwater chemistry.

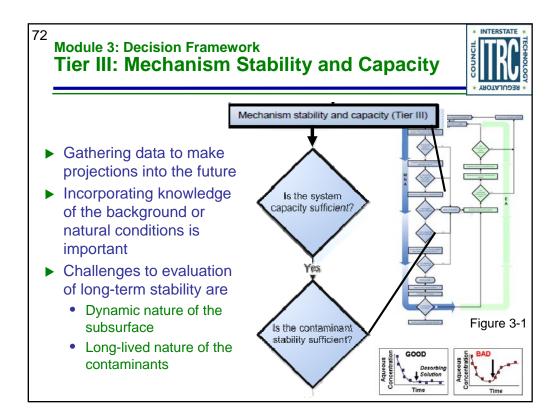
As discussed in section 2.5, the analyses associated with this tier are readily available from commercial laboratories.

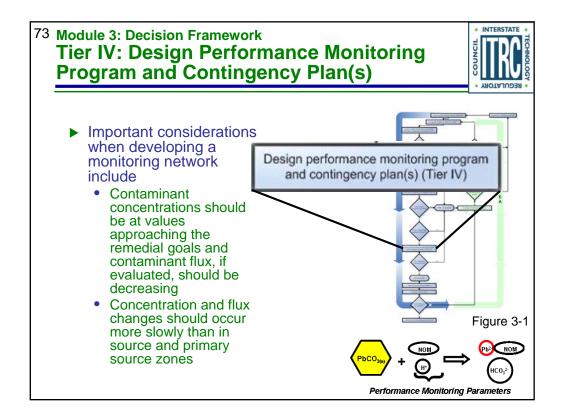


As outlined in Table 2.1 of the guidance document, the data types and analyses include: detailed characterization of system hydrology, detailed characterization of groundwater chemistry, subsurface mineralogy and/or microbiology, contaminant speciation, reaction mechanism evaluation.

While "reasonable" is determined by the decision-making parties, factors influencing that determination are site and contaminant characteristics, economics (use and value of property), etc.

Similar to Tier I, the majority of the analyses for Tier II are available from commercial laboratories.

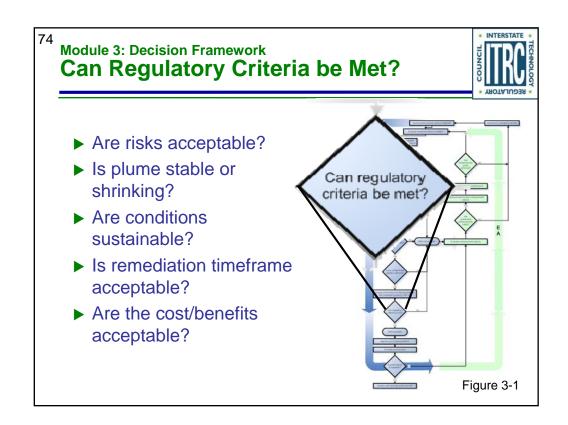




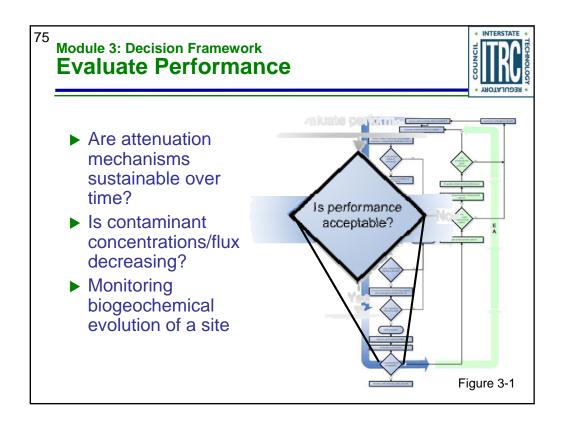
Up-gradient monitoring of controlling geochemical conditions can be incorporated in monitoring (See section 3.11)

There may be other state and program-specific regulations. These were addressed in Module 2 of the training and are addressed in Section 4 of the document.

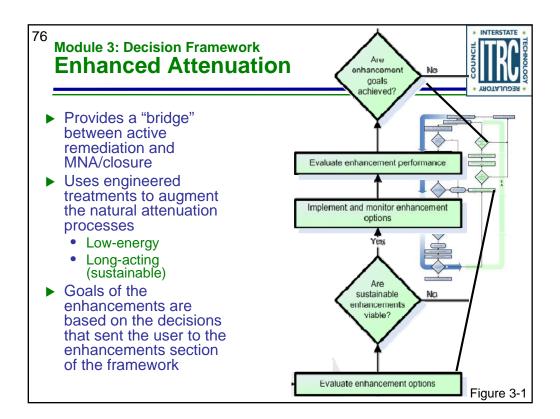
For a discussion on Mass Flux the ITRC in August 2010 published "Use and Measurement of Mass Flux and Mass Discharge". This document is available on the ITRC webpage under document number MASSFLUX-1 at http://www.itrcweb.org/guidancedocument.asp?TID=82



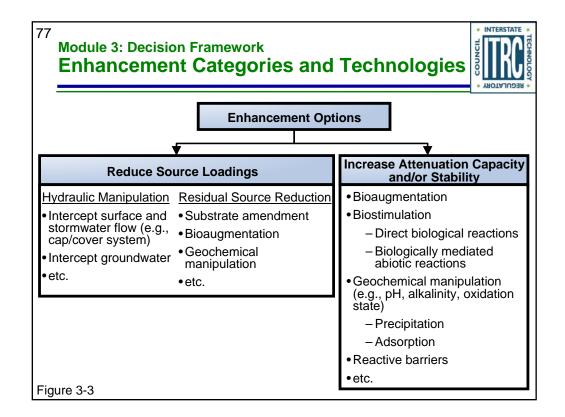
If each of the decisions have been answered in the positive, you have the technical basis for approving MNA.



For a successful MNA strategy, the site must be stable over the long-term when conditions evolve to the natural state. The parameters measured should support this evaluation.



An analysis similar to that conducted in Tier II and III would be conducted.



Technologies listed in the graphic (figure 3-3 of the Tech Reg document) are examples of types of treatments. They are listed in no particular order of importance. In 2010, the long-term effectiveness of these technologies at maintaining various metals and radionuclides in a stable form is being evaluated. For some contaminants present in the groundwater, such as I-129, technologies have yet to be developed, demonstrated and made commercially available.

Enhanced attenuation is based on a mass balance between contaminant loading into the system and the attenuation capacity of the system that will result in contaminants meeting the remediation goals for the system.

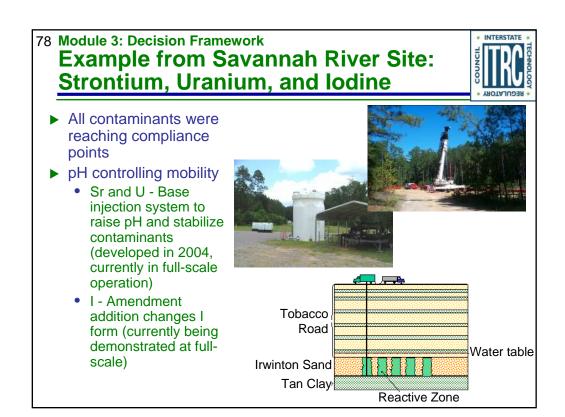
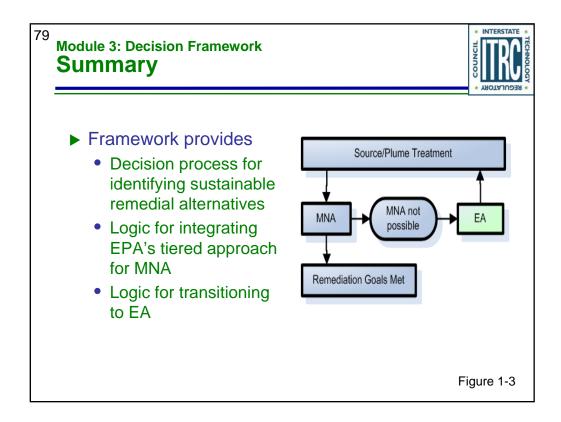


Diagram is a schematic of the target zone for the base injection. The top photo is of the installation of the barrier wall. The lower photo is of the above ground infrastructure associated with the base injection operation. Sodium hydroxide and tri-sodium phosphate are the base amendments that are injected periodically (injection frequency based on downgradient rebounding of pH) to maintain the pH at near natural pH levels (5.5 to 6). The treatment system consists of a funnel-and-gate setup, as represented by 3 black lines downgradient of the seepage basins in Figure B-8 of the Tech Reg document.

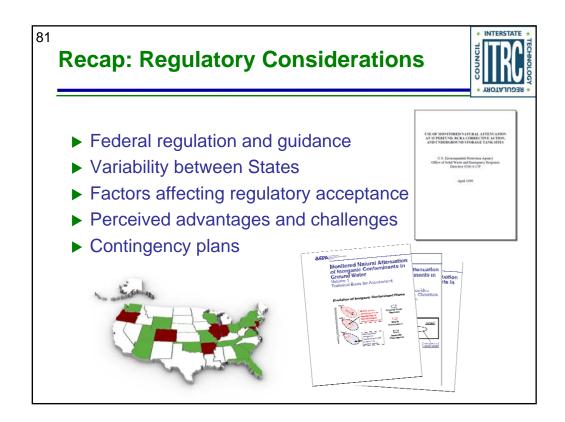


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A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater

Conclusions



Recap: Attenuation Processes Primer

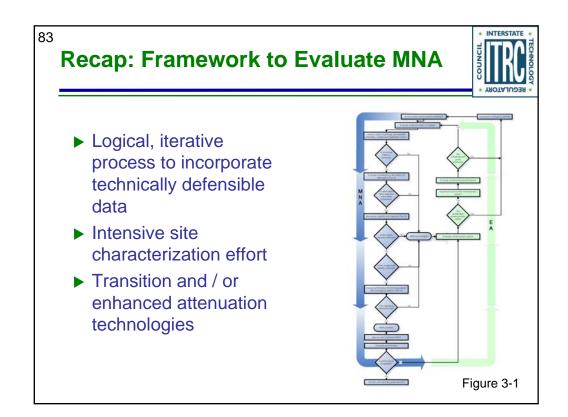
Metals / radionuclides versus organics

Dominant attenuation processes

Relationship between attenuation processes and aquifer properties

Non-destructive mechanisms

Non-destructive mechanisms

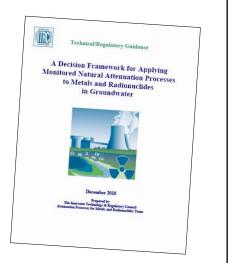


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Recap: Summary



- MNA is a viable remedial alternative, with associated advantages and challenges
- Decision Framework provides scientific process to assess MNA as a component of a site's remedial action



85 Thank You for Participating



- > 2nd question and answer break
- Links to additional resources
 - http://www.clu-in.org/conf/itrc/apmr/resource.cfm
- ► Feedback form please complete
 - http://www.clu-in.org/conf/itrc/apmr/feedback.cfm



Need confirmation of your participation today?

Fill out the feedback form and check box for confirmation email.

Links to additional resources:

http://www.clu-in.org/conf/itrc/apmr/resource.cfm

Your feedback is important – please fill out the form at: http://www.clu-in.org/conf/itrc/apmr/feedback.cfm

The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants

Helping regulators build their knowledge base and raise their confidence about new environmental technologies

Helping regulators save time and money when evaluating environmental technologies

Guiding technology developers in the collection of performance data to satisfy the requirements of multiple states

Helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations

Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

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Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches

Sponsor ITRC's technical team and other activities

Use ITRC products and attend training courses

Submit proposals for new technical teams and projects