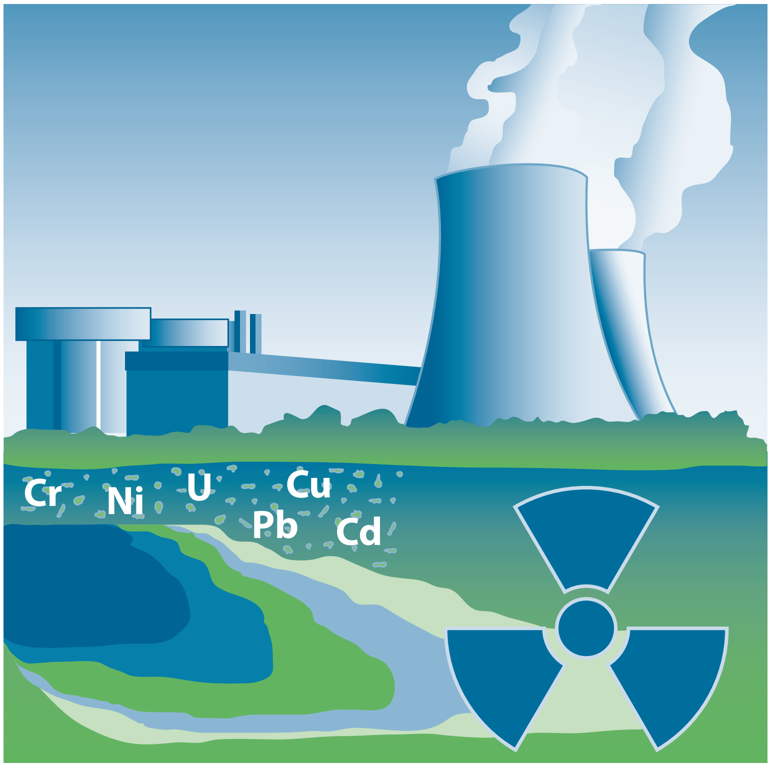
Technical/Regulatory Guidance

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



December 2010

Prepared by
The Interstate Technology & Regulatory Council
Attenuation Processes for Metals and Radionuclides Team

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APMR-1

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EXECUTIVE SUMMARY

Many sites across the United States have groundwater contaminated with metals or radionuclides—often at low levels, but above standards. Most potential engineered remedies are too costly or otherwise impracticable. In contrast, attenuation-based remedies rely on natural processes to sequester the contaminants of concern and are therefore less aggressive, less invasive, and less costly. While attenuation of organic contaminants is being increasingly accepted as a remedy, attenuation of metals and radionuclides involves more complicated or interdependent sets of processes and has rarely been applied.

Because technical guidance specifically addressing the use of attenuation-based remedies for metals and radionuclides has only recently been available, the application of attenuation remedies for metals and radionuclides has been inconsistent. To facilitate the acceptance of attenuation-based remedies for metals and radionuclides, the Interstate Technology & Regulatory Council (ITRC) developed this technical and regulatory guidance document, which builds on the U.S. Environmental Protection Agency's three-volume document for monitored natural attenuation. This ITRC document is intended for anyone involved with investigating, managing, or overseeing a site with metal and/or radionuclide contaminants, including public stakeholders, site owners, commercial operators, regulators, site managers, and investigators at all levels, including state and federal agencies. To determine the specific approach of this document, ITRC conducted a Web-based survey of state regulators and stakeholders to determine the existing state of knowledge and acceptance regarding the application of attenuation processes as a remedy. The document addresses issues identified in the survey and provides paths forward for resolving them. The guidance also includes recommendations for evaluating attenuation-based remedies in a consistent and technically defensible manner. A decision framework guides users through a series of decisions that help determine whether relying on attenuation processes is feasible and can lead to successful implementation. Finally, case study summaries demonstrate application of attenuation-based remedies to real-world scenarios. Full case studies are provided in Appendix A.

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1. INTRODUCTION

Techniques for removing or containing metal or radionuclide contaminants in groundwater are often inefficient and quite costly below certain concentrations—concentrations that may still be above regulatory criteria. Dealing with this dispersed low-level contamination may be especially challenging at many cleanup sites. In addition, intrusive remedial techniques may cause other environmental consequences and may expose workers to unacceptable risks. Understanding how and where attenuation processes may be effective in remediating a waste site is therefore a significant issue for these sites.

Integration of attenuation-based technologies into the remediation of metals and radionuclides contamination in groundwater may be a complex undertaking at many sites. While attenuation of organic compounds is predominantly based on biotic processes, attenuation of metal and radionuclide contaminants is predominantly based on abiotic processes that can be influenced by microbial processes. For metal and radionuclide contaminants in the subsurface, the interaction of groundwater with the soils and sediments in the saturated zone becomes very important because, in large part, the properties of the soils and sediments strongly control the attenuation processes. The role of cocontaminants may add to the complexity of the problem and the solution. Evaluating and incorporating attenuation-based technologies into treatment processes may require a new perspective and approach for many regulators and environmental professionals.

This document focuses on monitored natural attenuation (MNA) but also introduces the term *enhanced attenuation* (EA) as it applies to remediation of metals and radionuclides in groundwater. For clarity, both terms are defined below. See the Glossary (Appendix E) for additional definitions.

- **Monitored natural attenuation** is defined by the U.S. Environmental Protection Agency (EPA) as “reliance on processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a timeframe that is reasonable compared to that offered by other more active methods. The ‘MNA processes’ 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. These in situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.” Natural attenuation processes typically occur at all sites but to varying degrees of effectiveness depending on the types and concentrations of contaminants present and the physical, chemical, and biological characteristics of the soil and groundwater (EPA 1999). EPA’s guidance on MNA emphasizes that long-term monitoring is an important component of a remedy where natural processes are to be relied on to achieve cleanup objectives. Also, EPA generally expects that MNA will be appropriate only for sites with low potential for contaminant migration. Refer to Office of Solid Waste and Emergency Response (OSWER)

Directive 9200.4-17P (EPA 1999) for a discussion of criteria for sites where MNA may be appropriate.

- **Enhanced attenuation** is the use of low-energy, long-acting technologies in situations where MNA is not sufficiently effective or acceptable. EA can provide an effective and efficient "bridge" from higher-energy remedies to MNA with technologies that either increase the attenuation of the contaminants within the affected aquifer or reduce contaminant loading to the downgradient aquifer. Potential EA technologies optimize aquifer conditions to provide a sustainable treatment or at least minimize the energy needed to reduce contaminant loading and/or increase the attenuation capacity of an aquifer (ITRC 2008b). For purposes of this document, *sustainability* is defined as the ability of a system to maintain the important attenuation mechanisms through time.

This document is intended for anyone involved with evaluating, investigating, remediating, or managing sites involving metal and radionuclide contaminants in groundwater, including public stakeholders, site owners, regulators, site managers, and investigators at all levels, including state and federal agencies as well as commercial operations. This document provides the following:

- a decision framework (logic diagram) that incorporates key aspects of EPA's three-volume technical background series on MNA (hereafter referred to as EPA's three-volume MNA set) for metals and radionuclides in groundwater (EPA 2007a, 2007b)[1] within the larger evaluation framework of a contaminated site
- guidance on approaches and key issues associated with evaluating attenuation-based remedies (i.e., where MNA is a component of the response action) for metal- and radionuclide-contaminated sites where there are multiple contaminants
- a process to incorporate EA approaches into a treatment train for waste sites where the attenuation mechanisms are insufficient but remediation goals cannot be met with only source and plume treatments
- factors that regulators should consider when attenuation-based remedies are proposed for waste sites
- general discussion of methods for collecting or analyzing data needed to evaluate selected attenuation processes
- general discussion of EA categories
- site examples where MNA has been selected as a component of the response action
- background on geochemistry relevant to MNA for metals and radionuclides

This document does *not* provide the following:

- discussion of perchlorate and nitrate because the attenuation processes involved are significantly different than those for metals and radionuclides
- detailed discussion of methods and techniques for collecting or analyzing data needed to evaluate selected attenuation processes
- detailed discussion of EA technologies appropriate for metal/radionuclide-contaminated sites

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[1] At this writing, Volume 3 of the technical background series is in print but not yet released. It is mentioned here to be used as a resource when it is released.

In the past few years, MNA for organics has become widely accepted as a remedy for many contaminated sites. This document seeks to establish a knowledge base of attenuation processes and favorable subsurface conditions so that MNA can also be considered as a remedy for metals and radionuclides.

1.1 Scope of the Problem

EPA's definition of natural attenuation includes both organic and inorganic contaminants. This document covers metals and radionuclides; several technical and regulatory documents published previously by the Interstate Technology & Regulatory Council (ITRC) have targeted attenuation of organic contaminants (ITRC 1999b; ITRC 2007b, 2008b). The applicable attenuation processes are generally quite different for metals and radionuclides and result in contaminants remaining in the environment. Unlike organic contaminants, metals and radionuclides are not destroyed by those processes. These processes affect most metals and radionuclides by changing their valence state, which in turn affects their solubility and therefore mobility. For example, hexavalent chromium can be chemically or biologically reduced to the less soluble and less toxic trivalent chromium. In addition, the primary transport mechanism for inorganics is through groundwater, while organics have a variety of mobile phases and exposure routes. In the case of radionuclides, radioactive decay leads to less of the contaminant over time. However, radionuclide half-lives vary considerably, and many decay rates are too slow to be considered for a reasonable remedial timeframe. Table 1-1 differentiates the applicable attenuation processes.

Table 1-1. Applicability of different attenuation processes to organics versus metals and radionuclides

Process	Organics	Metals and radionuclides
Microbial	• Biodegradation—irreversible transformation to by-products, daughter products, or metabolites • Ultimate mineralization	• Biotransformation—change in speciation and formation of organo-compounds
Dispersion/ dilution	• Dissolved and colloidal phases	• Dissolved and colloidal phases
Sorption	• Tied to soil organic carbon	• Tied to mineral surfaces
Volatilization	• Tied to vapor pressure, Henry's law	• Potentially operable for mercury, iodine, radon, tritium, and carbon-14
Radioactive decay	• Not applicable	• Applicable to radionuclides
Biogeochemical	• Transformation to less soluble by-products or metabolites	• Precipitation and adsorption leading to metal sequestration • Changes in geochemical condition due to microbial respiration, including changes in oxidation-reduction potential (Eh) and pH, leading to reversible change in solubility
Transformation/ destruction	• Transformation to less soluble by-products, daughter products, or metabolites • Irreversible biological or chemical transformation to gaseous products—mineralization	• Not applicable

1.1.1 Types of Sites

Although elevated levels of metals and radionuclides do occur in nature, the majority of this contamination is a result of anthropogenic activities. Various sites have been identified as having metal and/or radionuclide contamination from a wide variety of waste release scenarios. Examples of activities that may contaminate sites with metals and radionuclides include the following:

- metals mining/excavating and ore processing
- primary metals industries, such as smelting and refining of ferrous and nonferrous metals
- rolling, drawing, and alloying metals
- industrial processes (manufacturing, casting, plating, electronics manufacturing, metals recycling, cement kilns, and utility operations)
- deposition of spent munitions (U.S. Department of Defense [DOD] facilities)
- waste deposition from production of nuclear weapons (U.S. Department of Energy [DOE] facilities)
- disposal (landfills, lagoons, wastewater residuals)
- agricultural applications of pesticides and herbicides (e.g., arsenic and lead)
- dispersal from mobile sources (cars, trucks, trains, etc.) and aerially deposited from vehicle emissions, etc. along transportation corridors

In the United States, radionuclide contamination is of particular importance in the vicinity of nuclear weapons production sites, at nuclear power plants, near nuclear waste disposal facilities, and in areas where uranium mining and milling have occurred. Beginning in the 1940s, the federal government built and used more than 20,000 facilities including uranium-production facilities, plutonium-production facilities, gaseous diffusion plants, production reactors, research reactors, chemical-processing facilities, hot cells, waste management facilities, and others (ITRC 2008a). These facilities are now part of DOE’s widespread nuclear weapons complex.

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Information System (CERCLIS) identifies contaminants of concern (COCs) addressed by the Superfund remedial response process (see Section 4). CERCLIS can generate a list of contaminant groups at sites with metal and radionuclide contaminants. The universe for these data is the National Priorities List (NPL) sites (proposed, final, and deleted sites) that contain the two groundwater contaminant groups shown in Figure 1-1. As the figure shows, metals are a common COC at NPL sites in most EPA regions. Radionuclide contamination is found at more than an order of magnitude fewer sites than metals contamination; however, the remedial response for radionuclides may be much more complicated.

1.1.2 Types of Contaminants

EPA’s three-volume MNA set (EPA 2007a, 2007b) focuses on 9 inorganic (including 7 metals) and 12 radioactive hazardous substances. Figure 1-2 highlights these contaminants. Other inorganic substances, such as perchlorate and nitrate, are not considered by this document because the attenuation processes involved are significantly different from those for metals and radionuclides. The term *metals* is used in this document as a generic term for metals and metalloids such as arsenic and selenium.

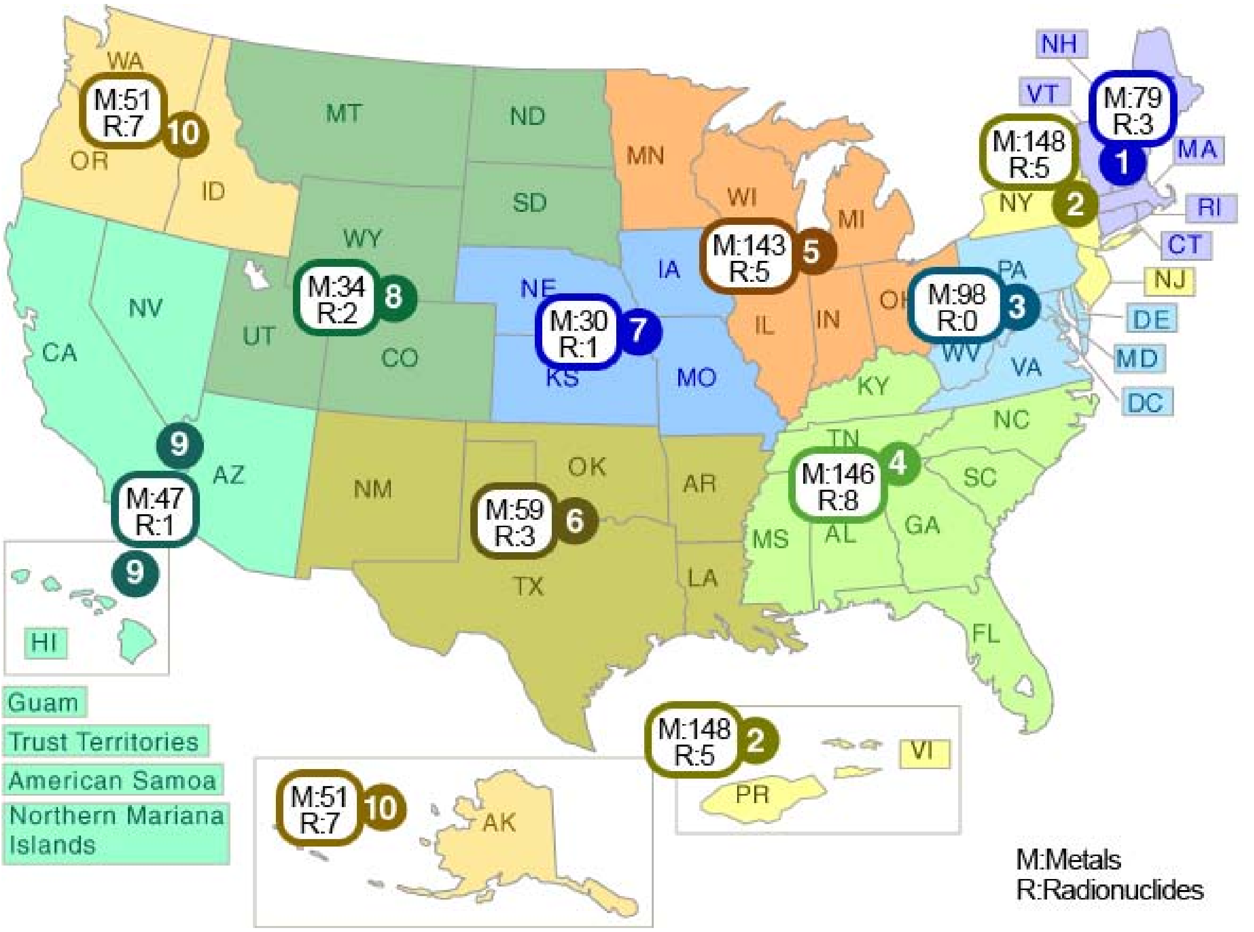


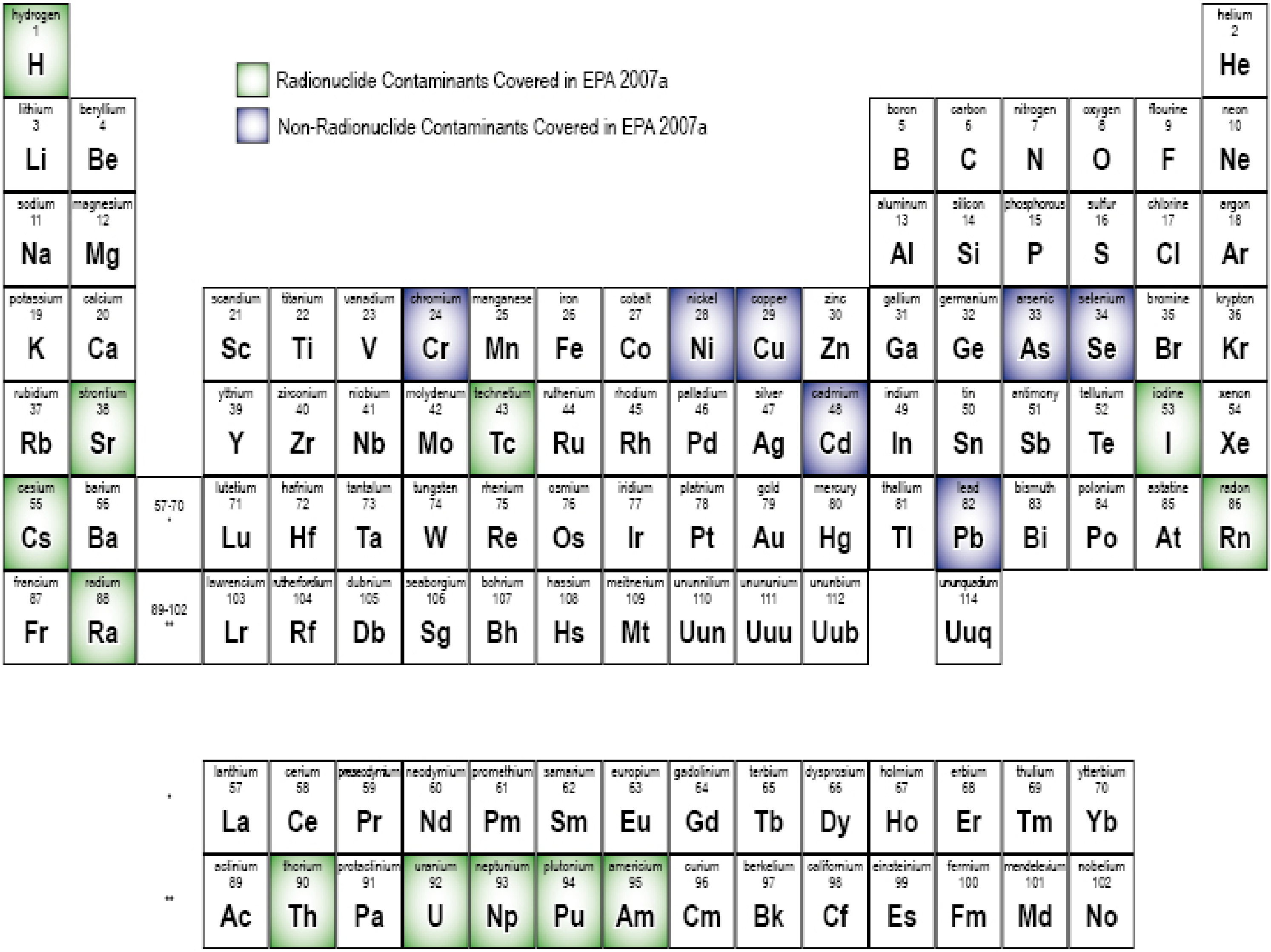
Figure 1-1. Groundwater contaminant group totals for NPL sites in EPA regions as of August 2010. (*Source:* CERCLIS)

EPA's selection of the nonradionuclide contaminants was based on several criteria (EPA 2007a):

- information regarding chemicals, specifically inorganic contaminants and metals, commonly found at Superfund sites (EPA 1994), considering toxicity, industrial use, and frequency of occurrence at Superfund sites
- chemical behavior, considering traits such as toxicity, ion charge (cation vs. anion), transport behavior, and redox chemistry to cover a broad range of geochemical behavior
- nomination by EPA regional staff of inorganic contaminants that occurred frequently or that were problematic in their regions

The selection of radionuclide contaminants was based on two criteria:

- high priority to the site remediation or risk assessment activities of EPA
- chemical behavior considering traits such as toxicity, cations, anions, conservatively transported, nonconservatively transported, and redox sensitivity



🟩 Radionuclide Contaminants Covered in EPA 2007a

🟦 Non-Radionuclide Contaminants Covered in EPA 2007a

🟩 hydrogen 1 H																		helium 2 He
lithium 3 Li	beryllium 4 Be													boron 5 B	carbon 6 C	nitrogen 7 N	oxygen 8 O	flourine 9 F	neon 10 Ne
sodium 11 Na	magnesium 12 Mg													aluminum 13 Al	silicon 14 Si	phosphorous 15 P	sulfur 16 S	chlorine 17 Cl	argon 18 Ar
potassium 19 K	calcium 20 Ca		scandium 21 Sc	titanium 22 Ti	vanadium 23 V	🟦 chromium 24 Cr	manganese 25 Mn	iron 26 Fe	cobalt 27 Co	🟦 nickel 28 Ni	🟦 copper 29 Cu	zinc 30 Zn	gallium 31 Ga	germanium 32 Ge	🟦 arsenic 33 As	🟦 selenium 34 Se	bromine 35 Br	krypton 36 Kr
rubidium 37 Rb	🟩 strontium 38 Sr		yttrium 39 Y	zirconium 40 Zr	niobium 41 Nb	molydenum 42 Mo	🟩 technetium 43 Tc	ruthenium 44 Ru	rhodium 45 Rh	palladium 46 Pd	silver 47 Ag	🟦 cadmium 48 Cd	indium 49 In	tin 50 Sn	antimony 51 Sb	tellurium 52 Te	🟩 iodine 53 I	xenon 54 Xe
🟩 cesium 55 Cs	barium 56 Ba	57-70 *	lutetium 71 Lu	hafnium 72 Hf	tantalum 73 Ta	tungsten 74 W	rhenium 75 Re	osmium 76 Os	iridium 77 Ir	platinum 78 Pt	gold 79 Au	mercury 80 Hg	thallium 81 Tl	🟦 lead 82 Pb	bismuth 83 Bi	polonium 84 Po	astatine 85 At	🟩 radon 86 Rn
francium 87 Fr	🟩 radium 88 Ra	89-102 **	lawrencium 103 Lr	rutherfordium 104 Rf	dubnium 105 Db	seaborgium 106 Sg	bohrium 107 Bh	hassium 108 Hs	meitnerium 109 Mt	ununnilium 110 Uun	unununium 111 Uuu	ununbium 112 Uub		ununquadium 114 Uuq				

*	lanthium 57 La	cerium 58 Ce	praseodymium 59 Pr	neodymium 60 Nd	promethium 61 Pm	samarium 62 Sm	europium 63 Eu	gadolinium 64 Gd	terbium 65 Tb	dysprosium 66 Dy	holmium 67 Ho	erbium 68 Er	thulium 69 Tm	ytterbium 70 Yb
**	actinium 89 Ac	🟩 thorium 90 Th	protactinium 91 Pa	🟩 uranium 92 U	🟩 neptunium 93 Np	🟩 plutonium 94 Pu	🟩 americium 95 Am	curium 96 Cm	berkelium 97 Bk	californium 98 Cf	einsteinium 99 Es	fermium 100 Fm	mendelevium 101 Md	nobelium 102 No

Figure 1-2. Radionuclide and nonradionuclide inorganic contaminants highlighted in EPA's technical background document. (EPA 2007a)

These contaminant characteristics allow coverage of the geochemical behavior of a wide range of radionuclide contaminants as well as the chemical classes that make up the periodic table. In addition, this selection accounts for many daughter and fission products.

Tables 1-2 and 1-3 display the total number of certain metals and radionuclides found in groundwater at NPL sites. As shown in Figure 1-1, metals are common COCs at NPL sites, the most common being arsenic, chromium, and lead. Among radionuclides, uranium, radium, strontium, and thorium are the most common COCs even though their numbers are an order of magnitude less than those of metallic hazardous substances (see Table 1-3).

Table 1-2. Specific metals found in groundwater at NPL sites as of August 2010
(*Source:* CERCLIS)

Hazardous substance	Number of sites	Distribution range
Arsenic	554	From 18 sites In Region 7 to 104 sites in Region 2
Cadmium	318	From 11 sites in Region 9 to 61 sites in Region 2
Chromium	440	From 15 sites in Region 8 to 93 sites in Region 2
Copper	216	From 7 sites in Region 7 to 51 sites in Region 2
Lead	458	From 19 sites in Region 7 to 93 sites in Region 2
Nickel	298	From 10 sites in Region 8 to 52 sites in Region 4
Selenium	93	From 1 site in Region 7 to 27 sites in Region 2

Table 1-3. Radioactive hazardous substances found in groundwater at NPL sites as of August 2010 (*Source:* CERCLIS)

Hazardous substance	Number of sites	Distribution range
Americium	3	From 0 sites in 8 regions to 2 sites in Region 4
Cesium	10	From 0 sites in 6 regions to 4 sites in Region 4
Iodine	5	From 0 sites in 8 regions to 2 sites in Region 4
Neptunium	6	From 0 sites in 7 regions to 3 sites in Region 4
Plutonium	5	From 0 sites in 6 regions to 2 sites in Region 4
Radium	11	From 0 sites in 6 regions to 5 sites in Region 4
Radon	3	From 0 sites in 9 regions to 2 sites in Region 2
Strontium	8	From 0 sites in 6 regions to 3 sites in Regions 4 and 5
Technetium	5	From 0 sites in 7 regions to 3 sites in Region 4
Thorium	7	From 0 sites in 5 regions to 2 sites in Regions 4 and 5
Tritium	9	From 0 sites in 5 regions to 4 sites in Region 10
Uranium	18	From 0 sites in Region 3 to 6 sites in Region 10

For more information on the documentation of MNA in the Superfund program, go to www.epa.gov/superfund/resources/gwdocs/monit.htm. For more information on the use of MNA in the Superfund program, see *Treatment Technologies for Site Cleanup, Annual Status Report, 12th Edition* (EPA 2007c) at www.cluin.org/asr (p. 4-8 and Appendix E of the report).

1.2 Challenges Addressed

The primary purpose of environmental cleanup is to protect human health and the environment from actual or threatened releases of hazardous substances or contaminants. One goal of this document is to identify barriers to the use of MNA for metals and radionuclides and to determine which barriers are technical or regulatory, and which may have resulted from a general lack of experience with attenuation processes. Key challenges addressed in this document are as follows:

<u>Technical Challenges (see Section 2):</u>

- Attenuation processes for metals and radionuclides usually do not result in the destruction of the metal or radionuclide.
- Attenuation processes are reversible for many of the contaminants.
- The processes involved are complex.
- The correct characterization data must be identified.
- Technical barriers to the use of MNA may have resulted from a general lack of experience with attenuation processes.

<u>Regulatory Challenges (see Sections 3 and 4)</u>:

- lack of consistent cleanup policies and decision criteria
- leaving contaminants in the subsurface at levels that exceed standards
- extending regulatory cleanup periods to accommodate longer attenuation timeframes
- identifying regulatory barriers to the use of MNA and determining which barriers may have resulted from a general lack of experience with attenuation policy and processes

<u>Stakeholder Concern Challenges (see Section 5):</u>

- risks to communities from metal and radionuclide contaminants that are left in place
- perception as a "do-nothing" remedy
- increased length of time and associated uncertainty with completing this remedy

1.3 Need for Guidance

With or without associated engineered remedies, MNA as a remedy has been accepted throughout the regulated community for organic groundwater constituents as a viable process for many years. Several policy and guidance documents exist to support attenuation of organics and to provide consistency in application and documentation. EPA's initial policy (EPA 1999) also emphasized the application of MNA to petroleum compounds and chlorinated solvents; metals and radionuclides were only briefly mentioned.

Attenuation of metals and radionuclides involves more interdependent sets of processes than attenuation of organic compounds. Thus, sites contaminated with metals or radionuclides, even at very low levels, can face the challenge of continued remediation and management for many years—even decades. These long periods of time result in extraordinary costs when using conventional treatments or at sites where complete cleanup and removal may not be achievable within economic constraints or technical feasibility.

The goals of site response actions are to protect human health and the environment by remediating contaminated soils, restoring contaminated groundwater to beneficial use, preventing migration of contaminant plumes, and protecting other environmental resources.

Stakeholders may be concerned about attenuation-based remedies because they are perceived as a "do-nothing" option. Communities generally do not favor prolonged cleanup approaches with uncertain funding and degree of risk and a potential to shift the burden for environmental cleanup to another generation. Significant uncertainties in attenuation efficacy and timelines may conflict with stakeholder expectations. Public acceptance may improve when there is a reliable scientific basis for evaluating whether MNA is or is not an appropriate remedy at a site.

When properly employed, MNA is not a "do-nothing" alternative; rather it is an effective knowledge-based remedy where a thorough engineering analysis provides the basis for understanding, monitoring, predicting, and documenting natural processes. 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. The compelling evidence needed to support proper evaluation of the remedy requires that the processes that destroy or immobilize contaminants be well understood and that their effectiveness at the site be documented (EPA 2001). MNA is not a "presumptive" or "default" remediation alternative and should be evaluated and compared to other viable remediation methods (including innovative technologies) during the study phases leading to the selection of a remedy (EPA 1999).

1.4 Proposed Framework

To facilitate the acceptance of attenuation-based remedies for metals and radionuclides, this document provides a framework, summarized in Figure 1-3, which builds on EPA's three-volume MNA set and provides guidelines for evaluating and documenting such remedies in a consistent and technically defensible manner. The framework is intended to emphasize the interrelationship among the source, the plume, and the attenuation-based remedies through feedback loops that foster understanding of the impact of each remediation option on the system. Section 3 of this document provides more detail and discussion of the framework.

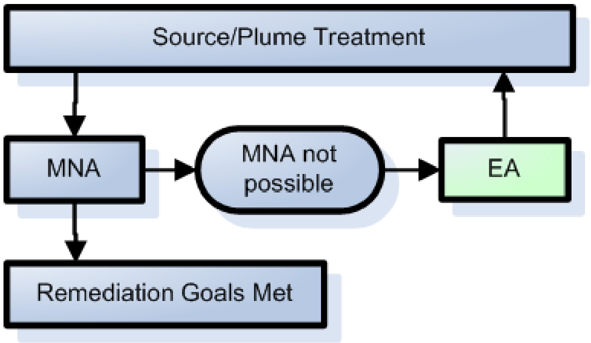


Figure 1-3. Simplified MNA decision framework for metals and radionuclides.

1.5 Relationship to Other ITRC Products

1.5.1 MNA and EA

The ITRC has produced several documents that discuss various aspects of MNA as practiced for sites with organic COCs in both the soil and groundwater. While this document focuses on metals and radionuclides, it is hoped the outcome will be a series of accepted practices for documenting both that a site is suitable for proposing that MNA of metals and radionuclides be implemented as well as identifying criteria for documenting the progress of the attenuation.

Other ITRC documents relating to natural attenuation include *Five-Course Evaluation Summary: ITRC/RTDF Training Course: Natural Attenuation of Chlorinated Solvents in Ground Water* (ITRC 1999a) and *Natural Attenuation of Chlorinated Solvents in Ground Water: Principles and Practices* (ITRC 1999b). These documents focus on organic contaminants. While a discussion of specific EA technologies is not part of this document, *Enhanced Attenuation of Chlorinated Organics—Electronic Resource Guide* (ITRC 2007a) focuses on technologies that can be implemented as EA treatments for chlorinated solvents. Some of these technologies, especially those that address reduction of source loading through reductions in flux through the source, are potentially applicable to metals and radionuclides. The classes of EA treatments for organics are consistent with those for metals and radionuclides.

The definition of EA and a decision framework documenting where it fits in the remediation process was first documented by ITRC in *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents for Groundwater* (ITRC 1998) and the technical and regulatory guidance document *Enhanced Attenuation: Chlorinated Organics* (ITRC 2008b). The decision framework for the organic contaminants was the basis on which the decision process supporting MNA and EA for metals and radionuclides was built.

This document seeks to begin to build the body of knowledge of attenuation processes and subsurface conditions for metals and radionuclides that will allow MNA of these constituents to become a remedy as accepted by the regulatory community as MNA for organics has become through the past few years.

1.5.2 Mass Flux/Mass Discharge

Estimations of mass flux and mass discharge may provide valuable insight into evaluations of plume stability; transitioning from source treatments to more passive treatments, including MNA; estimations of future risk and exposure; and system performance. However, the acceptance of mass flux/mass discharge estimations is not universal and requires development of a solid, defensible technical foundation and education for those who will propose remedial solutions based on their use and those who must make regulatory decisions. ITRC has published a technology overview titled *Use and Measurement of Mass Flux and Mass Discharge* (ITRC 2010) “intended to foster understanding of mass discharge and mass flux estimates through description of their development and use.” While this document was developed by the Integrated Dense, Nonaqueous-Phase Liquids (DNAPL) Site Strategy Team, and thus the focus of the case studies and example sites is organics, the material presented in the document is equally relevant to metals and radionuclides.

1.6 Document Organization

The remainder of this document is organized into sections that discuss the major issues associated with applying MNA at sites contaminated with metals and/or radionuclides. Section 2 provides a “primer” on geochemistry, reviews technical guidance from EPA, and presents a technical framework for investigating a site to determine the applicability of MNA. Section 3 presents the decision framework for determining the applicability of MNA as a component of a remedial action. Section 4 provides regulatory perspectives of federal and state agencies. Perspectives of public and tribal nation stakeholders are in Section 5. Section 6 presents real-world examples that illustrate key factors that impact the development of the conceptual site model (CSM) for a site.

2. PHYSICAL PROCESSES, SITE CHARACTERIZATION, AND MODELING APPROACHES

Historically, MNA has been applied to sites contaminated with organics, where natural attenuation processes may either transform organic contaminants to harmless products or mineralize contaminants to carbon dioxide. MNA has recently received increased visibility as a remedial approach for sites contaminated with metals and radionuclides. The conceptual paradigm of MNA as applied to metal and radionuclide contaminants differs from that applied to organic contaminants since metals and radionuclides cannot be transformed to harmless products. Metals can at best be sequestered to immobile and/or occluded forms that are rendered harmless to human and ecological receptors. Radionuclides, most of which are metals, can at best be attenuated in the same ways as stable metals and/or decay to harmless daughter products.

Regardless of the operative geochemical process of attenuation (e.g., precipitation, adsorption, radiological decay), metal and radionuclide contaminants (or the daughter products in the case of radiological decay) remain in place with any natural attenuation approach to site remediation. However, MNA can provide an effective site remedy through the stabilization and sequestration of the COC from mobile and bioavailable states, thereby effectively mitigating exposure to sensitive human and ecological receptors. Spatial and temporal changes in site geochemistry, which may result in mobilization of previously stabilized metal and radionuclide contaminants, must be accounted for when considering MNA as a remedial alternative. Since MNA of metal and radionuclide contaminants inevitably leaves the contaminant in place, MNA is generally acceptable only for sites that intrinsically have low potential for contaminant migration. The processes controlling EA and evaluation approaches/tools used for EA are the same as those for MNA, in part because the success of any EA application is predicated on stability and long-term sustainability of the attenuation process.

The objectives of this section are as follows:

- identify the geochemical processes that govern the environmental behavior and fate of metals and radionuclides at sites where MNA is being considered as a remedial alternative
- describe calculations and models useful for evaluating MNA and how they can be integrated into CSM development
- explicitly identify the uncertainties associated with MNA, how to approach site characterization for MNA implementation, and the challenges typical of an MNA groundwater remedy for metals contamination

To achieve these aims, this section summarizes the knowledge base of environmental fate and transport processes of metals and radionuclides in groundwater, outlines discrete steps for site characterization where MNA is being considered, and provides guidance to decision makers about the effectiveness of MNA at their particular site.

2.1 Geochemistry Primer

This section is a summary of geochemical concepts helpful to understanding attenuation processes of metals and radionuclides. With the exception of radioactive decay, the dominant attenuation mechanisms for metals and radionuclides involve chemical reactions that cause partitioning of the contaminant to immobile forms. Hence, a certain level of geochemical knowledge is required to understand the attenuation mechanisms. Many readers will have this level of knowledge and can skip this section. Others may find it a helpful introduction or refresher to geochemistry of metals and radionuclides in groundwater.

The geochemistry of aquifers concerns chemical reactions involving minerals and constituents dissolved in groundwater. At a given point, most aquifers are at near steady-state conditions geochemically, meaning that the reactions are very slow and only subtle changes in pore water composition and mineralogy occur with time. Faster reactions occur locally where there are changes in aquifer mineralogy or an influx of water with a significantly different composition than the pore water of the aquifer. A contaminant plume entering an aquifer is an example of the latter.

Contaminant plumes can induce a variety of reactions when they enter an aquifer. The nature of the reactions depends on the chemical composition of the contaminant plume, the chemical composition of the natural aquifer pore water, and the mineralogy of the aquifer. Attenuation mechanisms for metal and radionuclide contaminants are reactions that cause the contaminants to partition from being dissolved in the mobile pore water to being bound on or within immobile solids in the aquifer. In other words, attenuation is achieved by the contaminant transferring from a mobile to an immobile form. However, these are not the only reactions that must be considered.

Contaminant attenuation reactions or mechanisms are part of a network of potential reactions that are interrelated. The partitioning of a contaminant between pore water and aquifer solids is a balance between forces that tend to pull the contaminant into the pore water and those that tend to pull the contaminant into the solid. The forces that pull the contaminant into the pore water are summed up by the concept of aqueous speciation. The forces that pull the contaminant into the solid phase are attractions of two types. One is between the dissolved contaminant ion and other ions, forming a mineral that contains the contaminant (precipitation or coprecipitation). The other is between the contaminant ion and the surface of a mineral (adsorption or absorption).

Chemical reactions adhere to thermodynamic and kinetic principles and can be predicted if the right information is known. Equilibrium thermodynamics reveals what reactions are possible or what chemical conditions are required for reactions to be possible. However, some reactions in the environment proceed so slowly that they are not observable despite thermodynamic predictions that conditions are favorable for their occurrence. These are sometimes referred to as being kinetically controlled. Rates of kinetically controlled reactions are predictable for simple systems based on laboratory studies, but the subsurface is not a simple system. Variables such as temperature, surface area of minerals, and the presence in solution of constituents that inhibit reactions make reaction rate predictions difficult. In some cases reaction rates can be measured directly in the field, but often cannot. Reaction kinetics is an important aspect to geochemical reactivity in the subsurface. In many instances thermodynamically favorable processes, particularly environmental redox processes, are known not to occur on time scales relevant to site-specific consideration, For example, it can be shown that an aqueous solution containing a carbon source, such as sugar, and an electron acceptor, such as sulfate, will react to form sulfide and carbon dioxide. However, common experience tells us that in the absence of the right biological mediators, this reaction does not occur within relevant time scales (i.e., millennia). Thus, biotic mediation of most redox processes in groundwater environments is ultimately the determining factor for the rate at which a given chemical process occurs in the subsurface environment. The take-home message is that although a certain process is predicted to be thermodynamically favorable, this prediction does not immediately translate to the rate at which that processes will occur.

2.1.1 Equilibrium Constants

The equilibrium constant—the ratio of chemical species involved in a reaction at equilibrium—allows prediction of chemical reactions. As an example, the oxidative dissolution of the mineral pyrite by oxygen is described by the following reaction:

$$FeS_2 + H_2O + 3.5O_{2(aq)} = Fe^{+2} + 2SO_4^{-2} + 2H^+$$

The equilibrium constant for this reaction is as follows:

$$K_{eq} = \frac{\left(aFe^{+2}\right)\times\left(aSO_4{}^{-2}\right)^2\times\left(aH^+\right)^2}{\left(aFeS_2\right)\times\left(aH_2O\right)\times\left(aO_{2(aq)}\right)^{3.5}}$$

where aX is the chemical activity (a) of the constituent (X) in the reaction. Activity of a constituent in solution cannot be measured but is related to the concentration by an activity coefficient. The activities of pure minerals are equal to 1. The activity of water in most contaminant plumes is very close to 1. Hence, the equilibrium constant simplifies as follows:

$$K_{eq} = \frac{\left(aFe^{+2}\right)\times\left(aSO_4{}^{-2}\right)^2\times\left(aH^+\right)^2}{\left(aO_{2(aq)}\right)^{3.5}}$$

From a chemical analysis of the groundwater that includes concentrations of Fe^{+2}, SO_4^{-2}, and $O_{2(aq)}$, as well as pH, the activities can be calculated,[2] and the ion activity product (IAP) can be calculated. The IAP is the right side of the equilibrium constant equation. If the IAP is less than the equilibrium constant, then the reaction (i.e., oxidative dissolution) is thermodynamically possible. If the IAP exceeds the equilibrium constant, then the reaction is not possible, but the reverse reaction (i.e., precipitation) is possible.

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[2] Public domain and commercial software that perform these calculations is available.

Another valuable use of equilibrium constants is for understanding what reactions may take place as geochemical conditions associated with a contaminant plume change. If the geochemical evolution of a site is understood, an estimate of future groundwater composition can be made. With this information and the equilibrium constants of future potential reactions, the possible occurrence of reactions in the future can be determined. This is a powerful tool for assessing the long-term immobilization of metals and radionuclides.

A Note on Equilibrium Constants and Reaction Rates

Reaction rates are related to the equilibrium constants. Typically, the further a possible reaction is from equilibrium (i.e., the greater the equilibrium constant relative to the IAP), the faster the relative reaction rate will be. However, many reactions also have a relatively high activation energy that must be overcome before the reaction will proceed. The classic example is the reaction between oxygen and methane gas. Without an ignition source to overcome the activation energy, methane will not burn.

2.1.2 Aqueous Speciation

Most dissolved metals and radionuclides do not occur as a solitary ion in solution. They may form an ion unto themselves, but they also form ion pairs and/or combine with multiple ions forming more complicated aqueous complexes. The listing of these different dissolved forms of a contaminant, or at least the dominant ones, is called the aqueous speciation.[3] Naturally occurring anions that tend to form aqueous complexes with metal contaminants are hydroxyl (OH^-), carbonate (CO_3^{-2}), phosphate (PO_4^{-3}), sulfate (SO_4^{-2}), and chloride (Cl^-). Various soluble organic compounds bearing a negative charge can also form aqueous complexes with metals. These include carboxylic acids and fulvic acids. In addition, contaminant plumes may contain synthetic organic chemicals such as ethylenediaminetetraacetic acid (EDTA), which is specifically used to keep metals in solution during an industrial process. Hence, the nature of aqueous speciation for a metal depends not only on the chemical behavior of the metal, but on the concentrations of the potential anions that may bind it in aqueous complexes. Thus, it is important to obtain chemical analyses of contaminated groundwater that include all the constituents that may influence the speciation of metal and radionuclide contaminants.

Aqueous speciation for a metal is difficult to measure but can be calculated from thermodynamic relationships. Figure 2-1 is a calculated diagram of the aqueous speciation of uranium in oxidizing conditions showing fields where different species dominate. Calculation of the diagram requires assumptions for the phosphate and carbonate concentrations. In this case the phosphate concentration was assumed to be 10 µg/L, and the carbonate concentration was controlled by equilibrium with a partial pressure of 0.01 atm of carbon dioxide. Each line on the diagram is the set of points at which the species on either side have equal activities and—if an ideal solution is assumed—equal concentrations.

Uranium is an example of a contaminant with a complicated aqueous speciation because hydroxyl, carbonate, and phosphate ions all strongly bind with uranium in relatively stable aqueous complexes. The aqueous speciation is highly dependent on the concentrations of these anions and is also on the total concentration of uranium. However, the dominant control on aqueous speciation of oxidized uranium is the pH, which directly controls the concentration of hydroxyl ions by equilibrium with water. The pH also controls the concentrations of carbonate and phosphate ions. For example, the species of dissolved carbonate that forms the strongest

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[3] This listing should not be confused with isotopic speciation, which is a listing of the isotopes of an element present.

aqueous complexes with uranium is CO_3^{-2}, but it is part of the dissolved carbon dioxide system that consists of three species. The pH determines the speciation within this system and hence the concentration of CO_3^{-2}. At higher pH values, CO_3^{-2} is the dominant species and readily complexes with uranium, but at lower pH values, other uranium complexes are dominant.

Other metal and radionuclide contaminants vary in how complicated their aqueous speciation is relative to uranium. Some, like plutonium, are more complicated. Others, such as nickel, are much less complicated. Nevertheless, pH is a dominant influence on the aqueous speciation of all metals and radionuclides with the exception of tritium. Another important influence on aqueous speciation of contaminants is the oxidation-reduction potential (ORP). Like many other metals and radionuclides, uranium has multiple oxidation states, each of which forms multiple aqueous complexes.

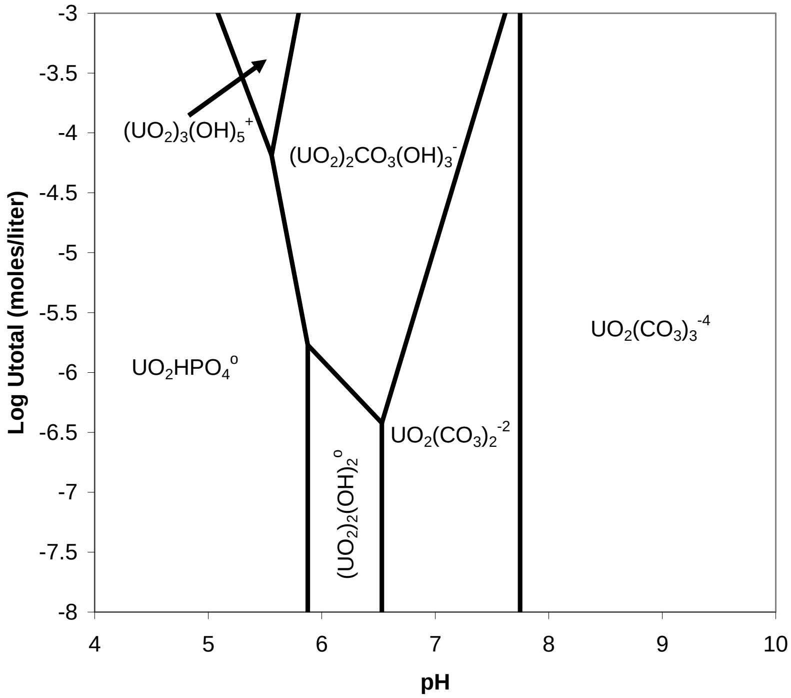

Figure 2-1. Calculated diagram of aqueous speciation of oxidized uranium in the presence of dissolved phosphate (10 µg/L) and carbonate (equilibrium with 0.01 atm CO_2).

A Note on pH

pH is defined as the negative log of the hydrogen ion activity:

$$pH = -\log a_{H+}$$

It is a measure of how acidic water is—low pH water is acidic. At a neutral pH of 7, activities of hydrogen ions and hydroxyl ions are equal. The pH of some common substances gives a relative understanding of pH values:

- lime juice ~2
- orange juice 3–4
- beer 4–5
- milk ~6
- seawater ~8

Uranium speciation illustrates why it is important to view contaminant plumes as systems of interrelated reactions. Contaminant concentrations alone reveal little about how natural processes will attenuate the contaminant or how a contaminant will respond to different remediation technologies.

2.1.3 Oxidation-Reduction Reactions

Oxidation-reduction reactions play multiple roles in attenuation processes of metals and radionuclides. They can directly affect the mobility of contaminants by changing the contaminants' oxidation state. They can cause precipitation of minerals into which contaminants partition. Alternatively, they can cause dissolution of minerals that could provide surfaces for contaminant adsorption.

Oxidation-reduction reactions, hereafter referred to as redox reactions, involve the movement of electrons from one chemical species to another. When a species is oxidized, it loses electrons. Another species must gain those electrons and be reduced. A classic example is the rusting of iron in which, in a simplified explanation, metallic iron atoms lose 3 electrons each to form Fe^{+3} ions. The Fe^{+3} ions are insoluble and can form a mineral such as goethite (FeOOH), which is similar to those associated with rust. If the species that gains the electrons is oxygen, the reaction is as follows:

$$Fe + 0.75O_2 + 0.5H_2O = FeOOH$$

The oxygen is sometimes referred to as an *oxidant*, because it is causing the oxidation of iron, or an *electron acceptor*, because it is receiving electrons from the iron. Conversely, the iron is the *reductant* or the *electron donor*. The oxidation of iron can be written without specifying an oxidant by using electrons as a component:

$$Fe + 2H_2O = FeOOH + 3e^- + 3H^+$$

The equilibrium constant for this reaction is as follows:

$$K_{eq} = (ae^-)^3 \times (aH^+)^3$$

For convenience, particularly for graphical purposes, equations like this are often written in logarithmic form:

$$\log K_{eq} = 3\log ae^- + 3\log aH^+$$

The activity of electrons can be treated similarly to the activity of hydrogen ions, and the quantity pe, the negative log of the electron activity, can be used. Then the equation is written as follows:

$$\log K_{eq} = -3pe - 3pH$$

Rearranging the equation to make pe a function of pH indicates that, at equilibrium and any given pH, there is an equilibrium pe. The log of the equilibrium constant for the oxidation of iron at 25°C is 2.48. Therefore:

$$3pe = -2.48 - 3pH$$

or

$$pe = -0.827 - pH$$

This relationship can then be graphed with pe versus pH so that it can easily be seen whether metallic iron or goethite is the stable form of iron at any value of pe and pH (Figure 2-2, left).

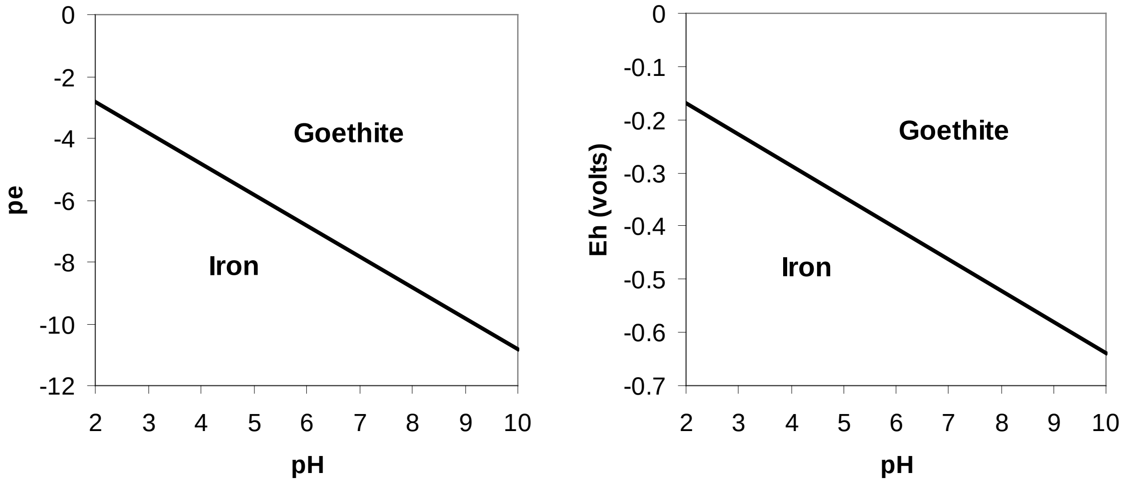

Figure 2-2. Comparison of pe-pH diagram (left) and Eh-pH diagram (right) showing stability fields of iron and goethite.

Unfortunately, unlike pH, pe cannot be measured with an instrument. Fortunately, a quantity related to pe, known as Eh, can be measured (Figure 2-2). Eh is a measure of the net electrical potential of all of the redox couples in an aqueous system, which commonly include Fe(II)/Fe(III), Mn(II)/Mn(III), O_2/H_2O, NO_3^-/N_2, and SO_4^{-2}/S^{-2}. Eh-pH diagrams are widely used in environmental studies to portray aqueous speciation and stability fields of potential minerals of metal and radionuclide contaminants. Returning to uranium speciation as an example, Figure 2-3 shows Eh-pH diagrams for uranium concentration of 100 µg/L and the same phosphate and carbonate concentrations as shown previously. The dashed lines indicate the limits of the stability of water, and thus no speciation is shown beyond those limits because, at equilibrium, water would not exist. Figure 2-3A shows only the aqueous speciation; Figure 2-3B shows stability fields for potential uranium minerals (yellow fields) at those conditions. The mineral stability fields indicate that the equilibrium solubilities of each mineral are less than 100 µg/L at conditions within the stability field. So, a conclusion that can be drawn from Figure 2-3B is that, over a wide range of pH, uranium is less soluble when it is reduced from the U(VI) to the U(IV) oxidation state.

Despite the usefulness of Eh-pH diagrams, the user must be cautious not to overinterpret them. They are equilibrium diagrams and show only what is possible. Furthermore, Eh measurements are a general indicator of the redox state of groundwater but do not mean anything about specific elements. Redox reactions are often kinetically controlled with very slow reaction rates at groundwater temperatures and in the absence of a catalyst to increase the rate. Hence, the fact that the state of the major redox couples indicated by a measured Eh suggests uranium should be reduced, or conversely oxidized, does not mean it is actually present in the predicted state. However, Eh-pH diagrams are a good starting place for formulating a conceptual model of contaminant behavior. Likewise, they often explain observations of contaminant behavior. Spatial and/or temporal trends in Eh measurements are also particularly useful for identifying the occurrence of redox reactions at a site. If large changes in Eh are observed from the core of a plume to the fringe, then there is a good chance redox processes are occurring, potentially causing significant geochemical transformations within the plume.

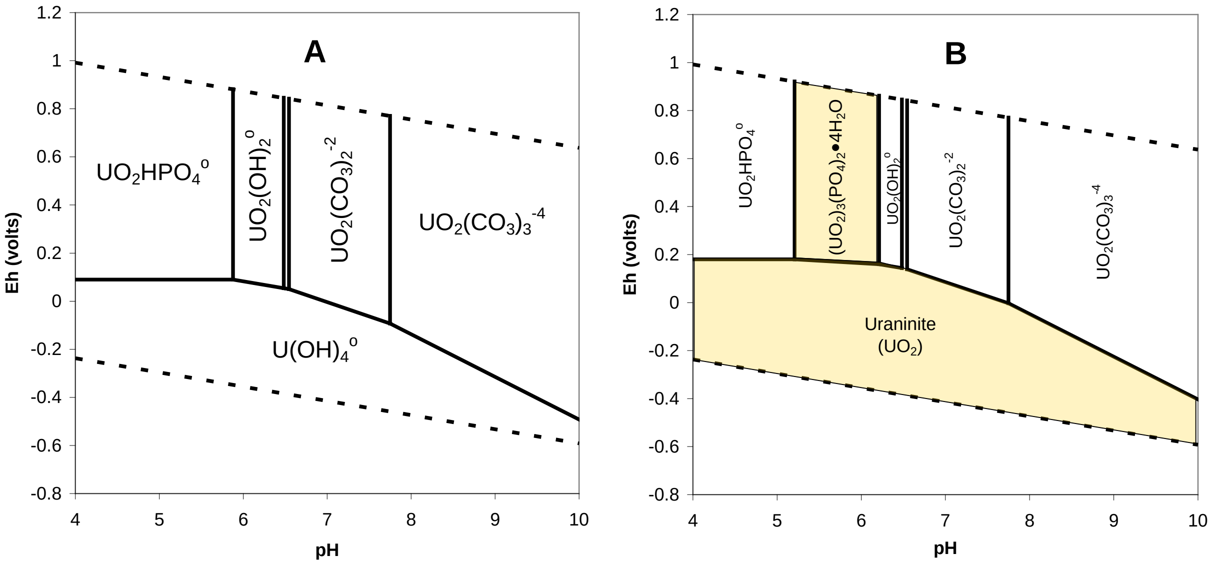

Figure 2-3. Eh-pH diagrams for uranium at a concentration of 100 µg/L, dissolved phosphate (10 µg/L), and carbonate (equilibrium with 0.01 atm CO_2). A shows only aqueous speciation; B shows stability fields for minerals $(UO_2)_3(PO4)_2{\cdot}4H_2O$ and uraninite.

2.1.4 Microbial Reactions

Microbes are ubiquitous in the subsurface and are involved in myriad geochemical processes. Their most important role in attenuation processes of metals and radionuclides is their ability to catalyze redox reactions. Microbes obtain their required energy from exploiting thermodynamically favorable reactions that are not at equilibrium. They do this by increasing the reaction rate, which increases the rate at which energy is available. This acceleration can have profound effects on metals and radionuclides because a change in oxidation state can greatly change the mobility of these contaminants. For example, Figure 2-3B shows the large stability field of the uranium mineral uraninite at reduced conditions. Under reduced conditions, uraninite has a much lower solubility than most oxidized U(VI) minerals. Thus, a change from U(VI) to U(IV) is likely to result in lower mobility, and greater attenuation, for uranium.

A Note on Simple Indicators of Microbial Activity

Although there are many more sophisticated ways to quantify microbial activity in groundwater, there are some simple indicators in spatial or temporal trends in groundwater chemistry. These can help decide whether more detailed methods are warranted:

- decrease in dissolved oxygen
- decreasing ratios of nitrate to chloride (or other relatively conservative tracers)
- increase in dissolved Mn or Fe
- decreasing ratios of sulfate to chloride (or other relatively conservative tracers)
- “rotten egg” smell of sulfide

Microbes can change the oxidation state of metals and radionuclides by directly catalyzing their oxidation or reduction reactions, but only if the reaction is thermodynamically favorable. In systems with an abundant and continuous supply of oxygen, microbes can catalyze the oxidation of metals and radionuclides by using the oxygen as an electron donor while the metal or radionuclide acts as the electron acceptor. In reduced systems, microbes can use oxidized forms of metals and radionuclides as electron acceptors while using a constituent such as organic carbon as an electron donor, resulting in the reduction of the metal or radionuclide.

Perhaps the most important role of a microbial community in attenuation of metals and radionuclides is their ability to catalyze reactions involving carbon as an electron donor using a variety of electron acceptors that are not contaminants. Oxidized aquifers have abundant potential electron acceptors in the form of iron and manganese minerals, nitrate in groundwater, and sulfate in groundwater or in minerals. When a source of organic carbon enters such an aquifer, for example as a constituent in a contaminant plume, microbes catalyze reactions between the electron-donating carbon and the electron acceptors, in a sequence that is most energetically favorable to the microbes. Electron acceptors that react to release the most energy are used first, and others are used sequentially in the order of the energy their reaction releases. In general, the sequence of electron acceptor use is as follows:

$$O_2 > NO_3^- > \text{Mn(III) or Mn(IV)} > \text{Fe(III)} > SO_4^{-2} > H_2O$$

This process leads to progressively more reducing conditions at which redox-sensitive metals and radionuclides may be reduced spontaneously or by microbially catalyzed reactions. Figure 2-4 shows this sequence in a generic plume containing a carbon source and the zones or gradients that are established by the sequential use of electron acceptors. Some contaminant metal and radionuclide reactions that may occur in these zones are also shown.

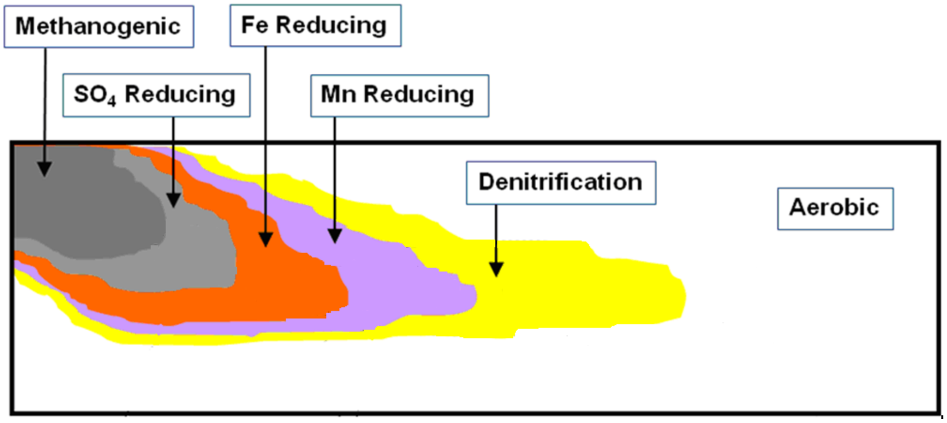

Figure 2-4. The zones of electron acceptor use in a plume containing an organic carbon source and some potential reactions that involve contaminants.

2.1.5 Aquifer Mineral Controls on Groundwater Chemistry

Reactions of groundwater with the natural minerals of the aquifer influence the groundwater chemistry. The degree of influence depends on the nature of the minerals. In sandy aquifers devoid of carbonate minerals, the influence is subtle because silicate minerals typically have low solubilities. Nevertheless, the chemical composition of the groundwater, particularly constituents such as aluminum and silica, reflects reaction with quartz, feldspars, micas, clays, or other prevalent silicates. In calcareous aquifers, those containing the calcium carbonate minerals calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$), the influence is more profound. Groundwater in calcareous aquifers generally has high concentrations of calcium, magnesium, and carbonate with pH values between 7 and 8.5, reflecting dissolution of the moderately soluble carbonate minerals. The presence of natural organic matter and colocated sulfide minerals causes groundwater to be reducing.

Aquifer mineralogy also affects contaminant plume chemistry. The pH of an acidic plume entering a calcareous aquifer is neutralized by dissolution of the carbonate minerals. These minerals are highly soluble in acid, so the aquifer has a large acid-buffering capacity. By contrast, the acid-buffering capacity of a sandy aquifer is much less. Dissolution of silicate mineral provides some buffering capacity, as does adsorption of hydrogen ions on clay mineral surfaces. Nevertheless, the acid-buffering capacity of a sandy aquifer is less than that of a calcareous aquifer. Redox conditions in a contaminant plume are also affected by aquifer mineralogy. The conditions of a plume entering an aquifer rich in organic matter and sulfide minerals are likely to become reducing. To a lesser degree, dissolution of Fe(III) minerals by a plume with chemically reducing conditions buffers the plume toward more oxidizing conditions. An effect associated with this may be release of natural trace elements such as arsenic originally bound to the dissolving Fe(III) minerals.

2.1.6 Waste Site Evolution

An understanding of waste site evolution is fundamental to evaluation of the permanence of attenuation of metals and radionuclides caused by natural or engineered processes. A contaminant plume is a transient perturbation of natural conditions within an aquifer. For most plumes these perturbations are significant because the chemical compositions of contaminant-bearing fluids are significantly different from that of the natural groundwater. The contrast between the geochemical conditions within the plume and the natural geochemical conditions of the aquifer dictate that conditions in the subsurface evolve as the plume moves. Hence, at any given location, natural attenuation mechanisms also evolve with time. A pendulum is a good model of waste site evolution (Figure 2-5). The natural condition is when the pendulum hangs vertically. When the pendulum is perturbed, it moves away from vertical, but when the force that perturbs it ceases, its natural tendency is to move back to vertical. Without artificial intervention, the further it is moved from vertical, the longer it will take to return to natural conditions.

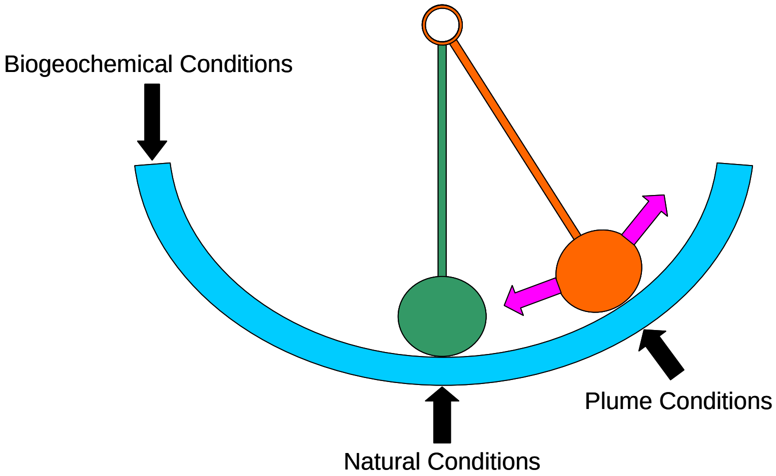

Figure 2-5. Movement of a pendulum as an analogy to waste site evolution.

In general, this principle is true for waste sites as well. Evolution of a waste site begins when a plume is introduced to the subsurface and ends when the subsurface has returned to near-natural geochemical conditions. The waste site may not return to exactly the conditions that existed before the plume was introduced because the plume may induce some permanent changes in mineralogy, microbiology, and hydrology, but it will always move in that direction. If a particular contaminant at a waste site is mobile at natural conditions, then natural attenuation alone is unlikely to be a successful remedy. On the other hand, if data suggest that a contaminant will be sufficiently attenuated at natural conditions, then natural attenuation may be an option that deserves further consideration. Knowing that a waste site will evolve toward natural conditions is the simplest form of using waste site evolution to predict the potential success of natural attenuation remedies. If further consideration of natural attenuation is warranted, then the analysis of waste site evolution should become more complex.

2.1.7 Geochemical Gradients

A premise stated early in this section is that aquifers are generally near steady-state conditions except at boundaries where the geochemistry of the aquifer pore water and aquifer mineralogy changes. A contaminant plume entering an aquifer perturbs this steady state, and chemical reactions occur as a response to this perturbation. Dissolution of minerals buffers pH and redox conditions. Organic carbon in plumes is oxidized by microbially catalyzed reactions involving aquifer-derived electron acceptors. These reactions establish geochemical gradients—zones of change in geochemical conditions. For example, in Figure 2-4 there is a geochemical gradient between aerobic and denitrifying conditions, denitrifying and iron-reducing conditions, etc. These gradients are moving, and the rate at which they move is informative about the geochemical evolution of the waste site. As the geochemical conditions evolve, attenuation processes of metals and radionuclides change. Thus, understanding the geochemical evolution of a waste site is critical to predicting whether, in the future, attenuation mechanisms will remain sufficient to prevent exposure of receptors to hazardous levels of contaminants.

When a contaminant plume is introduced to the subsurface, a geochemical gradient is created at the leading edge of the plume, at the interface of the contaminant plume and natural groundwater (Figure 2-6). Dilution of the plume, reaction with aquifer minerals, adsorption of plume constituents, desorption of natural constituents, and changes in microbiology can all occur at this gradient. In point of fact, different types of gradients move at different rates, though all are driven by the same hydrodynamic forces. Consider as an example that a leading gradient caused by dilution alone moves according to hydrodynamic forces and is unimpeded by chemical reactions. In contrast, a pH gradient is impeded by the buffering reactions associated with aquifer mineral dissolution and adsorption of free protons (H^+). Likewise, a leading redox gradient can be impeded by microbiological reactions and reaction with redox-sensitive aquifer minerals.

Trailing gradients form where natural upflow groundwater meets the infiltrating plume or enters the zone affected by the plume (Figure 2-6). As long as plume infiltration is relatively constant, the trailing gradient is stationary. Once plume flux from the vadose zone to the saturated zone is eliminated or substantially reduced, the trailing gradient migrates into and through the plume zone. Trailing gradients are controlled by hydrodynamic forces, dilution, reaction with plume-altered minerals, and the influx or elimination of nutrients which sustain microbial growth. Examples of reactions with plume-altered minerals are desorption of free protons from plume zone minerals and oxidation of reduced minerals created within the plume zone. It is often true that trailing gradients move much slower than leading gradients because the natural groundwater often has a much less aggressive chemical composition than the plume.

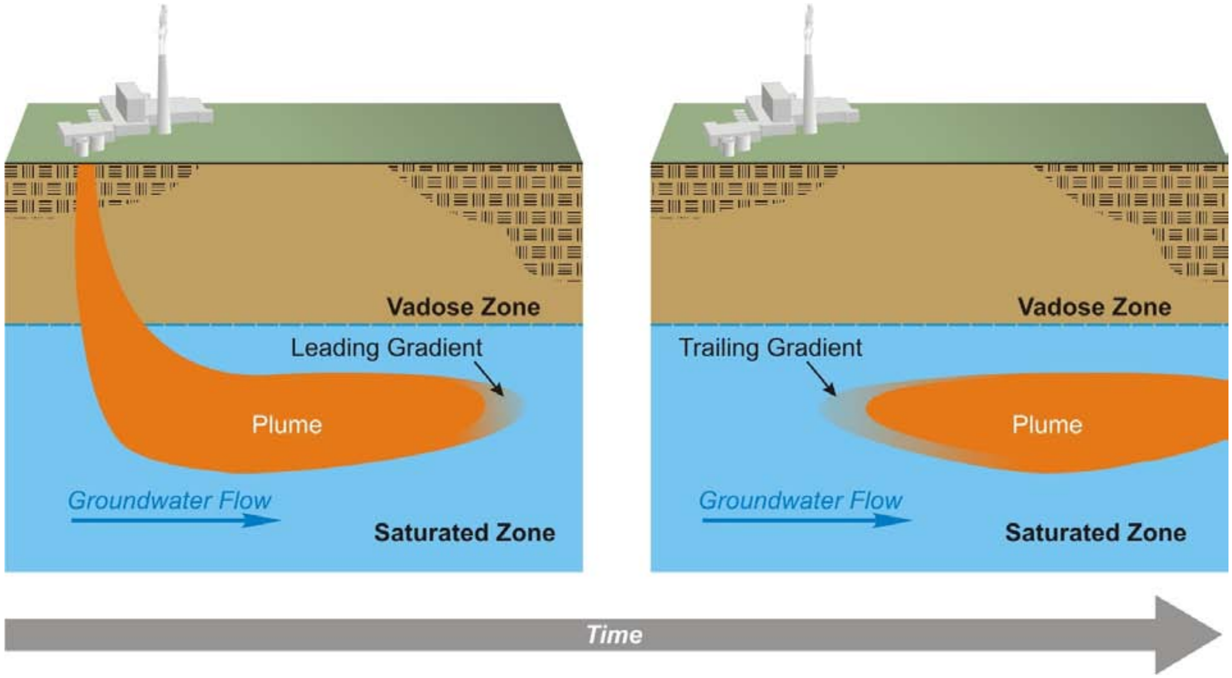

Figure 2-6. Formation of leading and trailing geochemical gradients as a plume evolves.

One way in which consideration of geochemical gradients simplifies long-term prediction of natural attenuation is that contaminants can be grouped by how their migration is controlled. Some contaminants will be controlled only by dilution, some predominantly by pH, and others predominantly by redox conditions. Large changes in contaminant mobility occur only across sharp gradients in these factors. Thus, the attenuation of contaminants is controlled by the migration rates of these gradients.

Geochemical gradients are also a useful tool to communicate contaminant mobility and waste site evolution to those that are not geochemists. It is easy to understand, without discussing specific mechanisms, that one group of contaminants may be following a particular geochemical gradient, while another may be stabilized within the plume zone. Subsequently, the group of contaminants that was stabilized in the plume zone may be mobilized as the trailing gradient passes. Likewise, it is easy to understand that contaminants that were immobilized in a treatment zone may be remobilized when the trailing gradient passes through the treatment zone.

2.2 Summary of Existing Guidance and Technical Resources

In 2007, EPA published the first two volumes of the three-volume MNA set (EPA 2007a, 2007b) called *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water*; the third volume is imminent but has not been released at this writing. This document set represents a technical resource for site managers to facilitate evaluation for the potential effectiveness of MNA as a remedial approach for metals and radionuclides in groundwater. The intention here is to describe the types of information provided in these documents and not to repeat the information provided there.

The first volume, *Technical Basis for Assessment* (EPA 2007a), contains the technical requirements for assessing the potential applicability of MNA as part of a groundwater remedy for plumes with nonradionuclide and/or radionuclide inorganic contaminants. The volume's three sections describe (1) the conceptual background for natural attenuation for inorganic contaminants, (2) the technical basis for attenuation of inorganic contaminants in groundwater, and (3) approaches to site characterization to support evaluation of MNA.

The first section of Volume 1 presents a tiered approach for site characterization to evaluate the potential for MNA as an effective remedial approach. The objective of the tiered approach is to provide site managers with a logical framework for an effective way to screen sites for MNA that is cost-effective because it prioritizes the data required for site evaluation. Conceptually, a tiered approach seeks to progressively reduce uncertainty as site-specific data are collected, thereby effectively managing project resources. Ultimately, the success or failure of MNA at any particular site will be determined by the operative physico-chemical processes and by the rate and extent of these processes. Thus, site evaluation for MNA requires collection of site-specific data that define the processes controlling contaminant transport.

The framework presented in this document is built around the tiered approach in EPA 2007a and is briefly discussed here. Table 2-1 summarizes the four tiers of MNA viability for different sites.

Table 2-1. Summary from EPA 2007a of the tiered approach to demonstrating MNA developed in that document

Tier	Objective	Potential data types and analysis
I	Demonstrate active contaminant removal from groundwater	• Groundwater flow direction (calculation of hydraulic gradients); aquifer hydrostratigraphy • Contaminant concentrations in groundwater and aquifer solids • General groundwater chemistry data for preliminary evaluation of contaminant degradation
II	Determine mechanism and rate of attenuation	• Detailed characterization of system hydrology (spatial and temporal heterogeneity, flow model development) • Detailed characterization of groundwater chemistry • Subsurface mineralogy and/or microbiology • Contaminant speciation (groundwater and aquifer solids) • Evaluate reaction mechanism (site data, laboratory testing, develop chemical reaction model)
III	Determine system capacity and stability of attenuation	• Determine contaminant and dissolved reactant fluxes (concentration data and water flux determinations) • Determine mass of available solid phase reactant(s) • Laboratory testing of immobilized contaminant stability (ambient groundwater; synthetic solutions) • Perform model analyses to characterize aquifer capacity and to test immobilized contaminant stability (hand calculations, chemical reaction models, reaction-transport models)
IV	Design performance monitoring program and identify alternative remedy	• Select monitoring locations and frequency consistent with site heterogeneity • Select monitoring parameters to assess consistency in hydrology, attenuation efficiency, and attenuation mechanism • Select monitored conditions that "trigger" reevaluation of adequacy of monitoring program (frequency, locations, data types) • Select alternative remedy best suited for site-specific conditions

For a site to pass through Tier I, it must be demonstrated that the extent of the plume is stable or shrinking due to attenuation of the contaminant. Time and spatial trends of contaminant concentration in groundwater are important indicators, but attenuation is not truly demonstrated unless it can be shown that contaminant is partitioning from the aqueous (groundwater) to the solid phase (aquifer minerals). The exceptions are radionuclides with half-lives short enough that radioactive decay accounts for plume stability. To pass Tier II, a viable process for aqueous to solid partitioning—an attenuation mechanism—must be demonstrated (see Figure 2-7). In addition, the rate of the attenuation mechanism should be sufficient to account for the stability of the plume demonstrated in Tier I. In Tier III the capacity of the aquifer to support or maintain the attenuation mechanism is measured. For MNA to be viable, the capacity must be sufficient to ensure the stability of the plume for some time agreed upon by site owners, regulators, and stakeholders. Furthermore, it must be demonstrated that the partitioning of contaminant from aqueous to solid phases is relatively irreversible under geochemical conditions that are likely to prevail in the future. Finally, Tier IV requires that a monitoring program be developed that will detect any future advance of the plume or other indication that failure of natural attenuation to meet remedial goals is imminent. As part of Tier IV, an alternative remedy should be selected that can be implemented if natural attenuation does fail.

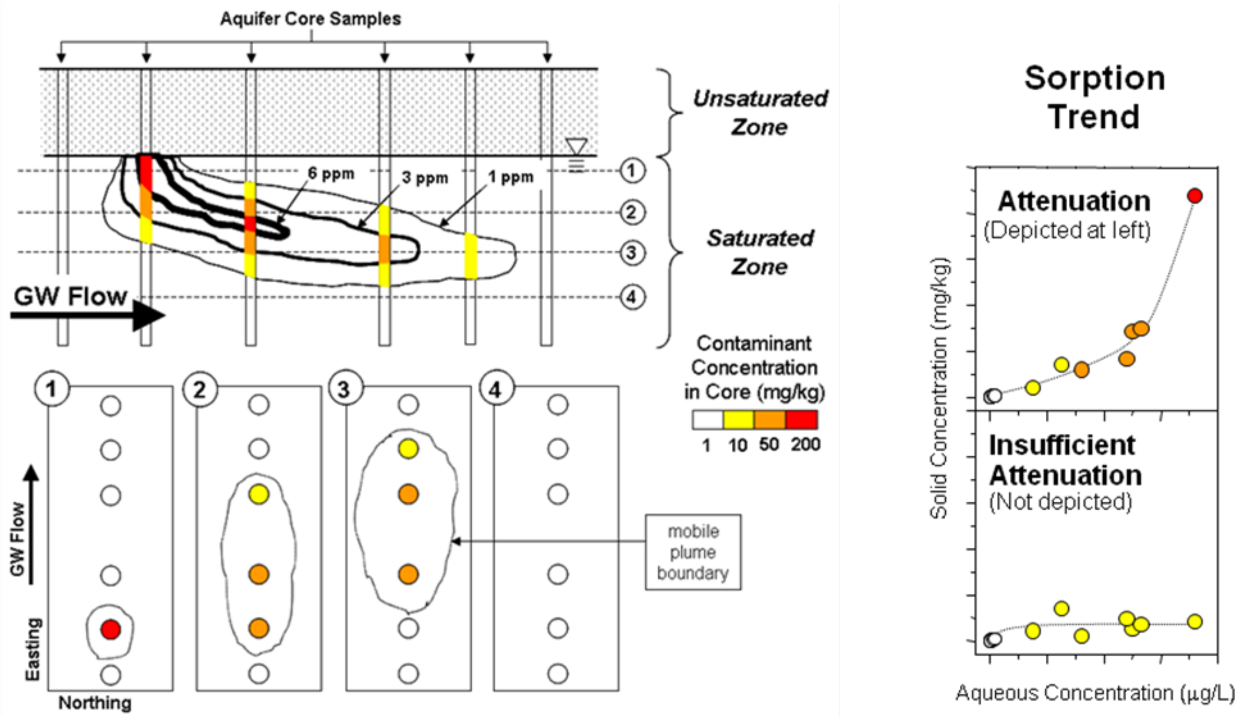

Figure 2-7. Illustration of how the migration of a generic plume boundary (left) is attenuated through the partitioning of the contaminant from the aqueous to the solid phase (right). Demonstration of ongoing sorption and aquifer capacity are critical to pass Tier 2.

The second section of Volume 1 provides a review of the physical and biogeochemical processes (e.g., sorption, precipitation, transformation, etc.) that govern contaminant transport in groundwater and provides a framework for considering the types of data that are often required to evaluate a specific site for MNA. Once the operative processes of metal attenuation are identified, the capacity of the subsurface aquifer to bind or sequester the contaminant must be determined.

The third section describes analytical techniques that are often used to provide a mechanistic understanding of the operative physico-chemical processes to assess the overall performance potential of MNA at a specific site.

The second volume in the set, *Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium* (EPA 2007b), consists of individual chapters that describe the natural processes that may result in the attenuation of the listed contaminants and data requirements to be met during site characterization. Emphasis is placed on characterization of immobilization and/or degradation processes that may control contaminant attenuation, as well as technical approaches to assess performance characteristics of the MNA remedy.

The third volume (not released at this writing but expected to cover assessment of radionuclides including americium, cesium, iodine, neptunium, plutonium, radium, radon, technetium, thorium, tritium, strontium), and uranium) consists of individual chapters that describe the natural processes that may result in the attenuation of the listed contaminants and data requirements to be met during site characterization. Emphasis is placed on characterization of immobilization and/or degradation processes that may control contaminant attenuation, as well as technical approaches to assess performance characteristics of the MNA remedy with focus upon radioactive decay. A tiered analysis approach is also presented to assist in organizing site characterization tasks in a manner designed to reduce uncertainty in remedy selection while distributing costs to address the following four primary issues:

- demonstration of dissolved plume stability via radioactive decay and/or active contaminant removal from groundwater
- determination of the rate and mechanism of attenuation by immobilization
- determination of the long-term capacity for attenuation and stability of immobilized contaminants
- design of performance monitoring program, including defining triggers for assessing MNA failure, and establishing a contingency plan

In addition to the three-volume MNA set briefly described above, there are two additional references describing processes of MNA for metals: a technical resource document for monitored natural recovery of contaminated sediments[4] and *Technical Guide: Monitored Natural Recovery at Contaminated Sediment Sites* (Magar et al. 2009). Both discuss technical aspects of natural attenuation of metals specifically applied to sediments; however, the geochemical processes which apply to metals sequestration and mobilization in sediments are also directly applicable to groundwater.

2.2.1 Technical Resource Document for Monitored Natural Recovery of Contaminated Sediments

The former document is a resource for remedial project managers (RPMs) describing field-scale geochemical processes and bench-scale tools that can be used to measure and/or predict natural

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[4] At this writing, the technical resource document is in development and not yet released. It is mentioned here to be used as a resource when it is released.

processes that contribute to the reduction of risk to human health and ecological receptors/resources at contaminated sediment sites. The goal of the document is to discuss natural physical, chemical, and biological processes that contribute to recovery processes associated with contaminated sediments and to present methods that may be used to measure and assess those processes at specific sites. The degree and number of technical tools that should be used for evaluating the appropriateness of MNA at contaminated sediment sites is detailed in this resource document. While the EPA document covers both organic and inorganic contaminants, an entire chapter is dedicated solely to natural attenuation process and temporal stability of metal contaminants under a natural attenuation scenario.

2.2.2 *Technical Guide: Monitored Natural Recovery at Contaminated Sediment Sites*

Issued through DOD's Environmental Security Technology Certification Program (ESTCP), *Technical Guide: Monitored Natural Recovery at Contaminated Sediment Sites* (Magar et al. 2009) outlines the principles and evaluation criteria for comprehensive and cost-effective evaluation of monitored natural recovery (MNR) as a remedial option at contaminated sediment sites, and like the aforementioned EPA document, it covers both organic and inorganic contaminants. This guidance presents a DOD framework for properly designing and implementing MNR and for predicting long-term MNR performance and potential human health and ecological risk reductions, providing RPMs and site owners with improved tools for more cost-effective sediment characterization and remediation. It also discusses how to incorporate potential impacts of major events (e.g., major storm events and human activity such as channel dredging) into decision making and provides requirements for monitoring after natural recovery is implemented. The document outlines the mechanisms by which shifts in geochemical conditions can remobilize metals in otherwise sequestered states. The guidance also addresses costs associated with site characterization, interpretation, modeling, and assessment in support of MNR.

2.3 Summary of Geochemical Processes Relevant to MNA of Metals and Radionuclides in Groundwater

There are four principal mechanisms by which metal and radiological contaminants are attenuated in the subsurface environment:

- sorption–desorption
- precipitation–coprecipitation–dissolution
- dilution–dispersion
- radiological decay

Metal solubility, sorption, and bioavailability depend primarily on metal speciation. Metal speciation, in turn, is determined by site-specific geochemical conditions. The ambient geochemical conditions of the groundwater aquifer solids which affect metal speciation include pH, Eh, alkalinity, natural organic matter (NOM), and chelating ligands (e.g., carbonate, phosphate, organic chelators, etc.). These geochemical conditions are often established by the dominant biogeochemical processes (e.g., aerobic vs. iron/sulfate-reducing conditions) and are expected to collectively govern metal speciation in groundwater (Figure 2-4). For example, groundwater with elevated concentrations of NOM is associated with low Eh (reducing conditions), which may lead to the reduction of metals such as arsenic or chromium, which are susceptible to redox processes. Within these four mechanisms, there are several geochemical processes that can contribute to the natural attenuation of metals in groundwater. The processes most important to consider for any contaminated-groundwater site include sorption/desorption, precipitation/dissolution, coprecipitation/dissolution, oxidation/reduction, biological stabilization, dilution/dispersion, and radiological decay. The extent to which these processes are relevant to a particular contaminant is site specific and can depend greatly on the nature of the subsurface material and aqueous geochemical conditions and the nature and extent of the contaminants present (mixed plume situations). Different background biogeochemical processes may create geochemical gradients along which metal speciation is expected to change.

2.3.1 Sorption–Desorption

In general, sorptive processes and precipitation are the two most important processes for natural attenuation of metals in groundwater. In the context of metals attenuation in groundwater, sorption can include *adsorption* onto the surface of aquifer solids (e.g., clay minerals, iron oxides, etc.) and *absorption* into the matrix of the aquifer solid substrate. Absorption is a physical process controlled by diffusion and capillary forces. Adsorption is more of a chemical process and, in most systems, is responsible for attenuation of a much larger mass of contaminants than absorption. Hence, the remainder of this discussion considers only adsorption.

The extent of adsorption for a particular metal onto a particular solid is quantified by a distribution, or partition, coefficient (K_d). Experimentally determined distribution coefficients for contaminants and a particular soil sample are sensitive to pH, alkalinity, salinity, and the solid:solution ratio used during the laboratory determination. Therefore, it is imperative that these factors be considered when applying K_d values where plume conditions (e.g., pH, ionic strength, etc.) may differ from the conditions used to measure the distribution coefficient. The presence of multiple potential sorbent phases in most aquifers can complicate estimates of metal adsorption; however, typically a single solid phase serves as the primary sorbent phase. For most uses, adsorptive processes are considered to be reversible, in a state of dynamic equilibrium, with the rate of adsorption approximately equal to the rate of desorption. Models of adsorptive processes can treat adsorption and desorption reactions separately. Explicit consideration of desorption reactions become important when a groundwater plume encounters a new water source (e.g., during upwelling or recharge) and the sorbed contaminants reach a new equilibrium under the newly established geochemical conditions, which determine new aqueous-phase contaminant concentrations.

Adsorption of metal and radionuclide contaminants is initiated by electrostatic attraction of the contaminant to an aquifer mineral surface. The contaminant may be weakly held at the surface by the electrostatic attraction alone or may become more strongly bound to the surface by chemical bonding. Contaminants that are weakly held by electrostatic forces typically have low K_d values, and those that are bound more strongly have high K_d values. Much more complicated and mechanistic treatments of adsorption are available in many textbooks (e.g., Stumm and Morgan 1996, Langmuir 1997), but it is not necessary to understand these to apply the framework presented in this document. On the other hand, it is imperative to qualitatively understand the sensitivity of adsorption to different geochemical conditions.

It is recognized that a brief discussion must speak in general terms about the geochemical influences on adsorption. It is a complicated process that varies greatly between contaminants and for each contaminant with different minerals. However, there are a few generalities that apply over a broad spectrum of metals and radionuclides.

For many metals and radionuclides and a given aquifer mineralogy, pH is the geochemical variable to which adsorption is most sensitive because pH has an influence on both the aqueous speciation of contaminants and the surface properties of minerals. In particular, the aqueous speciation of those contaminants that form strong hydroxyl or carbonate complexes is influenced by pH. The speciation, in turn, controls the charge on the contaminant ion and its hydrated radius—both important to electrostatic attraction toward mineral surfaces. The effect of pH on surface properties of minerals is more profound. The surface charge of most minerals that are capable of sorbing large amounts of metal and radionuclide contaminants varies with pH because, in water, hydroxyl groups capable of binding hydrogen ions form attached to the crystal structure at the surface of these minerals. The center of Figure 2-8 shows a schematic of the hydroxyl groups on a mineral surface at an intermediate pH. As pH increases, the concentration of hydrogen ions in the water decreases, and, in response, the surface hydroxyl groups give up hydrogen ions. The loss of hydrogen ions leaves a net negative charge on the surface. As pH decreases, the surface hydroxyls bind more hydrogen ions, resulting in a net positive charge. As Figure 2-8 shows schematically, as positive charge increases on the mineral surface, similarly charged cationic contaminants are repelled from the surface and do not adsorb. Conversely, when surface charge on the mineral is increased, cationic contaminants are attracted to the surface and adsorb readily (Figure 2-9). Anionic contaminants behave in an opposite manner.

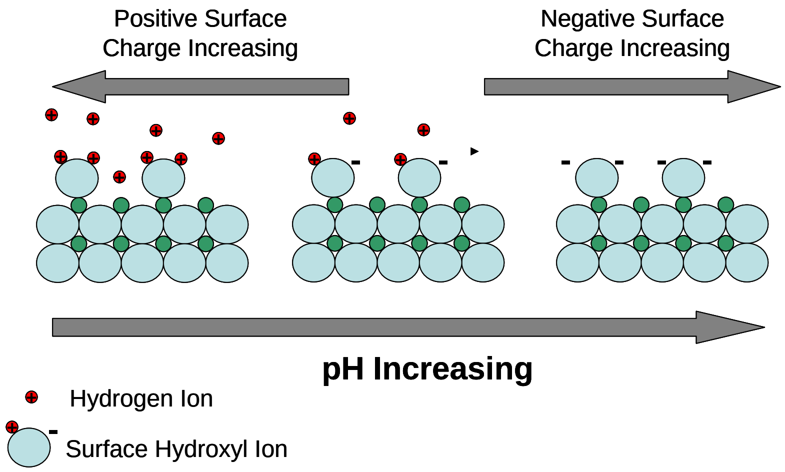


Figure 2-8. Schematic depicting how surface charge on a typical mineral surface changes with pH.

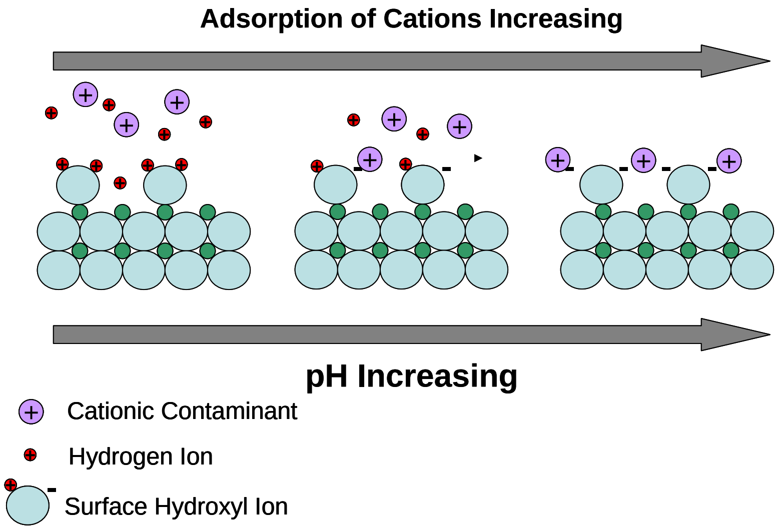


Figure 2-9. Schematic depicting adsorption of cationic contaminants with changing pH.

Ionic strength—loosely correlated to salinity, conductivity, or total dissolved solids—also influences adsorption of metals and radionuclides. The value of ionic strength affects the electrostatic surface properties of minerals, and hence adsorption. In addition, contaminants are more likely to form aqueous complexes that resist adsorption in high ionic strength solutions. If a significant fraction of the ionic strength is composed of an ion with similar properties to a contaminant, these ions compete with the contaminant for adsorption sites and reduce the adsorption of the contaminant.

Aquifer mineralogy is also important to adsorption of metals and radionuclides. In particular, the types and abundance of clay-size minerals and the presence or absence of calcite are important. Calcite in an aquifer controls the groundwater chemistry by buffering pH to values typically between 7 and 8.5 and adding carbonate alkalinity. The pH buffering affects adsorption as described above. The increased carbonate alkalinity can decrease adsorption of some contaminants, notably uranium, that combine with dissolved carbonate to form strong aqueous complexes. These complexes are usually anionic and thus sorb less at elevated pH.

Under a given set of geochemical conditions, adsorption of a contaminant is proportional to the number of adsorption sites available to the contaminant. This factor is controlled by surface area of the aquifer minerals. Thus, clay-sized particles can sorb far more metals and radionuclides than larger mineral grains because clay-sized particles have much higher surface areas. Clay-sized mineral type is important because different types of minerals have different surface properties. Clay-sized ferric iron oxides and hydroxides (e.g., hematite, goethite, ferrihydrite, etc.) commonly account for a significant amount of adsorption in aquifers, though other minerals may also be important. The amount of clay-sized minerals in an aquifer does not always correlate to the degree of contaminant adsorption. In many cases only a fraction of the clay-sized minerals present in an aquifer are in contact with passing groundwater and it is this fraction to which contaminants may sorb. For example, if a large fraction of the ferric iron minerals occurs in nodules, only a small amount of them are available for adsorption. The terms *effective surface area* or *reactive surface area* are often used to describe the surface area of minerals that is actually available for contaminant adsorption.

Mercury provides an example of how groundwater composition and pH affect adsorption. Figure 2-10 is an Eh-pH diagram showing the aqueous speciation of mercury. At mildly reducing conditions, the stable form of mercury is elemental mercury represented on the diagram as Hg^0. At these conditions the mobility of mercury is more limited by the low solubility of elemental mercury than by adsorption. Yet, at higher Eh values, the general solubility of mercury as Hg(II) is much higher, and its mobility is controlled by adsorption.

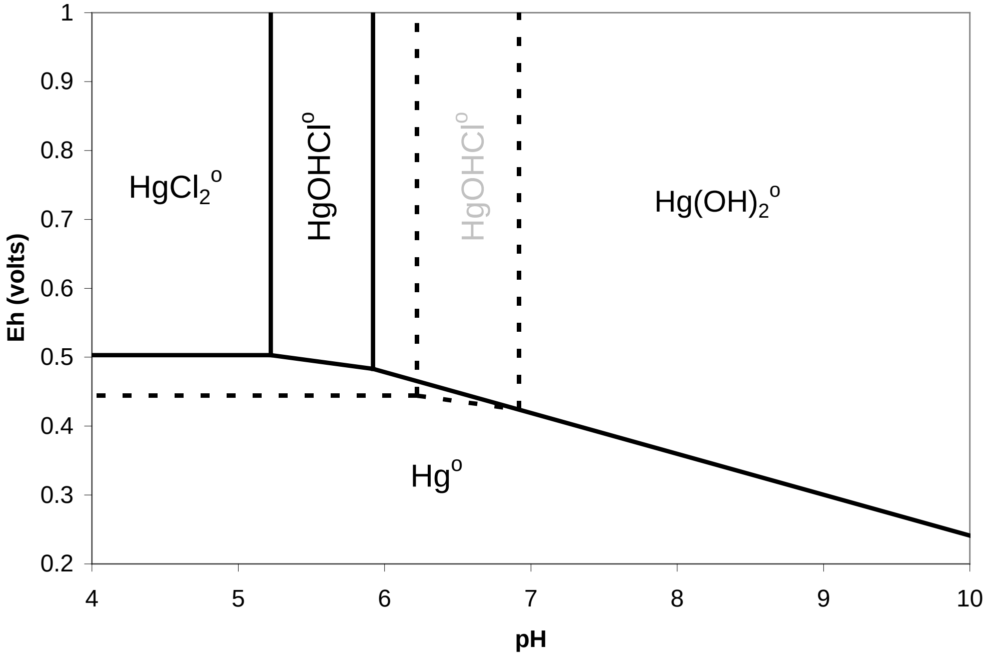


Figure 2-10. Eh-pH diagram showing aqueous speciation of mercury at chloride concentrations of 1 mg/L (solid line) and 10 mg/L (dashed line).

Over the range of pH shown in Figure 2-10, Hg(II) forms three dominant aqueous complexes, all of which are neutral in charge. The sorption of Hg(II) generally corresponds to the aqueous speciation. Adsorption is markedly increased when $Hg(OH)_2^o$ is the dominant species. This effect is not the result of electrostatic attraction because all three species have the same neutral charge. Instead, it is the result of chemical forces. More important for this example is that the speciation depends on the chloride concentration as well as the pH. At higher chloride concentrations (the dashed lines), the pH range at which the aqueous species $HgCl_2^o$ and $HgOHCl^o$ are dominant is expanded. When chloride concentration in groundwater is raised from 1 mg/L to 10 mg/L, the adsorption of Hg(II) is significantly reduced in the pH range of 6–7.

2.3.2 Precipitation–Coprecipitation–Dissolution

Precipitation, a common attenuation mechanism, is an example of chemical forces partitioning a contaminant into the solid phase, thereby reducing its mobility. Precipitation of a contaminant is a chemical reaction with an equilibrium constant. For example, precipitation of lead (Pb) as the mineral $PbCO_3$ occurs according to the reaction, where (s) denotes a solid:

$$Pb^{+2} + CO_3^{-2} = PbCO_{3(s)}$$

The reaction has an equilibrium constant of

$$K_{eq} = \frac{1}{(a_{Pb^{+2}}) \times (a_{CO_3^{-2}})}$$

Recall that the activity of a pure mineral such as $PbCO_{3(s)}$ is 1. However, precipitation reactions are generally considered from the point of view of dissolution of the contaminant-bearing mineral. Hence, the reaction is reversed and the equilibrium constant becomes as follows

$$K_{eq} = (a_{Pb^{+2}}) \times (a_{CO_3^{-2}}) = K_{sp}$$

where K_{sp} is called the *solubility product*. When the IAP, in this case $(a_{Pb^{+2}}) \times (a_{CO_3^{-2}})$, exceeds the K_{sp}, precipitation of the mineral is favored thermodynamically. When the IAP is less than the K_{sp}, dissolution of the mineral is favored. Once again, kinetics may prevent the actual precipitation of the mineral even though precipitation may be favored.

The terminology *saturated*, *undersaturated*, and *oversaturated* is often used in reference to the thermodynamic favorability of a precipitation-dissolution reaction. A saturated solution is at equilibrium with respect to the mineral, so K_{sp} = IAP. Precipitation is favored in a solution that is oversaturated with respect to a mineral (i.e., IAP > K_{sp}). Dissolution is favored in an undersaturated solution (i.e., IAP < K_{sp}). Many references use the concept of a saturation index (SI), which is the ratio of the IAP to the K_{sp}. When these are equal, the solution is saturated and the ratio is 1. The SI is commonly used in the logarithmic form where

SI = 0	solution saturated
SI > 0	solution oversaturated
SI < 0	solution undersaturated

Contaminants can also be attenuated by coprecipitation as a minor or trace element in a mineral composed of constituents that are not contaminants. For example, lead can be attenuated by coprecipitation in the mineral calcite ($CaCO_3$). Coprecipitation can occur in two ways. In the strictest sense of the word, *coprecipitation of lead* in calcite would mean that lead (Pb^{+2}) is incorporated into the crystal structure of calcite as a substitute for Ca^{+2}. In this case, the concentration of lead in the calcite would be governed by thermodynamic relationships and the ratio of lead to calcium dissolved in the groundwater. The term *coprecipitation* can also be used to describe a constituent that is physically incorporated into a mineral but is not actually part of the crystal structure of the mineral, which happens when a contaminant is precipitating at the surface of a growing mineral crystal and the contaminant is incorporated as inclusions in the mineral. Alternatively, in the case of microcrystalline masses of minerals such as iron hydroxides, contaminants can be coprecipitated by being adsorbed to the surface of microcrystals that are then aggregated into a mass of the mineral. In all of these cases of coprecipitation, remobilization of the contaminant depends on the dissolution of the host mineral.

Precipitation and dissolution of minerals are part of the network of reactions that make up an aquifer's geochemical system. As such, precipitation and dissolution of minerals depend not only on the chemical composition of the groundwater and the mineralogy of the aquifer, but on the other reactions that are occurring. These reactions include aqueous speciation reactions and dissolution and precipitation of minerals not directly associated with contaminants. Importantly, these factors and reactions may change substantially along geochemical gradients. Hence, conditions at a particular location that favor precipitation or coprecipitation of contaminants may change to conditions that favor dissolution of those contaminants as a geochemical gradient passes. As with sorption, prediction of long-term attenuation of metals and radionuclides by precipitation or coprecipitation relies on understanding the geochemical evolution of the system.

Identifying precipitation or coprecipitation of contaminants can be difficult. The contaminants are often at such low concentrations that there is often only a small chance of actually observing the minerals in which they occur. Use of groundwater analyses and saturation indices is valuable for indicating whether a contaminant is likely to be precipitating or coprecipitating, but these are not definitive. Therefore, multiple lines of evidence are usually required. These include spatial and temporal trends in contaminant concentration in groundwater, saturation indices, and contaminant leaching experiments on aquifer solids. The leaching experiments can be designed to target dissolution of specific minerals, or patterns in the concentration of contaminant in the leachate may indicate certain minerals are present.

It can be difficult to differentiate whether a contaminant has been adsorbed, precipitated, or coprecipitated. Nevertheless, it can be important for predictions of long-term contaminant attenuation. Attenuation mechanisms do not completely remove the contaminant from the groundwater, so there is always some contaminant being released from the aquifer solids. At constant groundwater composition, the curve of concentration released with time for a contaminant that was adsorbed is different from the curve for a contaminant that was precipitated. When groundwater composition is evolving, the release curves for adsorbed and precipitated contaminants can be very different.

The most common method to distinguish whether a contaminant is adsorbed or precipitated is leaching experiments on contaminated aquifer solids. Sequential extractions are one type of leaching experiment that can be effective and are relatively easy to perform. These involve sequentially leaching a contaminated sample with solutions that are increasingly more aggressive. Contaminants removed by the less aggressive reagents are generally considered adsorbed, and those removed only by the aggressive reagents are generally considered precipitated or coprecipitated. Sequential extractions can be ambiguous and must be interpreted with care. There are instrumental analyses that can distinguish adsorbed contaminants from those that are precipitated or coprecipitated; however, these can be expensive and are not always readily available to the average waste site owner.

2.3.3 Dilution–Dispersion

Dilution and dispersion of metals and radionuclides in groundwater can lead to localized contaminant concentration reductions and should be recognized in the development of the CSM. However, reliance on dispersion or dilution for contaminated sites is problematic because it may increase contaminant loading to downgradient receptors. Project managers should carefully evaluate the effects of increased loading on receiving bodies where dispersion can result in unacceptable risks to downstream areas or other receiving water bodies.

2.3.4 Radiological Decay

Radionuclide decay follows first-order kinetics, which means that the rate of the decay is proportional to the number of nuclei present. This process gives rise to a characteristic half-life for each radionuclide. A half-life is the amount of time required for half of the atoms of a particular radionuclide present to decay. Ten half-lives are required for the loss of 99.9% of any given radionuclide. Table 2-2 presents half-lives for common radionuclides. Radionuclides having very short half-lives typically decay too rapidly to affect the environment and do not adversely affect typical groundwater risk receptors. Radionuclides with very long half-lives may be persistent in the environment but may be of sufficiently low activity that little environmental damage is ultimately realized, depending on the size and extent of the contamination. The radionuclides with intermediate half-lives, such as strontium-90, present the greatest threat to ecosystem and human health receptors because they persist long enough to enter living systems and have sufficient radioactivity to cause damage to living tissue.

Table 2-2. Radioactive elements and associated half-lives

Radionuclide	Half-life
Americium-241	432 years
Carbon-14	5730 years
Cesium-137	30 years
Cobalt-60	5.25 years
Iodine-131	8 days
Plutonium-238	88 years
Plutonium-239	24,100 years
Radium-226	1620 years
Radium-228	5.75 years
Radon-220	55.6 seconds
Radon-222	3.8 days
Strontium-90	28 years
Technicium-99	211,000 years
Thorium-230	75,200 years
Thorium-232	1.4×10^{10} years
Tritium (hydrogen-3)	12.3 years
Uranium-234	2.45×10^{5} years
Uranium-235	7.04×10^{8} years
Uranium-238	4.46×10^{9} years

In addition to sorption, precipitation, and redox reactions, radionuclides exhibit radioactive decay characteristics, giving rise to a parent-daughter radioactive decay series for many of the radionuclides listed in Table 2-2. One notable radioactive contaminant which does not give rise to radioactive decay products is tritium. Given the relatively short half-life, the dominant attenuating mechanism of tritium (a radioactive isotopic form of hydrogen with a short half-life) is radioactive decay, rather than sorption or precipitation. Although tritium does not generate radioactive daughter products, those generated by some radionuclides may be more toxic, have longer half-lives, and/or be more mobile than the parent in the decay series.

2.3.5 Multiple Contaminant Plumes

The processes described above operate either individually or in concert to govern the attenuation of metal contaminants. Multiple processes may operate concomitantly to influence the fate of metal contaminants, particularly at mixed-plume locations. Complications arise when changes in geochemical conditions function to decrease the solubility of one metal but increase the solubility of another. An example is plumes containing both arsenic and chromium. Oxidized arsenic(V) species are typically lower in solubility and have a greater propensity for sorption onto aquifer solids, especially iron (hydr)oxides. In contrast, reduced arsenic(III) species are more mobile in groundwater. Alternatively, chromium is virtually immobile in its reduced chromium(III) form, whereas oxidized chromium(VI) is highly soluble and more toxic than chromium(III). Thus, geochemical site conditions such as a geochemical gradient of declining Eh may promote chromium attenuation and concurrently mobilize arsenic.

It is important to understand overall geochemistry of the contaminated site and its evolution through time. A comprehensive understanding of site conditions allows qualitative prediction of the behavior of multiple contaminants within a plume and the effects of natural or artificial changes in geochemical conditions. One way to approach this is by considering the effect of geochemical gradients on contaminant migration (Denham and Vangelas 2008). As discussed above, the evolution of a waste site can often be described by the migration rate of these gradients. In turn, the attenuation of groups of contaminants can be described by how the geochemical gradients affect their mobility. For example, anionic contaminants tend to sorb less as pH increases, while cationic contaminants tend to sorb more. Thus, as an acidic plume evolves and the trailing pH gradient migrates through the plume zone, the increasing pH tends to stabilize sorbed cationic contaminants but tends to release sorbed anionic contaminants. Using these general trends in contaminant behavior with an understanding of the migration of geochemical gradients can make assessing MNA and EA actions easier in plumes with multiple contaminants.

2.3.6 Geochemical Conditions

Ultimately, site-specific geochemical conditions determine the dominant pathways of metal and radionuclide fate and transport. Principal pathways of natural attenuation of metals and radionuclides in groundwater depend largely on the COC; each contaminant may have unique data needs and site-specific considerations. Table 2-3 shows the primary pathways and data needs for different metals, which may help to direct site characterization efforts for RPMs to identify of the potential pathways for metal sequestration and attenuation. The data requirements and principal pathways and special considerations for each element are adapted from Brady and Borns (1997) and Brady, Brady, and Borns (1997).

Table 2-3. Examples of natural attenuation pathways for metals and radionuclides

Metal/ radionuclide	Natural attenuation pathway	Data requirements	Special considerations
Americium Am(III)	Sorption to carbonate minerals	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable	Low pH destabilizes carbonates. High pH increases solubility of Am-carbonate minerals.
Arsenic As(III or V)	Sorption to iron hydroxides, formation of sulfides	Eh, and if Eh is low, sulfide levels	Low pH destabilizes carbonates, iron hydroxides. Low Eh dissolves iron hydroxides. Competition with phosphate for sorption onto oxides
Barium Ba(II)	Sorption to iron hydroxides, formation of insoluble sulfate and carbonate minerals	Sulfate levels, carbonate levels	Low pH destabilized carbonates, iron hydroxides. Low Eh dissolves iron hydroxides. If sulfides are present, precipitation is possible.
Cadmium Cd(II)	Sorption to iron hydroxides, carbonate minerals, formation of insoluble sulfides	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable; Eh, and if Eh is low, sulfide levels	Low pH destabilizes carbonates, iron hydroxides. Organic acids and chelates (e.g., EDTA) may decrease sorption. Low Eh dissolves iron hydroxides but may promote formation of sulfides.
Cesium Cs(I)	Sorption to clay interlayers	Clay content, cation exchange capacity	High NH_4^+ levels may lessen sorption. Subsurface characterization for clay content and mineralogy.
Chromium Cr(VI)	Reduction by organic matter and Fe(II), sorption to iron hydroxides, formation of insoluble $BaCrO_4$, formation of insoluble $Cr(OH)_3$	Eh, electron donor levels, and pH (reduction rates are faster at low pH)	Low pH destabilizes carbonates, iron hydroxides. Low Eh dissolves iron hydroxides. Consider potential reductants (e.g., sulfide and ferrous iron).
Cobalt Co(II)	Sorption to iron hydroxides, carbonate minerals	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable	Low pH destabilizes carbonates. Low Eh dissolves iron hydroxides.
Copper Cu(II)	Sorption to iron hydroxides, carbonate minerals, organic matter	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable	Low pH destabilizes carbonates. Low Eh dissolves iron hydroxides.
Iodine I(I)	Sorption to organic matter and sulfides	Metal sulfide mineral content	Does not sorb to other notable solid phases.
Lead Pb(II)	Sorption to iron hydroxides, organic matter, carbonate minerals, formation of insoluble sulfide and phosphate minerals	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable; phosphate concentration; Eh levels, and if Eh is reducing, sulfide levels; organic carbon content	Low pH destabilizes carbonate minerals, desorbs lead from iron hydroxides. Organic acids and chelates (e.g., EDTA) may decrease sorption. Low Eh dissolves iron hydroxides but favors sulfide formation.

Metal/ radionuclide	Natural attenuation pathway	Data requirements	Special considerations
Mercury Hg(II)	Formation of insoluble sulfides, and high affinity for portioning to organic matter	Eh, and if Eh is low, sulfide levels; organic matter content	Methylation leads for formation and bioaccumulation of highly toxic methylmercury.
Nickel Ni(II)	Sorption to iron hydroxides, carbonate minerals	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable; Eh, and if Eh is low, sulfide levels	Low pH destabilizes carbonate minerals, desorbs lead from iron hydroxides. Organic acids and chelates (e.g., EDTA) may decrease sorption. Low Eh dissolves iron hydroxides but favors sulfide formation.
Plutonium Pu(V or VI)	Sorption to iron hydroxides, formation of insoluble hydroxides	Iron hydroxide availability, pH, availability of reductants	May move as a colloid. Low Eh dissolves iron hydroxides.
Strontium Sr(II)	Sorption to carbonate minerals, formation of insoluble sulfates	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable	Low pH destabilizes carbonates.
Technetium Tc(VII)	Possible reductive sorption to reduced minerals (e.g., magnetite), formation of insoluble reduced oxides and sulfides	Eh, and if Eh is low, sulfide levels	Does not sorb to other notable solid phases.
Uranium U(VI)	Sorption to iron hydroxides, precipitation of insoluble minerals, reduction to insoluble valence states	Iron hydroxide availability, pH, availability of reductants	Low pH destabilizes carbonates, iron hydroxides. Organic acids and chelates (e.g., EDTA) may decrease sorption. High pH and/or carbonate levels decrease sorption. Low Eh dissolves iron hydroxides.
Zinc Zn(II)	Sorption to iron hydroxides, carbonate minerals, formation of sulfides	Iron hydroxide availability; pH, alkalinity, and Ca^{2+} levels to answer if calcium carbonate is stable; Eh, and if Eh is low, sulfide levels	Low pH destabilizes carbonates, iron hydroxides. Organic acids and chelates (e.g., EDTA) may decrease sorption. Low Eh dissolves iron hydroxides.

2.4 Role of Modeling in Tiered Analysis Approach

Modeling is an important tool for evaluating MNA of metals and radionuclides. Here modeling includes the processes of developing a CSM, mass balance calculations, and geochemical speciation calculations, as well as running predictive fate and transport models. Modeling of some sort is pertinent to each of the four tiers discussed in the EPA (2007a) approach to demonstrating MNA. It should be used in an iterative approach to characterization, evaluation of attenuation capacity, prediction of contaminant behavior, and establishment of a long-term monitoring strategy. The iterative approach of tiered analysis is designed to provide cost-effective guidance assessment to progressively reduce uncertainty as site-specific data are collected. Typically, the more complex the modeling approach, the more site-specific data are required, increasing costs but also mitigating site-specific uncertainty (Figure 2-11). The goal of modeling while moving through the tiered system of assessing MNA viability should be to facilitate this process, not just to predict contaminant concentrations at a particular point in space and time. Modeling should be used extensively to guide characterization, evaluate pieces of the conceptual model, and set the range that each important parameter must fall within for MNA to be a viable option.

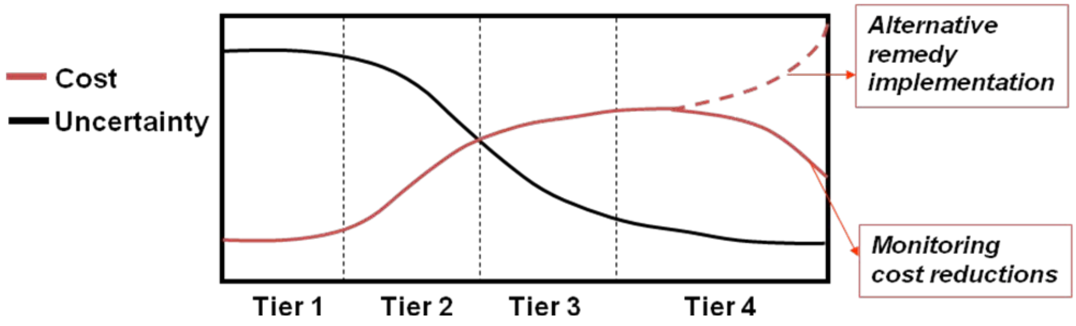


Figure 2-11. Illustration of the off-setting balance between cost of modeling and the uncertainty associated with modeling efforts.

2.4.1 Modeling, Development of CSMs, and Evaluation of MNA

EPA (2007a) contains an excellent discussion of modeling as it applies to the four tiers. The information presented here is intended to supplement that discussion by reiterating the most important points and showing how different types of models can integrate into conceptual model development and assessment of MNA through the four-tier system of EPA (2007a).

It is important to understand that the output of a model is only as good as the input. Therefore, primary emphasis should be on the parameters required to execute a model. The cost of collecting many of these parameters can be high, and the more complex modeling becomes, the more parameters are required. Hence, modeling should proceed from simple to more complex only as required. To some degree this is a natural progression as the process of evaluating MNA proceeds because in the earliest stages data required for complex models are often lacking. Yet, throughout the process the approach to modeling should always be to use the simplest model or calculation that can answer the question at hand or provide the information needed.

The CSM is a description of the contaminated site that includes the physical setting and dominant processes controlling contaminant behavior. These include factors controlling flow of the groundwater and attenuation mechanisms of contaminants. Additionally, processes controlling evolution of the waste site must be included so that the viability of MNA in the future can be assessed. This step is important because the mechanisms responsible for attenuation of inorganic contaminants are sensitive to geochemical conditions that will often change as the waste site evolves. In many cases, the CSM itself eliminates MNA from further consideration. For example, the CSM may describe an expanding plume, eliminating MNA as a remedial alternative.

Table 2-4 shows the integration of the CSM with the four-tier approach to assessing MNA of metals and radionuclides, and where various types of models can be used. If the point has been reached where MNA is being considered for metal or radionuclide contaminants, it is likely that development of the CSM is well under way and the Pre-Tier Analysis steps in Table 2-4 have been done. Yet, it is worth reemphasizing the importance of the site history, source identification, and the definition of waste site compartments. The site history is important because the spread of a contaminant plume often depends on the mode of contaminant release and the chemistry associated with that release. Contaminants disposed in solution may behave very differently than contaminants originally released as solids. Contaminants disposed as solids must undergo leaching from the solid phase into groundwater. This process may be slowed by solubility of the waste form or access of infiltrating water to the contaminant. Conversely, contaminants disposed in solution don't have these controls on their release to groundwater. The chemical nature of waste release at sites contaminated with metals and/or radionuclides strongly influences the degree to which contaminants are naturally attenuated in the subsurface. For contaminants disposed as solids, the solid phase the contaminant occurs in is important, but so are the other types of solids disposed. For example, in a landfill, degradation of organic matter may result in a mildly acidic chemically reducing pore fluid that has a profound effect on the attenuation of some contaminants. For contaminants released in solution, the chemical composition of the solution is important, particularly for waste process solutions because these are often designed specifically to keep the contaminants in solution. Thus, they are often acidic, alkaline, or have high concentrations of constituents which complex contaminants keeping them in solution (e.g., organic chelates). Likewise, mobility of redox-sensitive contaminants released with biodegradable organics may be affected by microbial processes operating on the organics. The flux/history is important because it defines the mass of contaminant that was released over time. The higher the mass released, the higher the probability that the attenuation capacity of the aquifer will be exceeded and the contaminant will migrate to exposure points.

Table 2-4. Integration of modeling, characterization, conceptual model development, and the tiered approach to evaluating MNA as an option

	Elements of conceptual model	**Characterization**	**Calculations/ modeling**
Pre-Tier Analysis	Spatial layout of site • source • potential exposure points/receptors	• Field site walk-over	
	Site history • inventory of contaminants released • mode of release • chemistry of release	• Records search • Personnel interviews	
	Define potential waste-site compartments	• Field site walk-down	

	Elements of conceptual model	Characterization	Calculations/ modeling
Tier I Analysis	Hydrogeologic environment • hydrogeological units affected or potentially affected • definition of flow regime • potentiometric surface defined	• Definition of hydrogeologic units from subsurface cores or geophysical logs • Hydraulic head measurements in wells • Stream base-flow measurements	• Hydraulic gradient calculations/flow net generation • Simple flow or transport modeling
	Spatial distribution of contaminants	• Groundwater analysis of contaminants • Surface water analysis of contaminants	• Aqueous speciation calculations
	Chemistry of plume	• Groundwater field measurements: pH, redox potential, alkalinity, dissolved oxygen • Groundwater laboratory measurements: major cations and anions, total organic carbon	
	Distribution of contaminants between aqueous and solid phases	• Bulk analysis of contaminant concentrations in aquifer solids	• Mass balance calculations (if natural background concentrations are known) • Probabilistic models
Tier II Analysis	Definition of contaminant/aquifer solid interactions • identify aquifer mineralogy • identify dominant attenuation mechanisms • measure attenuation mechanism rates • define geochemical heterogeneity	• X-ray diffraction, thermogravimetric analysis, etc. to analyze mineralogy • Sequential extractions, X-ray spectroscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy to identify specific attenuation mechanisms • Laboratory studies, in situ tests to measure attenuation rates • Use of geologic knowledge coupled with chemical and mineralogical analysis of aquifer solids to define geochemical heterogeneity	• Mass balance calculations • Reaction path modeling
	Detailed microbiology (if appropriate) • appropriate when sufficient carbon source is available to support biological mechanisms • appropriate when variation in nutrient chemical species (NO_3^-, SO_4^{-2}, O_2) cannot be explained by flow		• Reaction path modeling
	Detailed hydrogeology • measure key parameters • define hydrogeological heterogeneity	• Laboratory and/or field measurements of porosity and hydraulic conductivity • Variation in key parameters, geophysics, and use of geologic knowledge to define hydrogeological heterogeneity	• Analytical models of contaminant transport • Numerical flow models

	Elements of conceptual model	Characterization	Calculations/ modeling
Tier III Analysis	Measurement of attenuation capacity • quantitative mineralogy • flux of nutrients (if microbial processes are operable) • determine flux of contaminant from vadose zone	• More spatially dense quantitative mineralogy or use of heterogeneity information and less dense quantitative mineralogy • Lysimeter studies of nutrient concentrations in recharge	• Numerical reactive transport models
	Determine flux of contaminant from vadose zone	• Lysimeter studies of contaminant concentrations in vadose zone • Use of contaminant/tracer ratios and flow modeling	• Reaction path modeling
	Stability of contaminant stabilized zones • stability at conditions that reflect the geochemical evolution of the waste site	• Laboratory studies of contaminant stability • In situ push-pull tests of contaminant stability in stabilized zone	• Reaction path modeling • Numerical reactive transport models
Tier IV Analysis	Determine performance monitoring program		• Monitoring optimization models • Numerical reactive transport models
	Identify alternative remedy		• Reaction path models • Numerical reactive transport models

Definition of waste-site compartments is important because contaminants may behave differently in each compartment. Compartments may include things like organic-rich surface soils, the vadose zone, the saturated zone, and hyporheic zone. Many metals and radionuclides may be attenuated strongly in organic-rich compartments such as surface soils and the hyporheic zone. Yet, these zones are generally much smaller than the vadose and saturated zones.

Following the Pre-Tier Analysis (Table 2-4), the collection and analysis of data to support the tiered approach begins. From this point on in Table 2-4, the "Elements of conceptual model" and "Characterization" columns are essentially a summary of the discussions in EPA (2007a). The "Calculations/modeling" column shows at what point different types of models are commonly used. Table 2-4 is general guidance on the types of models that are commonly used in the process of evaluating MNA of metals and radionuclides and is not meant imply that these models must be used. Further discussion in this section is essentially an annotated list of the various types of models structured according to Table 2-4. As each type of calculation or model is introduced, a brief description is provided.

2.4.2 Tier I Analysis

2.4.2.1 Hydraulic gradient calculations/flow net generation

Hydraulic gradient calculations and generation of flow nets are done using hydraulic head measurements from multiple monitoring wells. They are essential at this point in the analysis for understanding groundwater flow directions. Most textbooks on groundwater describe these and their interpretation.

2.4.2.2 Simple flow calculations or transport modeling

Simple flow calculations or transport models are usually one-dimensional analytical solutions to equations governing flow through porous media. Again, they are usually described thoroughly in textbooks on groundwater. Though several computer programs that perform this type of modeling are available, it can often be done using a calculator. It is are important early in the assessment of MNA for estimating groundwater velocities and travel times and can be done in the Tier I analysis if values of hydraulic conductivity can be estimated from grain size or knowledge of other nearby sites. If estimates of hydraulic conductivity are reasonable but biased high, simple flow calculations or transport modeling can give a worst-case scenario of the travel time of a contaminant to a receptor. This may be important in the Tier I analysis for short-lived radionuclides such as cobalt-60, tritium, strontium-90, and cesium-137.

2.4.2.3 Aqueous speciation calculations

Aqueous speciation calculations are performed using computer programs that iteratively solve a series of reaction equations that describe formation of aqueous complexes composed of components within the system. For example, an element like copper in a simple sodium chloride solution occurs as several dissolved species combine with chloride or hydroxyl ions. The formation of each of these can be described as a reaction between hydroxyl or chloride ions and the Cu^{+2} ion. Aqueous speciation programs resolve all of these reactions, generally assuming equilibrium, and produce a concentration of each species at a given pH and redox potential. A chemical analysis of a groundwater can be entered into a program, and it will calculate the abundance of all aqueous species of which it has knowledge. To know about a species, the program must contain a reaction with an equilibrium constant for the formation of the species, as well as the concentrations of the components that make up the species. Most commonly available aqueous speciation programs have extensive thermodynamic databases that contain most of the species likely to be important to metal and radionuclide contamination. There is some variation in equilibrium constants used by different thermodynamic databases that leads to some uncertainty. However, more uncertainty in aqueous speciation calculations typically comes from incomplete or poor chemical analyses of groundwater entered by the user. Therefore, the data required to use aqueous speciation calculations are a chemical analysis of the groundwater that includes all of the major ions in solution, the contaminants, and any dissolved constituents that are specifically pertinent to a contaminant. For example, uranium can form dissolved phosphate complexes and relatively insoluble phosphate minerals. Hence, if uranium is a contaminant, chemical analyses of groundwater should include dissolved phosphate.

Aqueous speciation calculations are not valid for saline high-ionic-strength solutions unless there are special provisions within the program to account for these conditions because the general models used to calculate activity coefficients for each species are not valid at high ionic strengths, and specific ion interaction parameters must be used.

Most aqueous speciation programs also calculate the saturation indices of minerals in the thermodynamic database. The saturation index for a mineral is a ratio calculated from the speciation—usually expressed as the log of the ratio—that indicates whether or not the mineral is thermodynamically stable in the groundwater of interest. These should be interpreted as suggestions of what minerals might be present in contact with the groundwater or what minerals might precipitate or dissolve in response to changing geochemical conditions. The fact that a mineral is saturated or oversaturated (saturation index ≥ 0) does not mean it is present or will precipitate in a groundwater. The saturation index is only an indicator of what is thermodynamically possible; kinetic factors play a very large role in what minerals are actually present or will precipitate.

Aqueous speciation calculations can be done when data on bulk groundwater chemistry and contaminant concentrations are available. The dissolved species of contaminants give an indication of their mobility. For example, in many plumes with $pH < 6$, mercury may exist predominantly in the $HgCl_2^o$ complex that is likely to be more mobile than the $Hg(OH)_2^o$ complex. The saturation indices of contaminant minerals indicate whether precipitation is a possible attenuation mechanism. If a mineral with a contaminant as a component is saturated in groundwater, it suggests a mineral to look for to demonstrate that precipitation is an active attenuation mechanism for that contaminant. Saturation indices tell little about the possibility of coprecipitation of a contaminant.

2.4.2.4 Mass balance calculations

Mass balance calculations can be very useful for drawing conclusions about MNA based on the masses of contaminants, their distribution, and in some cases, the masses of reactants that act to attenuate contaminants. Mass balance calculations can be simple or complex. The simplest would be knowing the total source term of a short-lived radionuclide like cobalt-60 (half-life = 5.3 years) or tritium (half-life = 12.3 years). Simply applying radioactive decay to the source term may be useful in deciding whether MNA is a potential option. Mass balance calculations can become more complex as the conceptual model becomes more complete. When bulk concentrations of contaminant partitioned to aquifer solids are measured, simple mass balance calculations can be done to test, in a general sense, whether partitioning to the solid phase will sufficiently attenuate the contaminant. This use of mass balance calculations would be typical of Tier I analyses. More complex calculations can be done if specific reactions are known to cause attenuation of a contaminant. An example is an acidic plume containing a contaminant that is highly sorbed at $pH > 6$ flowing from the vadose zone into a calcareous aquifer. A mass balance calculation could be done to assess whether the aquifer contains sufficient calcite to neutralize all of the acid resulting in a sustainable $pH > 6$. If the answer is yes, then MNA is a potential option. Thus, the data required to perform mass balance calculations depend on the complexity of the calculations. For contaminants that also occur naturally, it is helpful if background concentrations are known (EPA 2007a).

2.4.2.5 Probabilistic models

Probabilistic models use Monte Carlo simulations to model contaminant transport using distributions of input parameters. The program selects values for each parameter based on the distribution provided by the user and calculates transport of a contaminant. This process is repeated to provide a distribution of results. Inherent in the distribution of results is their uncertainty. The narrower the distributions of the input parameters, the narrower the distribution of results. These types of models are useful in many ways. They can account for natural variability in measured parameters, help with understanding overall uncertainty of modeling results, and reveal the sensitivity of results to specific parameters. The latter use is most important in the early stages of considering MNA when characterization data are limited. Reasonable distributions of various contaminant transport parameters can be entered into a probabilistic model to determine how influential each parameter is on the final results. Characterization efforts can then be focused by putting more resources into measuring these parameters and less into measuring parameters to which the results are less sensitive. This is how probabilistic models can be most useful in Tier I analyses.

2.4.3 Tier II Analysis

2.4.3.1 Mass balance calculations

Mass balance calculations in this tier are more rigorous and can be done once specific partitioning mechanisms have been identified and quantified. The mass of contaminants can be compared with the mass of reactants to determine whether there are sufficient reactants to sustain MNA.

2.4.3.2 Reaction path modeling

Reaction path models combine aqueous speciation calculations, dissolution-precipitation thermodynamics, and mass balance calculations to model the chemical reactions in an aquifer system. The reactions can be between mixing water or groundwater and aquifer minerals and can include all attenuation mechanisms. Kinetics of reactions can also be introduced into reaction path models. Reaction path models are excellent tools for focusing in on geochemical and microbiological processes without the complications introduced by groundwater flow or when groundwater flow is not fully understood. For example, when aquifer mineralogy has been identified and attenuation mechanisms quantified, reaction path modeling can be done to identify dominant attenuation mechanisms under different scenarios. Reaction path modeling can also be done to test sensitivity of attenuation mechanisms to various geochemical parameters. For example, if it is found that a contaminant precipitates as a certain mineral, reaction path modeling can test the effect of changing pH on that attenuation mechanism. These models can also be used to estimate how much of a reactant (mineral surface, component of a contaminant-bearing mineral, etc.) is required to achieve an attenuation capacity that is sufficient for MNA to be appropriate. For example, if a reaction path model indicates that the aquifer material must be 50% clay to adsorb the expected mass of contaminant but observation shows the aquifer material is a clean sand, then MNA is unlikely to be appropriate.

2.4.3.3 Analytic contaminant transport models

Analytic contaminant transport models can be done when attenuation mechanisms have been identified and porosity and hydraulic conductivity have been measured. Analytic models or solutions are relatively simple and require few parameters, but often provide an elegant solution for contaminant transport problems. The key to analytic solutions is to have simple equations that describe the physical processes of contaminant transport. Analytic solutions have been used as a screening tool for MNA of metals and radionuclides (Brady et al. 1999). They are also excellent for examining sensitivity of natural attenuation to hydrogeological and geochemical parameters. In cases of relatively simple systems, analytic solutions together with the physical evidence for attenuation may be sufficient to demonstrate MNA is an appropriate remedy.

2.4.3.4 Numerical flow models

Numerical models are more flexible than analytic solutions and can incorporate heterogeneity, variations in reaction rates, etc. The trade-off for flexibility is complexity: taking full advantage of numerical models requires more characterization. However, with numerical models there is a broad spectrum of complexity. Rarely are the most complex models useful because parameterizing them at any reasonable cost requires estimations that increase uncertainty, which defeats the purpose of using an extremely complex model. Most numerical flow models also have simple geochemical capabilities, making them useful for bounding contaminant transport or testing the effects of geochemical heterogeneity on contaminant transport.

2.4.4 Tier III Analysis

2.4.4.1 Reaction path models

When quantitative mineralogy and nutrient flux are known, reaction path models can be used to determine whether passage of the plume through aquifer materials or a particular treatment is likely to alter flow properties by precipitation/dissolution of minerals or buildup of biomass. They can also be used to determine whether attenuation capacity is sufficient for MNA to be a viable option. Used in this way, they are more rigorous than mass balance calculations because they can consider reactant fluxes, mineral solubility, kinetics, microbial growth, etc. They are also useful in testing long-term stability of stabilized contaminants. Reaction path models can be used in concert with numerical flow models to estimate when active remediation of groundwater contamination can transition to MNA.

2.4.4.2 Reactive transport models

Reactive transport models integrate reaction path models with numerical flow models to solve the geochemical/microbiological system within each node of the model. In this way, they capture changes in geochemistry and/or microbiology along the flow path. They are used primarily to predict concentrations at a particular point in space and time. They are the most complex of models and are expensive to parameterize for multicontaminant systems or otherwise complex systems.

2.4.5 Tier IV Analysis

2.4.5.1 Monitoring optimization models

Monitoring optimization models are specialized to determine optimum monitoring well placement and sampling frequency.

2.4.5.2 Reaction path models

Reaction path models can be used at this point for testing potential alternative stabilization remedies.

2.4.5.3 Reactive transport models

Reactive transport models are useful in Tier IV for optimizing the monitoring program. They are also valuable for testing alternative stabilization remedies, other types of alternative remedies (groundwater capture, diversion, etc.), and future waste-site settings (different land-use scenarios, different climate scenarios, etc.).

2.4.6 Uncertainty in Modeling

One of the goals of modeling is to provide as reasonable a representation of reality as is possible or as is needed to answer a question of interest. Uncertainty is inherent in modeling and makes achieving this goal more difficult. Uncertainty in modeling can't be eliminated but can be managed. A major step in managing uncertainty is for site managers, regulators, and stakeholders to agree in advance what level of uncertainty is acceptable for a particular waste site. For predictive modeling, the uncertainty grows as the timeframe modeled increases, so it is important that these parties establish how far into the future predictions must be made. In perpetuity is not acceptable, because the uncertainty of the best model is 100% at an infinite time. It is also important to understand that modeling is being done to an accepted level of uncertainty rather than to a minimal uncertainty. If it can be agreed that the acceptable uncertainty is significantly higher than the minimal uncertainty, then simpler models requiring less parameterization can be used.

Uncertainty in modeling is different from error in modeling. Error is the degree to which the model results are different than the real system. This is often estimated by validating a model against a real system. This becomes difficult when modeling into the future. Uncertainty is a measure of the confidence in the model results. This can be estimated, even into the future, by understanding the confidence in each of the parameters that make up the model input. Careful modeling can capture uncertainty in the conceptual model, as well as apply uncertainty to the quality of data used as modeling input. Uncertainty is also introduced by the complexity or natural variation of the system being modeled. Models of complicated contaminants such as uranium, plutonium, or mercury (reactive, many pathways of transformation and/or transport) are likely to be more uncertain than models of simple contaminants such as tritium, strontium-90, or zinc (non- or moderately reactive, simple chemistry). Geochemical and hydrogeological heterogeneity, as well as fracture flow, introduce significant uncertainty in models. Regardless of the source of uncertainty, it is imperative in making remedial decisions to consider the confidence that can be placed on modeling results.

2.5 Analytical Methods to Support Evaluation of Natural Attenuation

Evaluating a site for natural attenuation processes of contaminants requires a suite of chemical, mineralogical, and microbiological analyses. This fact is evident in Table 2-4, which indicates such information is required in the evaluation Tiers I, II, and III. There are myriad possible analytical techniques to obtain this information. Each has its unique advantages and disadvantages that involve factors such as detection limits for specific constituents, accuracy, cost, and availability. Nevertheless, most of the required information can be obtained relatively inexpensively through commercial laboratories.

Tables 2-5 and 2-6 summarize analytical techniques commonly used in evaluating natural attenuation of contaminants. They cover only the most widely used and easily accessible techniques to provide a starting point for collecting the information needed to evaluate a site. The tables do not include radiological analyses. In most cases radionuclides are present at such low mass concentrations that they are difficult to detect using the analytical methods in the tables. Also, many radionuclides (e.g., H-3, Co-60, Sr-90, I-129, and Cs-137) have natural stable counterparts that are present at much higher mass concentrations. Hence, in environmental work radionuclides are usually analyzed by counting their decays or the decays of a daughter product with time. The methods for doing so are numerous and specific to each radionuclide but are readily available through commercial laboratories.

Table 2-5. Common groundwater analyses

	Analytes or purpose	**Method**	**Comments**
Field parameters	pH, Eh, dissolved oxygen, specific conductance, temperature	Electrode	Many tools available measure all of these either in a well or in flow-through cells during sampling
	Alkalinity	Colorimetric titration kit	
Metals	Most metals, including many contaminants	Inductively coupled plasma emission spectrometry (ICP-ES)	Commonly used for obtaining concentrations of major cations in groundwater for aqueous speciation analyses
	Many metals with poor detection limits by ICP-ES (As, Se)	Atomic absorption	
	Oxidation state of some metals	Ion chromatography (IC)	
Major anions	F, Cl, Br, NO_3^-, NO_2^-, SO_4^{-2}	IC	
Microbiology	Physiological types and numbers, overall biomass, specific organisms	Most probable number (MPN) analyses, cell counts, molecular tools, microcosms	Microbial analyses of sediment samples is preferred over analyses of groundwater samples, as groundwater may not be representative of all subsurface microbial activity; recommended only if a microbially mediated process is inferred to be relevant to the attenuation mechanism based on geochemical analyses

Table 2-6. Common aquifer solid analyses

	Analytes or purpose	Method	Comments
Partitioning of contaminant to soil	Adsorption or precipitation of contaminant	Chemical extractions followed by appropriate analysis (e.g., inductively coupled plasma mass spectrometry, ICP-ES)	Sequential extractions subject the sample to numerous extractions that each target a particular type of partitioning; gives information on attenuation mechanism
	Adsorption or precipitation of contaminant	Scanning electron microscopy with energy dispersive spectrometry	Can identify that contaminant is associated with particular minerals or has precipitated; useful only if contaminant is present at fairly high concentrations
Mineralogy	Identification of minerals in aquifer solids	X-ray diffraction	Generally minerals must be present at concentrations near 5 wt.% to be detected; various sample preparation techniques exist to concentrate and identify specific clay minerals; quantification can be achieved but is subject to many uncertainties
	Identification of minerals in aquifer solids	Thermogravimetric analysis	Can distinguish minerals, typically clays, that contain water from each other; some quantitative information
Bulk chemical composition	Elemental analysis of aquifer solid	X-ray fluorescence	Useful in conjunction with X-ray diffraction and thermogravimetric analysis to quantify mineralogy
Cation exchange capacity	Measures general adsorption capacity of aquifer solid	Various techniques that involving analyzing the amount of a common cation that adsorbs to a sample at a particular pH	Useful as a general indicator of adsorption capacity, but provides little information regarding specific contaminants
Microbiology	Physiological types and numbers, overall biomass, specific organisms	MPN analyses, cell counts, molecular tools, microcosms	Recommended only if a microbially mediated process is inferred to be relevant to the attenuation mechanism based on geochemical analyses

3. DECISION FRAMEWORK

3.1 Introduction to the Framework

MNA will likely be a component of the remediation strategy for groundwater plumes emanating from many waste units, including those with metal and radionuclide contamination. Since metals and radionuclides cannot be physically destroyed, their persistence in the environment leads to unique challenges and opportunities when evaluating and remediating sites with these contaminants. To foster efficiency in the evaluation process, a framework (Figure 3-1) has been developed to provide a logical process to incorporate collection of technically defensible data to support an evaluation of MNA as part of the characterization and monitoring of waste sites. As discussed in Section 2, some data used in an MNA evaluation are collected as part of the baseline characterization and ongoing monitoring of the waste unit, while other data are unique to understanding the attenuation of the contaminants present at the waste unit. The framework also introduces the concept of "transition" or "enhanced attenuation" technologies that are selected and designed based on the limitations identified during the MNA evaluation (see Section 3.16).

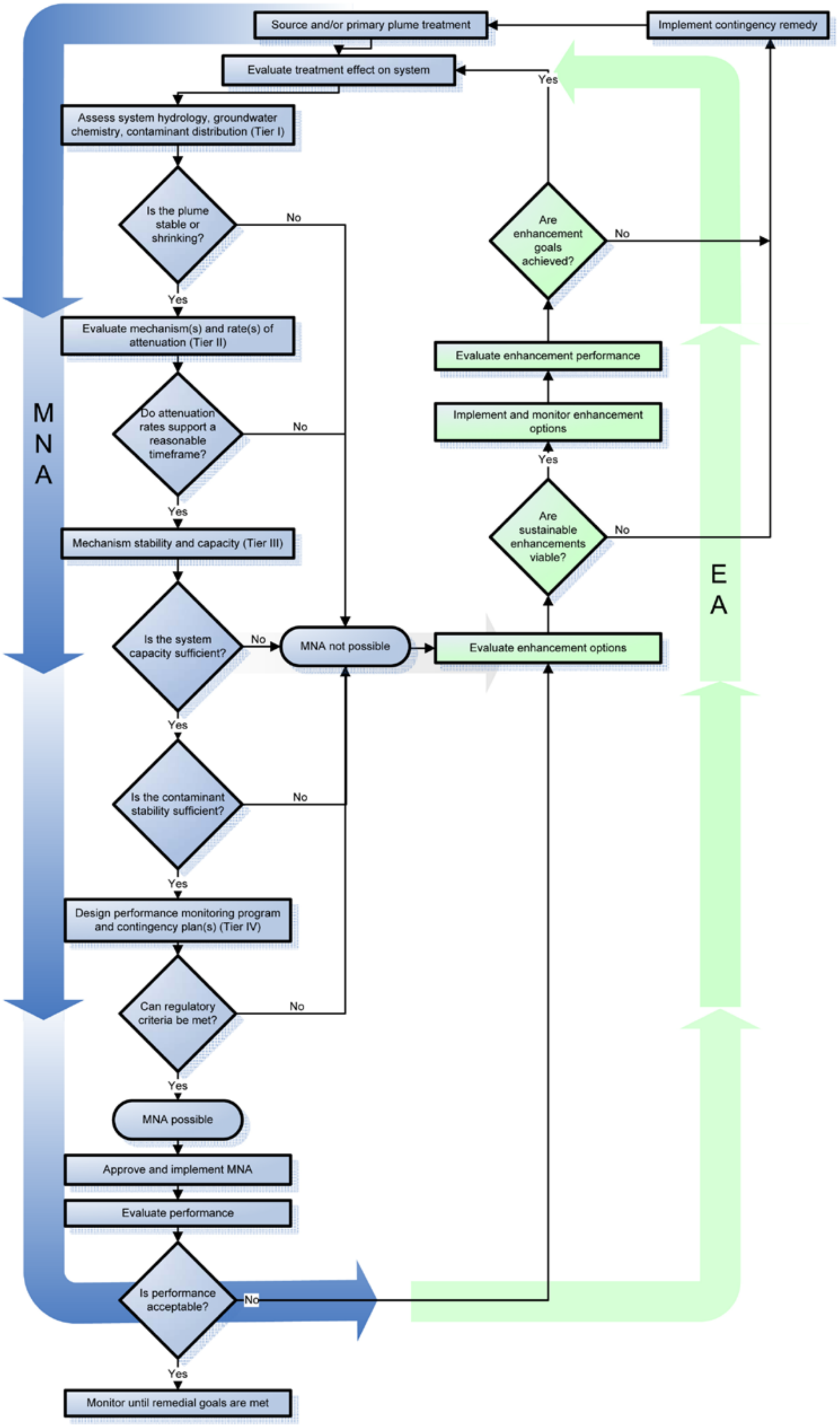


Figure 3-1. Decision framework for applying MNA to groundwater plumes contaminated with metals or radionuclides.

As established in Section 2.3.6, site-specific geochemical conditions determine the attenuation of metal and radionuclide contamination. Every remedial action implemented at a waste unit, be it removal or treatment, impacts the geochemistry of that unit and thus impacts the fate and transport of the remaining contaminants. In other words, actions at one point in the system have effects on other points in the system. This framework supports the evaluation of a contaminant plume as a system—a single entity—rather than individual disparate entities. By evaluating the plume in this manner, treatment trains or remedy combinations can be developed that work synergistically to facilitate reaching remedial goals. A process that provides an approach that combines technologies in a way that maximizes natural attenuation mechanisms will enhance cleanup of metal- and radionuclide-contaminated sites.

3.2 Key Feature/Factors When Using the Framework

Section 2 of this document summarizes the technical background provided in EPA's three-volume MNA set (EPA 2007a, 2007b). It further describes a tiered approach to evaluating the applicability of MNA to inorganic- and radionuclide-contaminated plumes. The framework in Figure 3-1 provides logic for integrating this tiered process into the remediation process and for transitioning from energy-intensive (labor, materials, costs) remediation technologies to attenuation-based approaches (MNA and EA). When working through the framework, each part must be considered sequentially, but extensive work or additional data are not always required. For example, much of the data required for Tier I are the traditional data collected to delineate contaminant plumes and in many cases already exist. The primary objective of progressing through the tiered evaluation steps is to reduce uncertainty in remedy selection.

Successfully working through the MNA framework and meeting remedial goals is often an iterative process. The tiered analysis process provides a means of organizing the data collection effort in a cost-effective manner that provides the ability to eliminate sites at intermediate stages of the site characterization effort. The framework can be exited at any time in the remediation process, and thus the point of exit is based on where one is within the process. For example, if the use of a source treatment allows the identified remedial goals to be met, then there is no reason to continue working through the framework and evaluating all the steps. One can also enter the framework at any time in the remediation process, assuming sufficient characterization has been conducted to indicate whether contamination is present at a level that requires action.

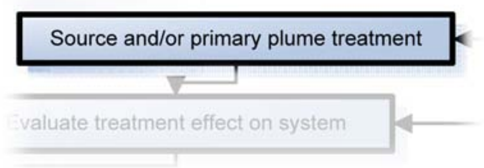
It should be kept in mind that at sites with multiple contaminants, MNA may be appropriate for some contaminants but not for others. An EA technology that will sustainably stabilize or detoxify one metal or radionuclide contaminant may not produce the same result in another metal or radionuclide. It is also possible that a remediation technology/approach for addressing one contaminant may have an adverse impact on another.

Contingency plans are referred to in two specific locations in the decision framework (Tier IV box along the MNA path and in a separate box in the upper right corner of the framework). However, contingency plans, whether informal or formal, should be available at each step in the process. For purposes of this document, a contingency plan is defined as a course of action to be followed if a preferred plan fails or an existing situation changes. The two specific references to contingency plans are discussed later in this section.

The following sections expand on each of the steps in the decision framework. The description works the MNA evaluation process (blue polygons along left side of the decision framework) and then moves to the EA evaluation process (green polygons along right side of the decision framework).

As each site is unique in both its subsurface properties as well as the contaminants that must be addressed, the guidance provided addresses key factors that should be considered for sites with metal and/or radionuclide contamination. There are many good references on how to collect and analyze samples, identify and understand key processes related to specific contaminants, design a variety of treatment systems, etc., and they will not be reiterated here.

3.3 Source and/or Primary Plume Treatment

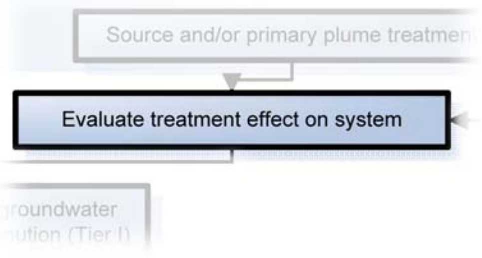


Essentially all regulatory guidance recommends, and regulators require, source/primary plume treatment. Specific to sites where MNA is being considered, the EPA states, "Control of source materials is the most effective means of ensuring the timely attainment of remediation objectives. EPA, therefore, expects that source control measures will be evaluated for all contaminated sites and that source control measures will be taken at most sites where practicable. At many sites it will be appropriate to implement source control measures during the initial stages of site remediation ("phased remedial approach") while collecting additional data to determine the most appropriate groundwater remedy" (EPA 1999). Appropriate actions may include removal actions, hydraulic control (e.g., caps, containment walls, and recirculation systems), and stabilization techniques to provide for long-term stabilization of contaminants. Both source and primary plume treatments are engineered and therefore are not part of the MNA process.

Because the framework is iterative, sources may be primary and secondary. In simple terms the primary source may be thought of as the original deposition of contaminated material. For mobile contaminants that are transported from the original source downgradient into a zone/environment that is conducive for immobilization, a new source may be formed—a secondary source. Thus, in repeated passes through the decision framework, the source being addressed may or may not be the original source.

Another twist on identification of a source involves radionuclides. For some radionuclides the secondary source may be a daughter product rather than the parent radionuclide. Depending on toxicity, the secondary source may be a greater issue than the original source.

3.4 Evaluate Treatment Effect on System



The traditional approach to evaluating treatment performance is focused on effectiveness of removal of contaminant (e.g., permeable reactive barriers [PRBs] or pump and treat) or effectiveness in limiting release of contaminant (e.g., caps). While important to the efficient operation of the treatment, the evaluation must be expanded when including attenuation-based remedies as part of the overall treatment process. As stated previously, attenuation-based remedies for metals and radionuclides generally focus on approaches that provide for long-term immobilization of the contaminants. Thus, the impact of the source and primary plume treatment on the overall system is paramount to facilitating conditions that support the long-term immobilization of the contaminants. In general, when the treatment moves the system in the direction of its natural biogeochemical evolution, it favors the long-term viability of attenuation-based remedies. The direction of natural biogeochemical evolution is always towards that of preplume conditions. For example, the pH of acidic or highly alkaline plumes eventually evolve toward the preplume pH by reactions with aquifer minerals and dilution. For contaminants that are less mobile at natural pH, treatment of an acidic or highly alkaline source that adjusts pH toward the natural tends to favor the long-term stability of the contaminants.

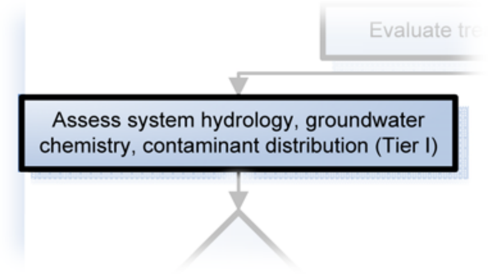
In addition to measuring effectiveness of removing contaminants or limiting their release, waste site remediation system evaluation should include the development of a decision process/strategy to identify when it is appropriate to turn off the source treatment and transition to and implement attenuation-based remedies and/or add an attenuation-based remedy to another portion of the system while the source treatment is operating. The point in time when it is appropriate to turn off the source treatment is when it is certain that post-treatment evolution of the waste site will not remobilize the stabilized contaminants. Thus, the system evaluation must include the information necessary to understand this evolution. The evolution depends on hydrology of the system, so the effect of the treatment on hydrology must be evaluated. The spatial and temporal variation of commonly obtained parameters—pH, bulk groundwater chemistry, and redox state—before and during treatment is also required to understand the overall waste site evolution. Additionally, mineralogical changes in the aquifer induced by the treatment must be known. Relatively passive source treatments such as capping are not likely to induce significant mineralogical changes in the aquifer. On the other hand, vigorous treatments such as reductive technologies do induce significant changes. Only by knowing the type of mineralogical change and its extent can the effect of the treatment on waste site evolution be determined.

If the treatment is primarily addressing the original source of the contamination—a basin, pond, landfill, etc.—it is important to understand the nature of that source. Waste release from landfill debris is different from waste release from solutions disposed in a basin. Likewise, the predominant chemistry of the waste should be understood because it will affect the waste release and subsequent migration.

When selecting an action that results in contaminated media being disposed of on land, an additional factor enters into the evaluation process. Because many of these contaminants are not destroyed (for this discussion, long-lived radionuclides will be considered not destroyed), risk transfer should be included in the evaluation of the overall impact of the action. This type of evaluation is identified in 42 U.S.C. 9621(b)(1)(A), “the long-term uncertainties associated with land disposal, and 42 U.S.C. 9621(b)(1)(G), “the potential threat to human health and the environment associated with excavation, transportation, and redisposal, or containment.”

3.5 Assess System Hydrology, Groundwater Chemistry, and Contaminant Distribution (EPA Tier I)

EPA (2007a) describes data collection and evaluation in this tier structure for the "Demonstration that the groundwater plume is not expanding and that sorption of the contaminant onto aquifer solids is occurring where immobilization is the predominant attenuation process." Another way to think about this tier is that the data collected and evaluated form the basis for the CSM for the contaminant plume system. Thus, these data should do the following:



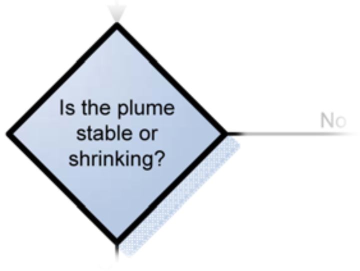
- delineate contaminant distribution
- define the hydrology of the system
- be sufficient to incorporate the evolution of biogeochemical conditions into CSM

The first two objectives are usually achieved by direct sampling of groundwater and aquifer material in monitoring wells and cored material. In addition, it is important to sample surface water that may receive groundwater discharges. These measurements provide the basis for determining contaminant distribution and are essential for understanding overall waste site evolution. Water levels obtained from the monitoring wells and stream base flows provide the basis for understanding the hydrology, which is essential to understanding contaminant distribution and overall waste site evolution.

As any sizeable contaminant plume is heterogeneous from both hydrogeologic and biogeochemical perspectives, it is important to have a basic understanding of those features controlling the contaminant plume system. Depositional processes cause sediments to be deposited in distinct volumes that have different hydrological and geochemical properties from one another. An aquifer is composed of groups of these volumes that may be as simple as a volume of sand in a layer with a few interspersed clayey lens volumes. Other aquifers may be much more complicated. However, it is important to recognize that the volumes that make up aquifer heterogeneity are not randomly distributed, but rather are controlled by the depositional environment of the aquifer lithology. Thus, maximum use of geologic knowledge in constructing the CSM helps in understanding heterogeneity. The important things to know are the relative number of volumes with distinct properties, their sizes, and their hydrological and geochemical properties. This technical knowledge, when integrated with regulatory and political factors, influence the approach taken as the evaluation of the system proceeds.

3.6 Is the Plume Stable or Shrinking?

After sufficient data have been obtained from the Tier I analysis, these data are analyzed to determine whether the contaminant plume is stable or shrinking. Most regulatory agencies consider a stable or shrinking plume to be the critical line of evidence for determining whether MNA is appropriate.



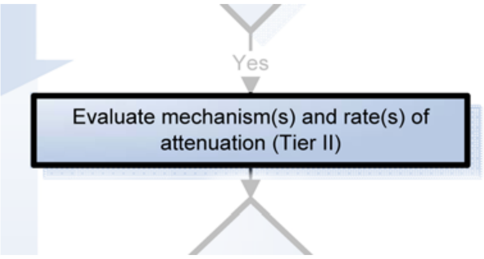
The OSWER directive on MNA (EPA 1999) indicates that sites where the contaminant plumes are no longer increasing in extent or are shrinking are the most appropriate for MNA remedies.

When there is a single contaminant, the analysis of plume stability is relatively straightforward, though not necessarily simple. Contaminant plumes that display stable or shrinking boundaries are most appropriate for consideration for MNA as a component of a groundwater remedy. Deviations from this criterion could potentially be considered for sites where knowledge of measured plume and aquifer characteristics provide a sound technical justification for attenuation downgradient of the existing plume. As an example, it is feasible that site conditions may be encountered where attenuation predominantly occurs at the plume leading edge or farther down gradient due to changes in groundwater chemistry.

For sites with plumes of multiple contaminants, answering this question may be complex. It is possible that in plumes with multiple contaminants, some contaminants may be stable and shrinking while others are not. This situation does not preclude an MNA remedy for select contaminants and an engineered (EA) remedy for others. The answer entails an evaluation with more complexities.

A “yes” answer indicates that the evaluation should continue based on the EPA tiered process. A “no” answer in this decision diamond indicates that additional engineered options should be evaluated through an EA evaluation process. This evaluation would be focused on the addition of a technology to reduce loading of contaminants from the source or a technology that would increase attenuation capacity within the plume that would be combined with the existing or a modified source treatment. The emphasis of the evaluation is to identify a combination of technologies that will support a stable and shrinking contaminant plume.

3.7 Evaluate Mechanism(s) and Rate(s) of Attenuation (EPA Tier II)

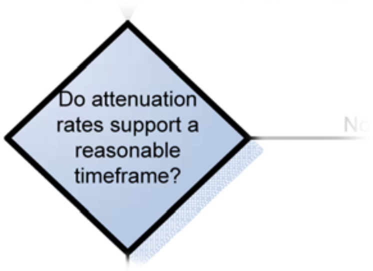


According to EPA (2007a), the purpose of Tier II data collection and evaluation is to “indicate whether MNA processes are capable of achieving remediation objectives, based on current geochemical conditions at the site. This data collection effort would also be designed to support identification of the specific mechanism(s) controlling contaminant attenuation.” Tier II emphasizes current conditions and attenuation based on those conditions. This step essentially identifies baseline attenuation conditions and continues the process of building a technically defensible CSM for the system. Thus, these data should do the following:

- delineate biogeochemical gradients
- organize contaminants based on controlling geochemical parameters
- identify the attenuation mechanisms controlling contaminant attenuation

While Tier I data needs are typical of most environmental investigations, Tier II data needs may be unfamiliar to many investigators. These data sets may include nonroutine groundwater chemistry parameters (e.g., mineralogy, major cations and anions in groundwater, etc.), soil samples to evaluate the presence of reactive soil minerals that will affect immobilization, and soil samples to measure immobilized contaminants. Tables 2-5 and 2-6 identify analytical techniques of particular value in understanding metals and radionuclides in the subsurface.

3.8 Do Attenuation Rates Support a Reasonable Timeframe?

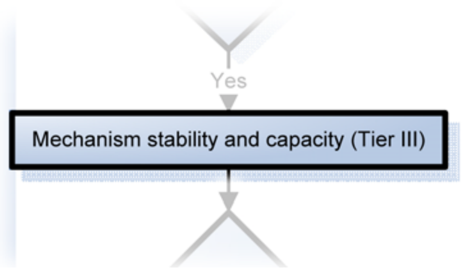


The attenuation rates being addressed by this question are the present day attenuation rates. When the biogeochemical conditions within the plume are different from the natural (precontaminant) conditions, the plume evolves toward those natural conditions affecting the attenuation rate(s) over time. Thus these rates are dynamic. If the system is unperturbed, the attenuation rates in many cases change slowly with time (hundreds to thousands of years).

The term *reasonable timeframe* is defined through an assessment of alternatives, including engineered active remediation and natural attenuation, with a comparison of the estimated timeframes to meet remedial end points. The natural attenuation timeframe must be comparable to active restoration, although allowance is made (EPA 1999) for the longer restoration timeframe required by the passive alternative as compared to more aggressive restoration alternatives. The decision on what is a reasonable timeframe rests with the decision makers for each individual site.

A “yes” answer to this question leads to the Tier III analysis. A “no” answer to this question leads to evaluating enhancement technology options. At this point, even though the attenuation mechanism does not support a reasonable timeframe, a strong attenuation mechanism(s) will have been identified that would support an enhancement. The contaminant plume system should be evaluated either prior to or as part of the enhancements evaluation to determine whether there is sufficient system capacity to result in long-term stability of the contaminant via the dominant attenuation mechanism.

3.9 Mechanism Stability and Capacity (EPA Tier III)

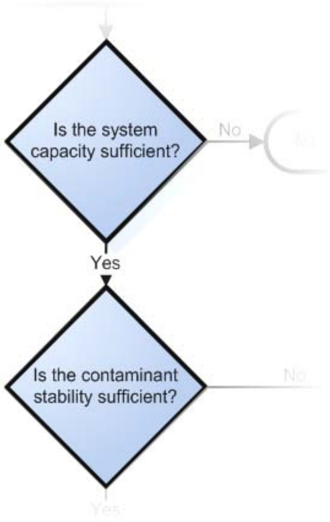


The objective of this tier is to “eliminate sites where site data and analysis show that there is insufficient capacity in the aquifer to attenuate the contaminant mass to groundwater concentrations that meet regulatory objectives or that the stability of the immobilized contaminant is insufficient to prevent remobilization due to future changes in ground-water chemistry.” (EPA 2007a). Similar to Tier II, data collected in this tier fill data gaps to continue the process of building a technically defensible CSM for the system. Thus, these data should provide evidence to support the near-term evolution of biogeochemical gradients affecting the site and an evaluation of the capacity of the system to attenuate the contaminants (system capacity).

A great challenge is evaluation of the long-term stability of these contaminants due to the dynamic nature of the subsurface environment and the long-lived nature of these contaminants. Institutional controls can aid in controlling human-induced impacts to the system. However, subsurface conditions, if no longer perturbed, return to natural conditions over time. By using knowledge of the natural conditions, the baseline attenuation mechanisms and rates in combination with knowledge of the system capacity, predictions of long-term stability of the contaminants can be made. It is important to consider that for multiple contaminant systems, the conditions that stabilize one or more contaminants may mobilize others.

3.10 Is the System Capacity Sufficient? Is the Contaminant Stability Sufficient?

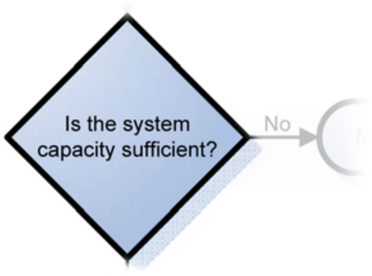
System capacity is based on the balance between contaminant mass moving through the aquifer as a function of time and the inherent ability of the system to alleviate the contaminant by various mechanisms. Hence, there is no fixed number for a high attenuation or low attenuation capacity because it is dependent on the mass of the contaminant. For metals and radionuclides, the dominant mechanism in most cases is immobilization. Under Tier II, the focus of data collection and evaluation was directed towards assessing whether the rate of the attenuation process(es) was sufficient to achieve the desired cleanup timeframe, with the *assumption* that sufficient capacity exists within the aquifer to attenuate the contaminants. Under Tier III, the data collection and evaluation process is directed towards verifying this assumption and confirming that sufficient capacity exits within aquifer.



A useful analogy is an advective transport breakthrough curve for a reactive constituent. It is possible that the evaluation process through Tier II may have been conducted during a time where reactive capacity exceeded the transported contaminant mass up to that point in time, thus preventing significant contaminant mass transport, i.e., prior to the rising limb of the breakthrough curve (attenuation is occurring—a mechanism is available). To determine that the attenuation capacity is sufficient and the contaminant will be stable for an agreed-upon timeframe (i.e., “breakthrough” will not occur at some monitoring location within the aquifer), one needs to verify that sufficient reactant mass is available within the aquifer. The Tier II evaluation provides a “snapshot” of how the system is (or has been) performing and the potential for performance into the future. Tier III assesses this potential.

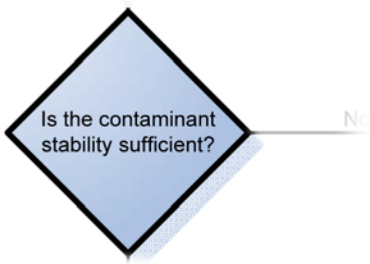
3.10.1 Is the System Capacity Sufficient?

A “yes” leads to an evaluation of the contaminant stability. A “no” leads to performing an evaluation of enhancement technology options. Even though the identified attenuation mechanism(s) do not support sufficient system capacity to balance or surpass the loading of the contaminants into the system, the introduction of an enhancement technology to the existing remediation system may result in the needed increase to the system capacity. In some cases this may be a straightforward



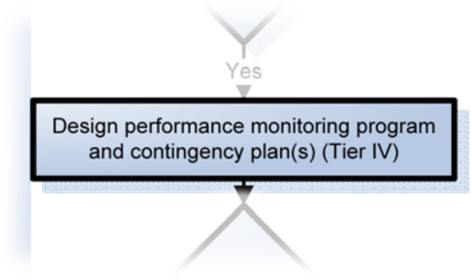
decision, as it is clear that the system capacity is insufficient. In those cases where it may not be straightforward, it may be worth evaluating enhancement options to determine whether a combination of remedies may yield a sufficient system capacity.

3.10.2 Is the Contaminant Stability Sufficient?



To proceed to this diamond, the system capacity has been identified as sufficient to attenuate the COCs. In this diamond the focus is on the long-term nature of that capacity. It is important that the attenuating mechanisms are strong enough and last long enough to allow the leading edge of the plume to shrink until the contaminant plume has dissipated. A "yes" response leads to the development of the performance monitoring program and contingency plan(s), as described in the first volume of EPA's three-volume MNA set (EPA 2007a). A "no" response leads to performing an evaluation of enhancement technology options. Even though there is not sufficient long-term stability of the attenuation capacity, the introduction of an enhancement technology to the existing remediation system may result in the needed long-term stability.

3.11 Design Performance Monitoring Program and Contingency Plan(s) (EPA Tier IV)



Section IC.4 of EPA's three-volume MNA set (EPA 2007a) provides an excellent summary-level discussion of the objective and approach to designing a performance monitoring program and contingency plans. EPA describes data collection and evaluation within this tiered approach as being structured to "[d]esign performance monitoring program based on the mechanistic understanding developed for the attenuation process, and establish a contingency plan tailored to site-specific characteristics."

There are several important considerations when developing a monitoring network to support an attenuation-based remedy. If an attenuation-based remedy is demonstrated to be a viable remedial option,

- contaminant concentrations should be at values approaching the remedial goals and contaminant flux, if evaluated, should be decreasing, and
- concentration and flux changes should occur more slowly than in source and primary source zones.

These conditions impact both the spacing of the monitoring points within the network, as well as the frequency of sampling.

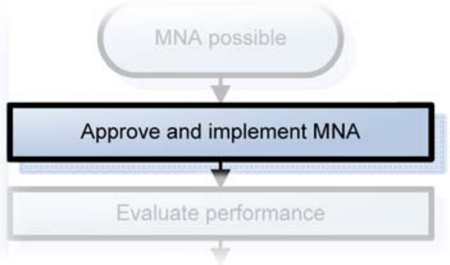
In addition, upgradient monitoring of biogeochemical conditions, such as pH and alkalinity, which have been identified as controlling factors in the attenuation processes, can provide early warning of changes to the more distal zone(s) in which attenuation-based remedies are being applied. This may be accomplished using existing monitoring networks supporting active treatments. Sampling frequencies in areas of active plume treatment may likely be at shorter intervals than in the downgradient zones where the attenuation-based remedies are in place. Early detection of a change to the system may mitigate the extent of the action(s) required to keep the system operating in a manner to reach the agreed-upon remedial goals.

Contingency plans are specific to the failure of MNA remedies due to unanticipated changes in site conditions, as described in EPA guidance on MNA for inorganics (EPA 2007a). For sites where treatment or remedies are added in a phased approach to address individual contaminants and/or different plume segments, contingency plans should be reviewed for continued applicability and, if need be, revised with each remedy addition or modification.

3.12 Can Regulatory Criteria Be Met?

At this point, the technical assessment is evaluated against applicable regulatory criteria. These criteria may differ depending on the regulatory program under which the site falls (e.g., CERCLA, Resource Conservation and Recovery Act [RCRA], state programs, etc.). While the analyses and decision steps above address many common regulatory criteria (e.g., compliance with applicable or relevant and appropriate requirements [ARARs], reasonableness of remedial timeframe, etc.), state or federal regulations may require explicit consideration of other criteria or analyses. Examples include risk assessment, cost/ benefit analysis, state and community acceptance, and specific state guidance and standards. Regulations may also require a comparison of MNA as a remedial approach against other alternatives, for example as prescribed and detailed by the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). Regulatory criteria that are not met for the site by MNA form the basis of criteria against which to evaluate the viability of enhancement options (see Section 3.17). Section 4 contains further discussion on this topic.

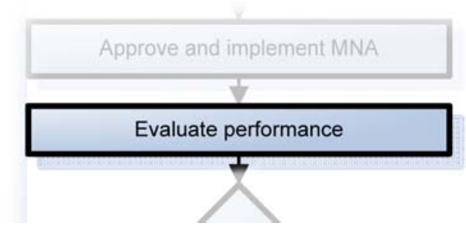
3.13 Approve and Implement MNA



If the previous five decision steps result in “yes” answers, then MNA is an appropriate remedy. This decision should be viewed as part of the total remedy and, in fact, may be implemented as part of a combination of several treatment technologies and/or enhancements implemented at various times and in various locations of the whole plume system.

An MNA remedy is approved and implemented based on technical evidence, as discussed in the EPA Tiers I–III, that system conditions exist such that the attenuation capacity is greater than the flux of the contaminants into the system at the present time and based on a reasonable projection of future conditions.

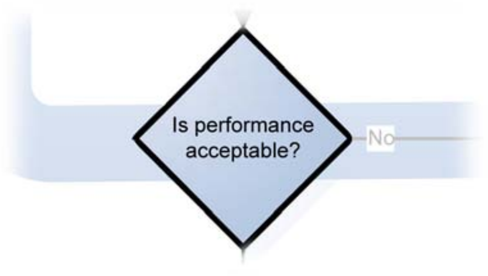
3.14 Evaluate Performance



Similar to sites contaminated with organic contaminants that are implementing MNA, it is important to monitor the system to ensure that the attenuation mechanisms identified as controlling the system will be sustainable over the time needed to have the plume diminish so that remediation goals are met and will remain below those values over time. A challenge with metal- and radionuclide-contaminated sites is that, in most cases, the contaminants are not destroyed but immobilized or detoxified, and this condition must be sustainable for timeframes of centuries to millennia. Understanding, through monitoring, the biogeochemical evolution of the system is important in evaluating performance. The knowledge gained in regards to understanding the controlling biogeochemical conditions from the investigations to evaluate Tiers I–III is the baseline for the performance evaluation.

Returning to the analogy presented in Section 3.10, the long-term system performance depends on the total contaminant mass that may need to be attenuated and on the extent that its release from source areas can be controlled. Information gathered in Tiers II and III is the input to developing the performance monitoring plan.

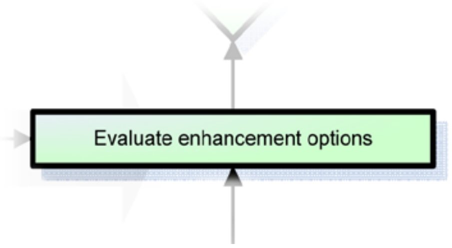
3.15 Is Performance Acceptable?



The long-lived nature of the majority of these contaminants does not typically mean that a "yes" answer indicates completion. An MNA remedy is approved and implemented based on technical evidence that the system conditions exist such that the attenuation capacity is greater than the flux of the contaminants into the system at the present time and based on a reasonable projection of future conditions. Acceptable performance indicates the system continues to operate within this "window" of acceptable conditions as indicated by the performance evaluation. Unacceptable performance means that conditions have changed and the system is no longer operating within that acceptable "window." Thus, contingencies (discussed in Section 3.21) need to be implemented.

A combination of decreasing contaminant concentrations and trends of decreasing contaminant flux from the source(s) through the distal portion of the plume(s) may be the ultimate best indicator of long-term acceptable performance. In most cases, maximum contaminant levels (MCLs) are the ultimate measure of success. The use of risk-based standards is becoming more common when it is impractical to reach MCLs. Decreasing concentrations or fluxes may be coupled with technical evidence that stabilized contaminants will not remobilize if subsurface biogeochemical conditions change.

3.16 Evaluate Enhancement Options



The framework incorporates the concept of EA that was defined by the ITRC Enhanced Attenuation: Chlorinated Organics Team and documented in *Enhanced Attenuation: Chlorinated Organics* (ITRC 2008b):

- "Enhanced Attenuation is a plume remediation strategy to achieve groundwater restoration goals by providing a 'bridge' between source-zone treatment and MNA and/or between MNA and slightly more aggressive methods."
- "EA is that 'bridge,' incorporating three important features: the evaluation of mass balance, defined as the relationship between mass loading and attenuation capacity of an aquifer, a decision framework that provides guidance for site decisions, and a toolbox of potential EA technologies (known as 'enhancements') that optimize aquifer conditions to provide a sustainable treatment or, at least, minimize the energy needed to reduce contaminant loading and/or increase the attenuation capacity of an aquifer."

As noted in the decision framework in Figure 3-1, multiple decision points could potentially bring the user to evaluating enhancement options. The process of evaluating enhanced attenuation options moves up the right side of the decision framework. Enhanced attenuation is defined as any type of intervention that might be implemented in a source-plume system to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention (ITRC 2008b). Enhanced attenuation is the result of applying an enhancement that sustainably manipulates a natural attenuation process. *Sustainability* in this context refers to the ability of a system to maintain attenuation mechanisms through time. Regardless of the sector of the plume (e.g. the source, aqueous plume, or dilute fringe) being remediated, the concepts of a mass balance and being able to increase attenuation capacity, reduce source loading, and/or increase stability are applicable.

Attenuation processes are targeted at specific species of metals and radionuclides of concern to human health or the environment. As a result, attenuation may not necessarily reduce the mobility of metals and radionuclides but may instead, for example, alter speciation to less toxic forms.

There are three classes of enhancements for metals and radionuclides, as shown in Figure 3-2. Typically, enhancements that reduce loading are implemented at the source. The source can be either a vadose zone or saturated zone source. Volumes that are considered "sources" tend to be small in dimension in comparison to the volume of the aqueous plume or the dilute/fringe portion of the plume. Reducing the source loading reduces the contaminant flux through the aquifer. Because mass flux is the product of groundwater flow and contaminant concentration, loading can be reduced by altering hydraulics to decrease the volumetric flow of water into or through the source or by decreasing the rate of contaminant transport from the source. Enhancements at the source may decrease loading to the degree that downgradient attenuation capacity can be sustained over the agreed-upon remediation timeframe.

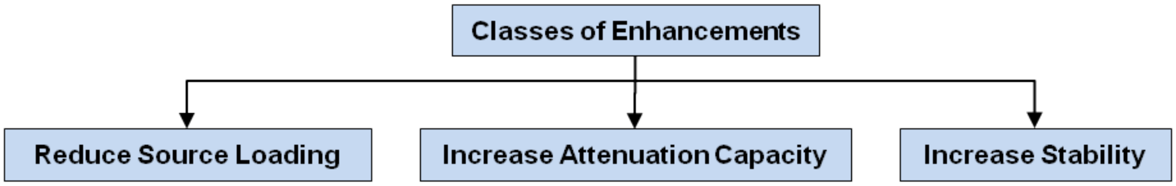


Figure 3-2. Classes of enhancements

The second and third classes of enhancements involve increasing attenuation capacity and/or increasing contaminant stability. Unlike attenuation of organic contaminants, for which degradation mechanisms are relevant and reliable, attenuation of metals and radionuclides, for the most part, relies on processes that decrease contaminant mobility or toxicity under current and future groundwater conditions. The second class of enhancements may increase capacity in the aquifer to attenuate contaminant mass to groundwater concentrations that meet objectives. This approach decreases the mass flux of contaminants coming from the source by increasing the ability of aquifer solids to remove contaminants from groundwater.

Specific to metals and radionuclides are the third class of enhancements that increase stability. Immobilized metals and radionuclides must be sufficiently stable to prevent remobilization due to future changes in groundwater chemistry. Future changes in groundwater chemistry could result in a release of a metal or radionuclide from aquifer solids due to desorption or dissolution of precipitates. Enhancement options that increase stability therefore include manipulation of geochemical factors influencing remobilization, such as pH, oxidation state, and alkalinity.

The evaluation of enhancement options includes the following steps:

1. Define the goals of enhancement.
2. Identify potential technologies for enhancing attenuation.
3. Evaluate the ability of the options to meet the stated goals.

The goals of the enhancement may or may not be the final remedial goals for the site. As indicated at the beginning of this section, EA may be used as a bridge between more aggressive technologies and MNA. The goal of EA may therefore be to increase attenuation capacity to the point where MNA is effective without enhancements, for example (see decision framework), or to implement a technology that will support the long-term stability of the existing sufficient attenuation capacity. In addition costs, low risk/toxicity, etc. may be important in the evaluation of enhancement technologies. Depending on site conditions, a variety of potential technologies exist for EA to reduce source loading, increase attenuation capacity, or increase stability. Figure 3-3 lists example technologies.

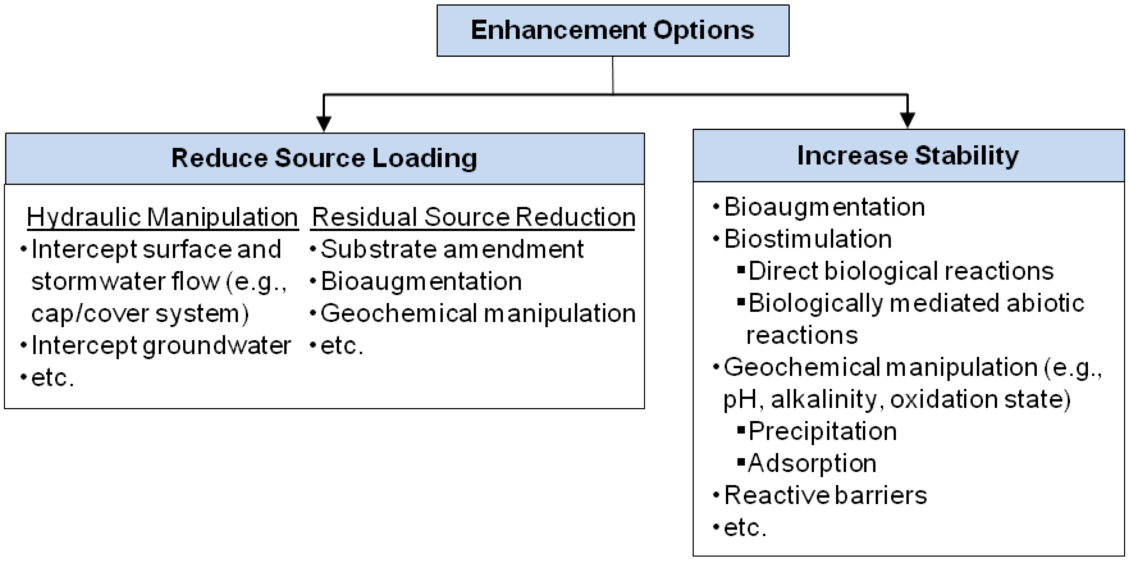
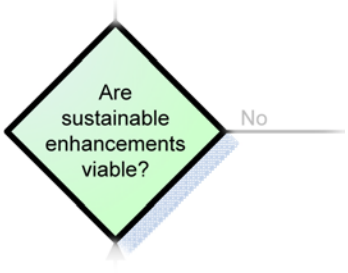


Figure 3-3. Examples of enhanced attenuation technologies for metals and radionuclides in the subsurface.

After potential enhancement technologies have been identified, their ability to meet the defined goals of enhancement is evaluated. This evaluation can rely analysis similar to those described earlier for Tiers II and III, depending on the specific goals of enhanced attenuation. For example, if the goal of enhancement is to increase the stability of the immobilized contaminant, additional bench-scale tests could be conducted to assess contaminant stability after simulated enhancements.

3.17 Are Sustainable Enhancements Viable?

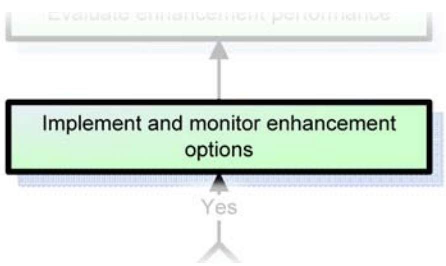


At this point, the technical assessment of potential enhancements options is evaluated against the goals for the enhancement (e.g., reduce contaminant loading from the source). For an enhancement to be viable, implementation of the technology will result in a change in the mass balance of the system, favoring attenuation of the contaminants and resulting in stabilization and ultimate shrinkage of the plume.

A “yes” response leads to implementing and monitoring the enhancement. This decision should be viewed as part of the total remedy and may in fact be implemented as part of a combination of several treatment technologies implemented at various times and in various locations of the whole plume/system.

A “no” response leads to reevaluation of the source and/or primary plume treatments, as neither MNA nor enhancements were deemed as capable or remediating the contaminant plume based on the existing conditions and available data.

3.18 Implement and Monitor the Enhancement(s)

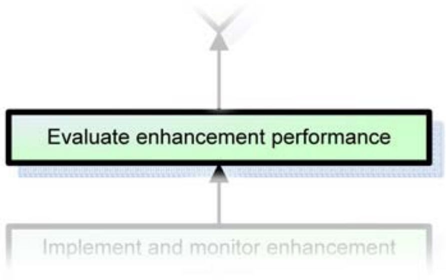


Though they are engineered treatments, enhancement technologies are implemented and monitored with an emphasis on the attenuation of the contaminants, reduction of mass flux, modification of the mass balance of the system, and long-term stabilization and ultimate shrinkage of the plume.

Both monitoring of the operation of the system and the long-term monitoring may include some elements of traditional active system monitoring. However, there must be elements related to the areas of emphasis mentioned in the previous paragraph. Otherwise it will be difficult to determine whether the enhancement is meeting the goals for which it was designed and when the enhancement is no longer needed, allowing the natural attenuation processes to take over until remediation goals are met.

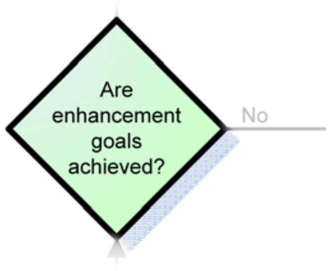
Monitoring must ensure that the enhanced attenuation mechanisms identified as controlling the system will be sustainable until enhancement goals are met (enhancement goals may or may not be remedial goals). As noted in Section 2, understanding the biogeochemical evolution of the system through monitoring is important to performance evaluation. Analyses similar to those employed in Tiers I–III assist in understanding the controlling biogeochemical variables of the system. These analyses act as the baseline for the performance evaluation.

3.19 Evaluate the Enhancement(s) Performance



The performance of the enhancement is evaluated against the enhancement goals, which are aimed at reducing contaminant loading to the system, increasing the attenuation capacity of the system, or increasing the stability of immobilized contaminants. The goals of the enhancement, as stated in previous sections, may or may not be the final remediation goals for the site.

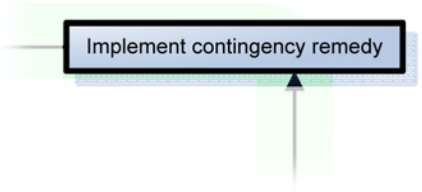
3.20 Are Enhancement Goals Achieved?



If enhancement performance is found insufficient to meet enhancement goals within the required timeframe, it may be necessary to implement contingencies prior to reevaluation of source and/or primary plume treatment measures to determine whether additional measures in this area are warranted.

If enhancement performance is determined to be sufficient to meet goals, the decision framework directs the user to “evaluate the treatment effect on the system.” In reality, this is a component of the evaluation of the enhancement performance.

3.21 Implement Contingency Remedy



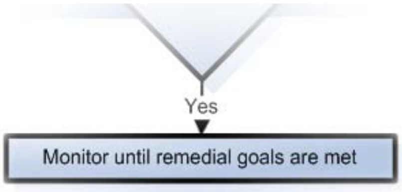
As defined in Section 3.2, a contingency plan is a course of action to be followed if a preferred plan fails or an existing situation changes. EPA describes a contingency remedy, plan or measure as "a cleanup approach specified in a remedy decision document that functions as a 'backup' remedy in the event that the 'selected' remedy fails to perform as anticipated" (EPA 2004b).

The contingency is implemented to keep the restoration of the contaminated groundwater progressing toward reaching the agreed-upon remediation goals. These contingencies may take various, site-specific forms. Examples of contingency action may include, but not be limited to, the following:

- optimization of source and or plume treatments
- implementation of an alternative EA technology (several reasonable options were identified during the original evaluation)
- initiate the process for evaluating a technical impracticability (TI) waiver

This last option is feasible only if compliance with ARARs is technically impracticable from an engineering perspective (40 Code of Federal Regulations [CFR] 300.430(f)(ii)(C)(3) and 42 U.S.C. 9621(d)(4)(C)), i.e., all viable options have been explored. As stated in a draft document by the ITRC Remediation Risk Management Team, "A TI waiver does not constitute an exit strategy that disregards the ARAR, but provides a protective alternative. A TI waiver is the requirement of an alternative strategy to (1) prevent further migration of the plume, (2) prevent exposure to the contaminated groundwater, and (3) evaluate further risk reductions."

3.22 Monitor Until Remedial Goals Are Met



This is the ultimate goal. Due to the fact that many of these contaminants are not degraded to innocuous end products but remain in their original state, reaching remedial goals will most likely take long periods of time. Long-lived databases will be a necessity to act as the repositories for the historical record of these sites. The historical record will provide the data needed to demonstrate the contaminant concentrations and contaminant fluxes have decreased both spatially and temporally.

3.23 Decision Framework Summary

The decision framework provides logic for integrating EPA's tiered process for MNA of inorganics (metals) and radionuclides into the remediation process and for transitioning from energy-intensive (labor, materials, costs, etc.) remediation technologies to attenuation-based approaches (EA and MNA). It also is intended to set forth a process that will produce CSMs that take a systems approach to remediating a site rather than a series of disparate parts. Metal and radionuclide sites, in particular, benefit from this approach because the contaminants, except for short-lived radionuclides, are not destroyed but remain in the system unless physically removed. Thus, actions taken in one sector of the contaminant plume (be it in the unsaturated or saturated zone) have an impact on contaminant fate and transport in downgradient sectors of the plume. Some sites, as documented in selected Appendix A case studies, have followed the logic process laid out in this section. The process depicted by the decision framework should facilitate investigations that will be conducted in a more timely and cost-efficient manner and will result in remediation technology choices that work in concert to restore groundwater to beneficial use.

4. REGULATORY PERSPECTIVES

The decision framework (Figure 3-1) asks the question, "Can Regulatory Criteria Be Met?" The answer requires first identifying which regulatory authorities might apply to a site. One goal of this document is to identify barriers to the use of MNA for metals and radionuclides and to determine which barriers are technical or regulatory and which may have resulted from a general lack of experience with attenuation processes. As stated in the National Research Council report (NRC 2000), "natural attenuation is an established remedy for only a few types of contaminants," which does not include metals and radionuclides. This statement is still largely true because MNA of metals and radionuclides was not considered an available remedy when many of the current regulations were written. However, federal and state regulations and guidance are now beginning to include some provisions pertinent to using MNA. This section provides an overview of state and federal regulatory systems with authority over MNA, summarizes current regulatory positions of federal and state regulatory agencies, and provides an overview of factors for regulatory acceptance, as well as perceived advantages and disadvantages.

4.1 Federal Policy and Guidance

4.1.1 U.S. Environmental Protection Agency

In 1980, Congress passed Public Law 96-510, also known as CERCLA. This act and subsequent reauthorization acts in 1986 and 1990 (i.e., Superfund Amendments and Reauthorization Act of 1986 [SARA] and the Omnibus Budget Reconciliation Act) provide statutory requirements for remediation of sites where hazardous substances have been released into the environment. All remedial actions at CERCLA sites must be protective of human health and the environment and comply with ARARs unless a waiver is justified. Cleanup levels for response actions under CERCLA are developed based on site-specific risk assessments and/or ARARs. The determination of whether a requirement is applicable or relevant and appropriate must be made on a site-specific basis (see 40 CFR §300.400(g)).

EPA expects to "return usable ground waters to their beneficial uses whenever practicable" (see 40 CFR §30 0.430(a)(1)(iii)(F)). In general, drinking water standards provide relevant and appropriate cleanup levels for groundwaters that are a current or potential source of drinking water. However, drinking water standards generally are not relevant and appropriate for groundwaters that are not a current or potential source of drinking water (see 55 FR 8732, March 8, 1990). Drinking water standards include federal MCLs and/or nonzero maximum contaminant level goals (MCLGs) established under the Safe Drinking Water Act (SDWA) or more stringent state drinking water standards. Other regulations may also be ARARs as provided in CERCLA §121(d)(2)(B). CERCLA and other regulatory authorities, particularly those pertaining to radiological contamination, are discussed in Section 2.3 of *Determining Cleanup Goals at Radioactively Contaminated Sites* (ITRC 2002).

The 1999 OSWER directive's (EPA 1999) definition of MNA identifies several physical, chemical, and 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. The directive goes on to state a preference for those processes, including biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical/biological stabilization, transformation or destruction of contaminants, that permanently degrade or destroy contaminants, and for use of MNA for stable or shrinking plumes.

The 1999 OSWER directive contains no specific applications of MNA as a remedial approach for inorganic contaminants. The key policy concerns are that the specific mechanisms responsible for attenuation of inorganic contaminants should be known to be occurring at a particular site and that the stability of the process should be evaluated and shown to be protective under anticipated changes in site conditions. The 1999 OSWER directive provides the context for EPA's expectations for evaluating the feasibility of employing MNA as part of a cleanup remedy for contaminated groundwater.

Different federal and state remedial programs may have somewhat different remedial objectives. For example, the CERCLA and RCRA corrective action programs generally require that remedial actions do the following:

- prevent exposure to groundwater contaminated above acceptable risk levels
- minimize further migration of the plume
- minimize further migration of contaminants from source materials
- restore groundwater conditions to cleanup levels appropriate for current or future beneficial uses, to the extent practicable

Achieving such objectives could often require that MNA be used in conjunction with other "active" remedial methods. For other cleanup programs, remedial objectives may be focused on preventing exposures above acceptable levels. It is therefore important to be aware of federal and state statutory and regulatory requirements, as well as policy considerations that apply to specific sites.

Technical information in EPA's three-volume MNA set (EPA 2007a, 2007b) can be used as a point of reference to evaluate whether MNA by itself, or in conjunction with other remedial technologies, is sufficient to achieve site-specific remedial objectives. This three-volume MNA set is discussed in Section 2, and it serves as a technical background document for EPA's new policy on MNA of metals and radionuclides.[5]

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[5] At this writing, EPA's new policy on MNA of metals and radionuclides is in development and not yet released. It is mentioned here to be used as a resource when it is released.

4.1.2 U.S. Department of Energy

While supporting the implementation of MNA as a remediation approach in appropriate settings, DOE has issued no policies, orders, or notices specifically addressing this topic. Three DOE guides include mention of MNA within the context of the topic of the document. In 1999, the DOE Office of Environmental Restoration issued to its facilities complex-wide two guidance documents to facilitate implementation of MNA at waste sites where it would be potentially viable. As characterization, monitoring, and decision-making tools, as well as enhancement/transition technologies advance, these two guidance documents remain timely in their approach to evaluating, selecting, and monitoring MNA remedies:

- *Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* (DOE 1999a) provides a decision-making framework for evaluating the efficacy of MNA as a remedial alternative consistent with applicable regulations and the EPA's OSWER Directive 9200.4-17P.

- *Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites* (DOE 1999b) provides technical direction on the role of monitoring for effective implementation of a natural attenuation remedy, key considerations for designing a natural attenuation monitoring network, and statistical approaches for interpreting data and refining CSMs. Important points made in this document are that review of monitoring data against the CSM is an ongoing iterative process and that defined contingency actions are a necessity for all MNA strategies.

The three DOE guides mentioned in the first paragraph of this section tie back to DOE Order 540.1A requiring all site contractors to comply with DOE Acquisition Regulation (DEAR) Clause 970.5204-2, "Laws, regulations, and DOE directives." Within this clause is stated, "In performing work under this contract, the contractor shall comply with the requirements of applicable Federal, State, and local laws and regulations…." DOE facilities that have identified soil and/or groundwater contamination are listed either as a facility (e.g., Savannah River Site) or as an individual waste unit (e.g., Hanford 100-Area) on the NPL. Thus, environmental waste site cleanup at DOE sites is regulated under RCRA or CERCLA. Unique to DOE facilities is disposal of radioactive materials. DOE Order 5820.2A establishes policies, guidelines, and minimum requirements for managing radioactive and mixed waste facilities. Similar to DOE Order 540.1A, the management of these facilities is to be protective to the groundwater in accordance to federal, state, and local laws and regulations.

DOE guides provide information that may be useful in implementing a specific DOE order and are not requirements. The three DOE guides are identified below, and the context in which MNA is discussed or identified is described.

- *Implementation Guide for Integrating Environmental Management Systems into Integrated Safety Management Systems* (DOE 2004b). "This document provides discretionary guidance for implementing the requirements of Department of Energy (DOE) order (O) 450.1, *Environmental Protection Program*, dated 1-15-03. DOE O 450.1 requires implementation of sound stewardship practices that are protective of the air, water, land, cultural and ecological resources impacted by DOE operations, and by which DOE meets or exceeds compliance with applicable environmental, public health and resource protection laws, regulations and DOE requirements in a cost-effective way. This objective is to be accomplished by implementing Environmental Management Systems (EMSs) as part of existing Integrated Safety Management Systems (ISMSs) established pursuant to DOE P 450.4 *Safety Management System Policy*, dated 10-25-96, at DOE facilities. This Guide provides suggested approaches for meeting the requirements of DOE O 450.1." MNA is mentioned in Appendix A, "Additional Guidance Documents," with two entries under "Ground Water Protection": *Final Directive on the Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (June 9, 1999) and *Monitored Natural Attenuation in Environmental Restoration* (February 17, 1999).

- *Ground Water Surveillance Monitoring Implementation Guide for Use with DOE O 450.1, Environmental Protection Program* (DOE 2004a). "The purpose of this guidance is to assist Department of Energy (DOE) sites in establishing and maintaining surveillance monitoring programs to detect future impacts on ground water resources from site operations, to track existing ground water contamination, and to assess the potential for exposing the general public to site releases." In this document MNA is used to provide context for examples related to monitoring network design. There is no specific language related to designing monitoring networks for MNA remedies.

- *Ground Water Protection Programs Implementation Guide for Use with DOE O 450.1, Environmental Protection Program* (DOE 2005). "The purpose of this Guide is to highlight the benefits, goals, and objectives of a successful site-wide ground water protection program (GWPP) that is consistent with the requirements for an environmental management system (EMS) in DOE O 450.1, *Environmental Protection Program*…. This Guide is a broad, comprehensive description of an effective GWPP which can be adapted to the site-specific issues." As in DOE G 450.1-6, MNA is used to provide context for examples related to developing an effective GWPP; there is no specific language related to developing a GWPP for remedies that include MNA. The guide does state, "[G]round water protection goals can be used as the basis for evaluating performance on monitored natural attenuation remedies."

4.1.3 U.S. Nuclear Regulatory Commission (NRC)

The NRC scope of responsibility includes regulation of commercial nuclear power reactors; nonpower research, test, and training reactors; fuel cycle facilities; medical, academic, and industrial uses of nuclear materials; and the transport, storage, and disposal of radioactive materials and waste. It derives its authority over the use of radioactive materials from the Atomic Energy Act (AEA) and the Energy Reorganization Act of 1974. The NRC has not developed a specific policy or guidance for applying MNA at sites covered by its regulations.

4.2 State Policies and Guidance

Different, and often multiple, divisions of state government may have jurisdiction over remedial efforts at different contaminated sites. In RCRA-authorized states, the RCRA-equivalent state regulations can be considered ARARs under CERCLA or may be applied directly. These state regulations apply in lieu of federal regulations, and while most state solid and hazardous waste regulations are based on the federal requirements, some states have developed regulations more stringent than the federal program. State regulations, therefore, include the basic list of RCRA metals but may also specify additional metals. States also develop and promulgate regulations and standards to protect groundwater and surface water from toxic levels of certain metals. These water regulations and standards are consistent with, and sometimes more stringent than, federal regulations in the Clean Water Act (CWA).

NRC relinquishes its AEA authority to a state once it has sufficient staff and resources, regulations, and a radiation protection program in place that meets NRC's compatibility requirements. Currently, 37 states have an agreement with NRC to assume that authority. Besides this AEA authority over certain classes of radioactive materials, most states have radiation control regulations for radiation sources other than those three classes (source, by-product and special nuclear material). The only exception is with the Uranium Mill Tailings Radiation Control Act of 1978 (UMTRCA) Title I Sites (inactive or abandoned uranium and thorium mills). NRC retains jurisdiction of Title I sites even in agreement states. EPA regulations for the UMTRCA program allow the use of "natural flushing" if a plume will meet standards in 100 years and institutional controls are in place to protect human health and the groundwater is not or is not expected to become a source of drinking water. This concept is similar to MNA. EPA standards for Title I sites are in 40 CFR 192, and natural flushing is described at 192.12(c)(2).

MNA of metals and radionuclides was not considered an available remedy when many of the current state regulations were written. In some cases, however, MNA seems to fit the intent of the existing regulations even if it is not specifically mentioned as a remedy. The following subsections discuss pertinent policies and guidance from several states. Appendix B provides links to additional resources.

4.2.1 Alaska

The Division of Spill Prevention and Response of the Alaska Department of Environmental Conservation (DEC) has developed guidance (Alaska DEC 2000) for evaluating and approving cleanup plans which incorporate natural attenuation as a remedy. The purpose of the guidance is to clarify its policy regarding the use of natural attenuation for the cleanup of contaminated soil and groundwater at sites regulated under the Alaska Administrative Code of Regulations (18 AAC 75 Article 3). The Alaska DEC considers natural attenuation to be one of many remedial options that may be effective, by itself or in combination with other remedies to clean up contaminated groundwater within a reasonable timeframe. Alaska DEC does not view natural attenuation to be a "no-action" remedy but rather considers it to be a means of addressing contamination under a limited set of site circumstances where its use meets the applicable regulatory requirements.

The guidance suggests that, "Natural attenuation should be selected only where it will be fully protective of human health, safety, welfare and the environment." Where natural attenuation's ability to meet these expectations is uncertain and based predominantly on predictive analyses, decision makers are encouraged to incorporate contingency measures into the remedy. Source control and performance monitoring must be fundamental components of any natural attenuation remedy. A site where natural attenuation is selected as a remedy receives a No Further Remedial

Action Planned letter. Long-term monitoring and institutional control are required, and site closure occurs only after cleanup levels for groundwater are met.

The following topics are all developed in this guidance:

- advantages and disadvantages of natural attenuation
- demonstrating the efficacy of natural attenuation through site characterization
- sites where monitored natural attenuation may be appropriate
- reasonableness of remediation timeframe
- performance monitoring
- contingency remedies
- decision documentation

Attenuation of metals and radionuclides is also specifically addressed. It emphasizes knowing what specific mechanism (type of sorption or redox reaction or radioactive decay) is responsible for the attenuation of inorganics because some mechanisms are more desirable than others. Determining the existence and demonstrating the irreversibility of these mechanisms are key components of a sufficiently protective natural attenuation remedy. Natural attenuation of inorganic contaminants is considered most applicable to sites where immobilization or radioactive decay is demonstrated to be in effect and the process/mechanism is irreversible.

4.2.2 Colorado

Colorado regulations do not specifically address natural attenuation; they also do not prevent applying MNA as a potential remedy. Typically, available federal policy and guidance are followed when Colorado regulations and guidance do not cover a specific situation or contaminant. As a RCRA-authorized state, Colorado can implement corrective action at facilities with releases of hazardous waste. A nonpresumptive remedy such as MNA will likely require additional investigations since the outcome is less certain (CDPHE 2002a).

Water in Colorado that is affected by sites contaminated by metals and radionuclides is generally required to meet specific state surface water and groundwater standards. Site-specific standards can also be established, often guided by ambient antidegradation principles. Of the various groundwater use classifications, “surface water quality protection” is the underlying default use.

In establishing default inorganic soil remedial objectives, the Colorado Department of Public Health and Environment (CDPHE) recognized that the fate and transport of inorganic constituents in the environment is controlled by complex chemical interactions, both in the soil column and the underlying aquifer (CDPHE 1997). These complex interactions make modeling the fate and transport of inorganic constituents highly site specific, compared with modeling the fate and transport of organic constituents. To develop remedial objectives that would be protective of all types of inorganically contaminated environments, a conservative approach was taken that did not consider the adsorption and transformation of inorganic constituents. By negating the effects of adsorption and transformation, transport models simply simulate the flushing and dilution of an “inert constituent” through the vadose zone to a monitoring well. All of the contaminant mass input to the column is partitioned to the water phase. The contaminant concentration in the leachate at the bottom of the vadose zone is divided by the contaminant concentration at the monitoring well, resulting in a "dilution factor" that can be used to calculate inorganic soil remedial objectives. Default inorganic remedial objectives were calculated by multiplying the groundwater standard for an inorganic constituent by 22 to obtain the remedial objective for that constituent in soil. If a facility does not agree with using this dilution factor for inorganics, the facility can propose other methodologies or site-specific calculations for review and approval by CDPHE.

In practice, especially at smaller sites, MNA has been accepted as a remedial option where it has been demonstrated that the plume is stable, concentrations are declining, and there are no risks of exposure. Internal guidance acknowledges, "[T]here may be circumstances where the extent and degree of on-site groundwater contamination does not warrant the continued collection and evaluation of groundwater data. Long-term monitoring of on-site groundwater that contains contamination in excess of established state standards may not be necessary if all of the following conditions are satisfied" (CDPHE 2002b):

- The source area has been successfully remediated and is no longer contributing to groundwater contamination that will exceed state standards.
- The groundwater contamination is of limited extent, and site conditions are such that it will have little to no opportunity to migrate laterally off site or vertically into deeper water-bearing zones.
- The contaminants are demonstrated to readily naturally attenuate and do so within reasonable timeframes.
- Data are available that clearly and convincingly demonstrate constituents are naturally attenuating.
- Several years worth of data is available showing a clear and consistent downward trend in contaminant concentrations.
- Data show the trend in contaminant concentrations will not be asymptotic and that the standards will be achieved in the near future.
- All of the above occur without having to operate and maintain active remediation systems.
- An environmental covenant is placed on the property to restrict the use of this contaminated groundwater and prohibit activities that may in some way change environmental conditions resulting in an expansion of the plume.

Where these circumstances exist, the expectation is that the residual contamination will drop below the state standards within a reasonable timeframe through natural processes without the aid of active systems. Environmental covenants between the facility and the state can ensure that exposures to contamination will be prevented by restricting groundwater uses where necessary, which adds a layer of assurance while MNA is ongoing. Removing the restrictions of an environmental covenant could eventually be justified with sufficient data.

Once plume stability has been demonstrated, generally with several years of monitoring data on a site with no known exposure pathways, monitoring may sometimes be discontinued even if concentrations remain above standards (within the site boundary). This practice has been applied at sites with groundwater contaminated with organic compounds, but there are no regulatory barriers that would prevent the same practice from being applied for metals and radionuclides.

4.2.3 Florida

Florida rules and policies do not specifically address MNA for metals and radionuclides. Metals and radionuclides are treated the same as other COCs, which is to say that they are addressed on a case-by-case evaluation. Remedial action plans, including those proposing MNA, are reviewed and approved based on site-specific conditions. Rule requirements for MNA can be found in Chapter 62-780.690, Florida Administrative Code.

Generally, Florida regulations follow the guidance of EPA Directive 9200.4-17 except that dilution is not included in the definition of natural attenuation and is not considered to be an acceptable mechanism for natural attenuation. The state has adopted natural attenuation default criteria (NADCs), which for metals and radionuclides equal 10 times the groundwater cleanup target levels (GCTLs). These are not standards, but guidance values. For groundwater contaminant concentrations less than the NADCs, MNA is considered an acceptable remedy as long as all applicable rule requirements are met. MNA is also allowed if contaminant concentrations are above the NADCs subject to demonstrating that MNA will be a successful strategy. Appendix B provides a link for a list of site-specific conditions and geochemical parameters that may be evaluated in an effort to demonstrate that MNA is a viable option. MNA is more often implemented after other remedial measures have been completed.

The required analytical data must be evaluated annually to verify progress of site rehabilitation by natural attenuation. If the annual rate of expected cleanup progress is not achieved, then the next submitted monitoring report must be signed and sealed by an appropriate registered professional and include a proposal to do one of the following:

- perform a supplemental site assessment and submit a supplemental Site Assessment Report
- continue the implementation of the approved Natural Attenuation with Monitoring Plan
- prepare and submit a Remedial Action Plan

4.2.4 New Jersey

The New Jersey Department of Environmental Protection has regulations to address natural groundwater remediation in the Department’s Technical Requirements for Site Remediation, N.J.A.C. 7:26E. Natural groundwater remediation is defined as any form of groundwater remediation where only degradation, retardation, and dispersion mechanisms are used to achieve applicable standards. For sites with active groundwater remediation, the definition also applies to portions of the plume that are not captured by the active groundwater remediation but are anticipated to be naturally remediated after separation from the source plume. Groundwater remediation proposals that include natural attenuation are evaluated on a case-by-case basis. When selecting the remedy for a site or area of concern, the remedial action needs to ensure protection of the public health and safety and the environment based on factors that include remedial goals and objectives, implementability, reliability, effectiveness, future site use, and surrounding land uses.

The regulations specify that natural remediation of free and/or residual product will not be allowed. For dissolved-phase contamination, natural groundwater remediation may be implemented if the department determines that active groundwater remediation is impracticable or not cost-effective. Such decisions are made on a case-by-case basis.

The person responsible for conducting the remediation is required to demonstrate to the department that groundwater contaminant concentrations will decrease to applicable remediation standards through degradation, retardation, or dispersion under present site conditions.

Pursuant to the regulation, specific site conditions are evaluated to determine the viability of natural remediation, including contaminant mass, as determined by free or residual product and dissolved-phase delineation and dissolved contaminant concentrations; dissolved oxygen content of groundwater; presence or absence of microorganisms in soil and groundwater; groundwater flow velocity; applicable physical and chemical characteristics of contaminants and contaminant degradation products present in both soil and groundwater; sorptive and desorptive characteristics of the soil; and other applicable physical and chemical characteristics of soil.

In addition, the regulations state the following:

- All soil contamination in the unsaturated zone has been or will be remediated to the applicable numeric soil remediation standard in accordance with a schedule approved by the department.
- Groundwater contamination has been delineated to the remediation standard applicable to the nearest downgradient receptor.
- groundwater contaminated above the applicable standard will not reach the nearest downgradient receptor, as estimated by an appropriate groundwater flow/contaminant transport model.
- The fate of the contaminant plume has been documented.
- Contaminant levels in groundwater do not present a vapor risk to any receptors.
- Predicted impacts to potential receptors are consistent with the current and potential groundwater uses based on a 25-year planning horizon as projected by local and county land-use documents.
- All necessary access agreements needed to monitor the groundwater quality have been obtained.
- A classification exception area shall be established for the area of the aquifer impacted by the migrating contaminant plume.

Monitoring and performance requirements for natural remediation are also specified in the technical requirements to monitor plume characteristics and movement, calibrate the model used to estimate the eventual extent of the plume, and assess the effectiveness of the natural groundwater remediation.

4.2.5 Tennessee

To date, Tennessee does not have an official position on MNA of inorganics (i.e., metals and radionuclides). Each site or situation is evaluated on a case-by-case basis. In general, MNA is evaluated based on an analysis of cost-effectiveness, technological feasibility, the nature of the threat or risk posed to human health and the environment, and the extent to which MNA would eliminate threats to human health and the environment. Further, MNA may be used in combination with other remedial actions to achieve water quality criteria. If the work is done under the Hazardous Waste Management Act Part 2, the four criteria mentioned above are required by Tennessee Code Annotated (TCA) 68-212-206(d).

4.2.6 Texas

The Texas Commission on Environmental Quality (TCEQ) employs a site cleanup remedy selection process that includes two remedy standards, one of which must be applied to the remedy chosen. The selected remedy must address both human health and ecological exposure concerns. Remedy Standard A is a "pollutant cleanup" standard that requires all affected media to be "decontaminated" or removed. Remedy Standard B is an "exposure prevention" standard that allows removal, decontamination, or control remedies to be selected. Either standard may be applied to the affected property. Additional information can be found in the Texas regulatory guidance document "Application of Remedy Standards A and B," RG-366/TRRP-28, available at www.tceq.state.tx.us/remediation/remguidance.html.

Texas Risk Reduction Program guidance on MNA ("Monitored Natural Attenuation Demonstrations," RG-366/TRRP-33, currently under revision) addresses only groundwater remediation but does not preclude the use of MNA for soil remediation. A number of decision trees are used to evaluate the appropriateness of MNA as a remedy. Acceptance of MNA as a decontamination or control remedy for an affected property is predicated on the rigorous evaluation of MNA lines of evidence. Three lines of evidence may be used:

- The primary line of evidence (PLOE) is based on historical groundwater data that demonstrate a clear trend of decreasing contaminant concentrations (for decontamination) or stable concentrations (for control) over time and distance.
- The secondary line of evidence (SLOE) extends the PLOE and is based on geochemical signatures or "footprints" in the groundwater that demonstrate the type of natural attenuation processes that are occurring. The SLOE also includes the calculation of site-specific biodegradation rates that may also be employed to estimate remediation timeframes.
- Other lines of evidence (OLOE) include predictive modeling studies or other laboratory/field studies that demonstrate an understanding of natural attenuation processes working at the site and their effectiveness in eliminating and/or controlling contaminant migration.

Decontamination by MNA is considered to be a permanent, destructive remedy such as biodegradation. Perceived decreases of dissolved metal concentrations (i.e., PLOE) are typically attributable to precipitation to a solid phase. However, since such reactions typically are thermodynamically reversible, the remedy is not considered to be permanently destructive, and MNA is not considered acceptable for metals decontamination.

While Texas rules and guidance do not specifically exclude metals from decontamination by MNA, the planned revision to the guidance will include a statement that explicitly cautions persons regarding the use of natural attenuation as a decontamination remedy for metals. However, proposals for the use of natural attenuation for metals decontamination in Texas are considered on a case-specific basis. TCEQ technical staff has developed acceptable methodologies to demonstrate whether or not metal sequestration is sufficiently permanent when using enhanced in situ techniques.

The TCEQ Remediation Division does not address radionuclides. However, in general, radioactive decay would fit into the SLOE (the determination of degradation rates). Since the decay constant (λ) of an isotope is known, that parameter could be used for modeling. The permanence of radionuclide transformations to the solid phase may be considered similarly to other metals.

4.2.7 Washington

Regulatory protocols used by the Department of Ecology for applying natural attenuation are located in the Washington Administrative Code under Expectation of Cleanup Alternatives in WAC 173-340-370 (7). Washington state expects that natural attenuation of hazardous substances (excluding radionuclides) may be appropriate at sites where the following apply:

- Source control (including removal and/or treatment of hazardous substances) has been conducted to the maximum extent practicable.
- Leaving contaminants on site during the restoration timeframe does not pose unacceptable threat to human health or the environment.
- There is evidence that natural biodegradation or chemical degradation is occurring and will continue to occur at a reasonable rate at the site.
- Appropriate monitoring requirements are conducted to ensure that the natural attenuation process is taking place and that human health and the environment are protected.

For radionuclides, the state follows federal cleanup standards.

Taking the above regulation into consideration, sites that contain metal or radionuclide contamination pose special problems for remediation by natural attenuation. Radionuclides are considered to be naturally attenuated if their interactions with soils result in transport times to possible receptors much greater than their radioactive half-life. Simply put, if the radionuclides are relatively immobile (through sorption processes or slow groundwater movement) and will not reach the accessible environment before they decay to a safe level, then natural attenuation may be a feasible remedial alternative.

Performance monitoring for natural attenuation is meant to track contaminant concentrations but may also include tracking those parameters, which serve as indicators of how well attenuation is working. The main purpose of detection monitoring is to establish whether attenuation mechanisms have failed to achieve the desired reduction in contaminant concentrations, thereby requiring the implementation of previously agreed-upon contingency measures. The detection monitoring system (sentinel wells) should be constructed somewhere between the downgradient edge of the plume and the nearest potential receptor. More specifically, sentinel wells should be sufficiently far from potential receptors so that contingency remedial actions, if required, can be effectively implemented. They should also be sufficiently far from the leading edge of the plume to account for the range of possible plume expansion based on the uncertainties evaluated within the conceptual model.

4.3 Regulatory Acceptability of MNA for Metals and Radionuclides

4.3.1 Survey of State Regulators

To determine the specific approach of this document, the APMR Team conducted a Web-based survey of state regulators and stakeholders to determine the existing state of knowledge and acceptance regarding the application of attenuation processes as a remedy at sites with groundwater contaminated with metals and/or radionuclides. Members of the APMR Team evaluated results from the survey (detailed findings are provided in Appendix C) and found that there appears to be a lack of knowledge with respect to the technical and regulatory aspects of attenuation for radionuclides. Further, responses to the survey suggested a greater level of uncertainty in understanding the importance of the various attenuation mechanisms associated with radionuclides than those associated with metals. However, respondents appeared comfortable with their knowledge associated with attenuation of metals and the importance of the various attenuation mechanisms. Survey findings also indicated a lack of governing policies and guidelines for evaluating the viability of attenuation-based remedies for sites with metals and/or radionuclide contamination. The APMR Team took these apparent competencies and deficiencies into consideration while developing this document and determining its scope and focus.

Through a short questionnaire sent to state regulators, the APMR Team also solicited information regarding how policies in various states apply MNA as a remedy. Regulators in 24 states responded to the seven questions. The information compiled from this questionnaire supplements the survey described above and is presented in Table 4-1. While some significant information could be compiled, the phrasing of a couple of the questions may have led to some ambiguity, which therefore limits the conclusions that can be reached.

All the responding states except Pennsylvania (96%) are “RCRA authorized.” Regulations in all but two of the states (Illinois and Maryland) allow MNA as a remedial option for organic constituents. MNA for cleanup of metals and radionuclides is allowed in all responding states except Arkansas, Illinois, Maryland, and Oregon. New York, for example, “does not have official (in writing) MNA guidance,” but for organics and some metals, “MNA remedies … are frequently selected on a case-by-case basis.” Of those four states where MNA of metals and radionuclides is not allowed, only Illinois will not allow MNA of metals or radionuclides, even on a case-by-case basis.

MNA has been applied explicitly or implicitly at sites with metal or radiological contamination in about 71% of the 24 states responding to the survey; MNA has not been specifically applied at such sites in seven of the responding states.

All states responding except Oregon and Wisconsin reported that they use MCLs for groundwater cleanups, though both those states also indicated that their groundwater standards are more stringent than MCLs. Nine other responding states (total of 42%) also have groundwater standards lower than MCLs. It is unclear, however, if respondents meant any standards are lower or only standards for metals or radionuclides. For instance, Wyoming does not have lower values for metals and radionuclides, but does for other constituents.

Table 4-1. State policies on applying MNA as a remedy (✓ indicates a positive response, x indicates a negative response)

State	AR	AZ	CO	CT	FL	GA	IL	IN	MD	MO	NJ	NY	OH	OK	OR	PA	SC	TN	UT	VA	VT	WA	WI	WY
1. Is your state RCRA authorized?	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	x	✓	✓	✓	✓	✓	✓	✓	✓
2. Do your state's regulations allow for the selection and implementation of monitored natural attenuation (MNA) as a remedy for organics (e.g., petroleum and/or solvents)?	✓	✓	✓	✓	✓	✓	x	✓	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
3. Do your state's regulations allow for the selection and implementation of MNA as a remedy for metals and/or radionuclides?	x	✓	✓	✓	✓	✓	x	✓	x	✓	✓	✓	✓	✓	x	✓	✓	✓	✓	✓	✓	✓	✓	✓
4. If your state does not have official guidance regarding the selection of MNA as a remedy for metals and/or radionuclide contamination, may the remedy be approved on a case-by-case basis? Leave blank if your state has official guidance regarding the selection of MNA as a remedy for metals and/or radionuclide contamination.	✓	✓	✓	✓		✓	x	✓		✓		✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
5. Has MNA been applied (either explicitly or implicitly) as a remedy at sites with metal and/or radionuclide contamination?	x	✓	x	✓	✓	✓	x	x	x	✓	x	✓	✓	✓	x	✓	✓	✓	✓	✓	✓	✓	✓	✓
6. In your state, are MCLs used for groundwater cleanup?	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	x	✓	✓	✓	✓	✓	✓	✓	x	✓
7. Are some of your state's groundwater standards lower (i.e., more stringent) than MCLs?	x	x	✓	✓	x	x	x	x	x	✓	✓	✓	x	x	✓	x	x	x	x	x	✓	✓	✓	x

4.3.2 Factors Affecting Regulatory Acceptability

MNA of metals and radionuclides in groundwater involves more complex and interdependent processes than does MNA of organic compounds; however, many of the factors that must be considered by regulators are the same. Most state and federal regulatory programs have incorporated MNA of organic compounds into their policies because practical experience and knowledge of the processes involved have reached a level where the perceived risk is tolerable. Regulatory acceptability of MNA of inorganics lags behind because a similar base of knowledge and practical experience has been lacking.

The list of factors that affect regulatory acceptability of MNA is based partly on the results of the survey of state regulators in Appendix C. Another source was a "consensus report" on the use of bioremediation for radionuclides and metals contamination, produced by a working group consisting of 11 regulators from 8 states, organized by Oregon State University (State Regulators Consensus Workshop 2005). State regulators on the APMR Team also added their perspectives.

In general, for MNA to be considered as a remedial option, regulators must have the following:

- confidence in the technology prior to full-scale application
- adequate site characterization
- an adequate performance monitoring plan
- a commitment to long-term stewardship

The following list of factors is not necessarily exhaustive; the factors do not constitute absolute requirements, are not listed in any particular order, and are not of equal importance in determining acceptability. The importance of each factor depends on site-specific environmental conditions, hydrogeology, land ownership, and current regulatory requirements. Information on each of these factors is provided in Section 2 and in EPA's three-volume MNA set (EPA 2007a, 2007b). Specifically, factors that might be considered while evaluating the acceptability of MNA as a remedy may include the following:

- Contaminant source material: Removal of source material is generally a prerequisite for consideration of MNA as a remedial option.
- Plume stability: Contaminant plume must be stable or shrinking.
- Monitoring duration: Conditions that allow shorter-term operations, surveillance, and monitoring favor MNA acceptability (e.g., radionuclides with shorter half-lives).
- Potential receptors: Sites where human or ecological receptors are currently impacted or where failure of a natural attenuation remedy might result in unacceptable exposure are typically not good candidates for MNA.
- Stability of end products under ambient conditions: Conditions where contaminants are incorporated into the mineral structure favor long-term stability.
- Certainty of site characteristics: The fewer assumptions or complex characteristics, the better.
- Availability of other remedies: MNA may not be the first choice if other viable and cost-effective remedies are available.

- Case studies: The existence of applicable successful case studies for the contaminants of concern helps to lower perceived risk but does not guarantee success.
- Remedy reviews: Periodic reviews are normally required for any remedy that does not meet free release (no-further-action) criteria.
- Contingencies: Contingency plans must be part of an MNA remedy decision in case of failure or deviation from expected results.
- Institutional controls: An MNA remedy should establish institutional controls sufficient to prevent unacceptable exposures during the period of remediation.
- Adequate hydrogeological and geochemical characterization.
- Monitoring program: Carefully designed monitoring programs match parameters to remediation objectives and focus on the direct contamination, contaminant indicators, or the conditions necessary for the desired reactions.
- Timeframe: Determining a reasonable timeframe for achieving and maintaining remedial goals for an attenuation-based remedy is a complex and site-specific decision. Establishing a generic time period that would be applied at all sites or facilities, therefore, is not appropriate. Factors that should be considered when evaluating the length of time appropriate for remediation include the following:
    - proximity of contamination to human and ecological receptors
    - current and potential use of the aquifer (e.g., state/federal classification)
    - current and future geochemical and hydrogeological conditions
    - magnitude, mobility, and toxicity of the contaminants
    - comparative timeframe for active remedial alternatives
    - reliability of institutional controls over long time periods
    - public acceptance of the extended time for remediation
    - uncertainties in all of the above

4.4 Advantages and Disadvantages of Natural Attenuation

The validity of MNA needs to be measured against all the requirements and potential disadvantages that should be considered during site characterization and evaluation of cleanup alternatives. These lists are modified from EPA’s OSWER Directive (EPA 1999) and Alaska DEC guidance (Alaska DEC 2000). From the perspective of regulators, these are the advantages and disadvantages of MNA.

Potential advantages of natural attenuation of metals and radionuclides include the following:

- as with any in situ process, generates smaller amounts of remediation wastes
- reduced potential for cross-media transfer of contaminants commonly associated with ex situ treatment
- reduced risk of human exposure to contaminated media
- less intrusion into the subsurface and fewer structures on the surface
- potential for application to all or part of a given site, depending on site conditions and cleanup objectives
- use in conjunction with, or as a follow-up to, other (active) remedial measures
- generally lower overall remediation costs than those associated with active remediation

Potential disadvantages of natural attenuation of metals and radionuclides include the following:

- Contaminants persist in the subsurface because, except for radioactive decay, they are not degraded by natural attenuation processes.
- Longer timeframes required to achieve remediation objectives may not meet regulatory requirements.
- Site characterization may be more complex and costly.
- Toxicity of transformation/daughter products may exceed that of the parent compound.
- Long-term monitoring will generally be necessary.
- Institutional controls may be necessary to ensure long-term protectiveness.
- Potential exists for continued contaminant migration and/or cross-media transfer of contaminants.
- Hydrologic and geochemical conditions amenable to natural attenuation are likely to change over time and could result in renewed mobility of previously stabilized contaminants (or naturally occurring metals), adversely impacting remedial effectiveness.
- More extensive education and outreach efforts may be required to gain public acceptance of an MNA remedy.

5. TRIBAL AND STAKEHOLDER ISSUES

This section primarily addresses the concerns of those tribal governments and stakeholders affected by sites that are candidates for restoration by attenuation. Stakeholders include people in communities living near contaminated facilities, site-specific advisory boards, local governments, and a variety of nongovernmental organizations. These concerns include community participation, long-term monitoring and maintenance, future use, health and safety, and specific tribal issues.

5.1 Community Participation

As noted in a National Research Council review (NRC 2000), there are important communication issues associated with proposing “natural attenuation” as a remediation option at a site, especially to nontechnical audiences. Many stakeholders may be concerned about attenuation-based remediation because it appears to be a “do-nothing” option or because of its long-term nature. Lessons learned from earlier attenuation projects along with the application of new technologies and procedures form the basis for the development of “supportable” (from the stakeholder perspective) projects using attenuation to remediate metals and radionuclides. Communication with stakeholders seeks to fill in gaps in understanding, reveal differences of opinion, and build a common view of the advantages and disadvantages presented by applying MNA.

Prior to beginning attenuation projects, the public must be fully informed of planned activities and potential consequences. Attenuation-based restoration projects, perhaps more than any other type of restoration, may require the community to coexist with some residual level of contamination for an extended period. Attenuation-based projects should always include communicating this temporal component.

A community relations plan similar to that required under CERCLA (EPA 2005) should be developed, and interested parties should be involved in the planning process. This process not only serves the purpose of keeping the public informed, but also provides guidance to communities about the timing of potential construction and transport of waste materials through populated areas. EPA believes that receiving new information and comments from the community is crucial and required by statute and regulations. In many instances, communities are able to provide valuable information on local history, citizen involvement, and site conditions.

It is important to consider the local culture in remediation decisions. Does any local population practice subsistence fishing? Do they consume shellfish or amphibian species that tend to accumulate metals and radionuclides?

Regulations covering environmental cleanup typically require certain levels of public involvement through advisory boards, public comment periods, and technical assistance. Under a CERCLA action, for example, the lead agency normally conducts community interviews and develops a community relations plan to help determine the community's level of interest in the site, its major concerns, and potential issues. The lead agency creates an information repository and administrative record for every site and makes it available to community members. The lead agency also typically develops a document specifically for the community, which explains the various cleanup options under consideration, holds at least one meeting to explain the options, and invites the community to submit comments on them. At Superfund or DOD sites, EPA or DOD also may make funding available to community members so they may obtain technical assistance to better understand the often complex issues. By identifying the public's concerns, EPA and the lead agency are able to fashion a response that is protective of human health and the environment and that more effectively addresses the community's concerns and needs.

DOE's national cleanup program includes consultation with a national Environmental Management Advisory Board as well as site-specific advisory boards. These boards provide advice and recommendations concerning environmental restoration, waste management, and technology development. Among the wide variety of topics addressed by the advisory boards are future use, risk management, appropriate cleanup levels, economic development, and budget prioritization. Advisory board membership reflects the diverse groups affected by DOE cleanup activities, such as local governments, tribal nations, environmental and civic groups, labor organizations, universities, and industry.

5.2 Long-Term Monitoring and Maintenance

Stakeholders may be concerned that attenuation-based restoration of radionuclide and metal contamination may require a more detailed characterization of the site or that attenuation will require extensive long-term monitoring to ensure public health and ecological parameters are met. Perhaps more than other environmental restoration techniques for metals and radionuclides, attenuation depends strongly on balancing relationships between the contaminated media and the geochemistry at a specific site—a dynamic stasis of sorts. Significant uncertainties in attenuation cleanup efficacy and timelines may conflict with stakeholder expectations. Consequently, stakeholders should receive additional communication of technical information, results of monitoring, and prognoses. As an important precept, the pertinent subsurface conditions must be documented and monitored efficiently and effectively for the life of the facility to ensure that contaminants are not moving. If monitoring indicates that contaminants are mobile in the environment, there must be a commitment by the responsible party that the remedy will be revisited and selection of attenuation will not hinder future investigations and consideration of other means to remove the contaminants.

Communities generally do not favor prolonged cleanup approaches with uncertain funding, with a commensurate degree of risk, and a shift of the burden for environmental cleanup to another generation. Thus, contaminant removal through conventional means (e.g., pump and treat) may be preferred unless it can be demonstrated that attenuation may produce an equal protection of the public health and the environment with an added cost-benefit. The public generally is not concerned with simply reducing the overall restoration costs but may be more concerned with removing the contamination quickly and gaining access to the land—or lifestyle—before the contamination occurred. Many factors must be considered when determining the restoration path, including the projected cost of ongoing surveillance and maintenance and agreements among the facility owners, tribal governments, state regulators, local community planners, and various stakeholders. In all cases, the process must have the goal of minimizing exposures to workers and the public, maximizing protection of the environment, and satisfying the concerns of the various stakeholders.

Stakeholders will also be concerned about what will happen if attenuation does not proceed at the projected rate. Stakeholders may expect that target contamination levels be set for future dates and for reassessment of the cleanup strategy if monitoring shows that targets are not being met by natural attenuation.

5.3 Future Use

The public should be full partners in future land-use decisions. Generally, the public favors site cleanup that leads to unrestricted use. Depending on the site-specific characteristics, attenuation-based restoration may require restricted access and/or institutional controls for a long period of time while the restoration proceeds. If unrestricted use is not possible, the smallest area possible should be set aside, and institutional and engineering controls should be incorporated into the activity. These should include a surveillance and monitoring system, and permanent markers should be developed for contaminated sites. If land use does lead to unrestricted use, a long-term stewardship program must be developed to ensure that the contaminants are reduced to acceptable levels or eliminated. If attenuation is selected, the site should be visibly marked and documented for long-term identification.

5.4 Health and Safety

During attenuation, the general public's exposure to contaminants should be negligible. Worker health and safety should also be positively affected. A related stakeholder concern is that the strictest cleanup standards be applied. Cleanup standards may differ from site to site based on risk assessments, site conditions, or state regulations; however, communities generally want to see the strictest standard that has previously been applied nationally. Communities often ask for cleanup standards that result in risk levels below 10^{-6} (i.e., no excess cancer risks greater than one in one million).

Establishing contaminant background levels is related to establishing cleanup levels. This can sometimes be very contentious since man-made contaminants that were produced or handled at these facilities often have few benchmarks with which to establish background levels. Lead agencies should expect that this may become an issue and be fully prepared to back up their decision.

Isolation of waste should be reliable and permanent, and contaminants should be stable and or stabilized to ensure immobilization. The immobilized contaminants should be able to withstand foreseeable environmental changes for the life of the contaminant.

5.5 Issues Specific to Tribes

There is no "one-size-fits-all" method for addressing tribal issues. Tribes are different from public stakeholder groups because tribes have government-to-government relationships with federal, state, and local governments, and this status must be respected. Each tribe is a unique entity culturally, governmentally, and socially. Thus, since a comprehensive discussion of tribal issues cannot be presented, this section provides general guidelines and issues pertaining to tribes.

There is no overarching "Native American" view or policy on natural attenuation. Tribes share many concerns with the dominant culture. However, tribes have further concerns specific to their own interests that may not be present in public stakeholder groups. Some tribes view any level of contamination of their land and natural and cultural resources as a grave insult. Many (if not all) tribes have areas that are culturally significant and even sacred. Examples of these may be springs, mountains, hunting areas, plant-gathering areas, or burial sites. Some tribes consider certain natural structures/features as a living being, to be protected and afforded all the rights of a human tribal member.

In situations that concern culturally significant/sacred areas, rules that nontribal environmental professionals rely on may be superseded. Seemingly ordinary flora and fauna may have tremendous cultural/religious importance to a tribe. Items of great significance may include birds and feathers, small game, large game, and flora (herbs, grasses, trees). These items may be used in ways that the dominant culture has not considered or valued and has not, as yet, added into standard risk assessment scenarios.

As to risk assessment, tribal pathways and lifeways are unique and different from the dominant culture, and tribal uses of natural materials are unique. Tribal risk assessment may not follow traditional models. There are often additional exposure pathways not adequately accounted for in traditional models. Much of the pathway and exposure information may be proprietary and might not be shared beyond the tribe. Standard exposure pathways are reflective of the dominant culture and may not address all exposure pathways from traditional and cultural activities. For example, if there is radionuclide contamination of a body of water, the sweat lodge ritual may pose an inhalation risk that might be overlooked by site assessors who do not practice this ritual themselves.

Regarding the government-to-government relationship, some guidelines may ease and facilitate successful interaction and decisions. Consultation should occur early in the decision-making process and allow enough time for tribal meetings and decisions. Consultation should follow an approved tribal protocol or policy if one exists.

The issue of proprietary information is important. For example, data collected on tribal land may or may not be shared with any outside group. Even within a tribe, certain internal information may not be accessible by all tribal members due to inner society restrictions or traditions.

When interacting with tribes, keep in mind that political boundaries are a creation of the dominant culture; areas of tribal concerns may go beyond modern political boundaries to ancestral homelands. For example, the Los Alamos National Laboratory (LANL) in New Mexico sits entirely on the ancestral homeland of the Pueblo de San Ildefonso. Every activity of LANL affects the tribe, even those that do not reach the current political boundary. The same may be true of any tribe.

6. APPLYING MONITORED NATURAL ATTENUATION—HOW TO START

While this document seeks to begin to build the body of knowledge of attenuation processes and subsurface conditions to support assessment of MNA as a component of a remedial action, the idea of assessing metal and radionuclide groundwater plumes may seem daunting; thus, the question may still remain, “How do I begin?” The intent of this section is to use real-world examples to highlight how to begin an evaluation of a site using types of data with which many environmental technical personnel are familiar.

The discussion in Section 2 focuses on a basic understanding of the geochemical conditions of the subsurface, a necessity at any potential MNA site. The more complex a site, the greater the level of geochemical expertise required. However, using information that is typically collected during a site characterization effort provides much of the information to begin developing a robust CSM and begin evaluating whether MNA or EA is a viable option for a remedial site. This section looks at a few examples from field sites to highlight the concept of “start with what you know” within the context of real-world settings. These examples also provide evidence that the standard data set collected at many sites can yield invaluable information to make a reasonable initial assessment of whether MNA or EA is a potentially viable component of the remedy. These examples investigate natural attenuation using many of the principles set forth in the three-volume MNA set (EPA 2007a, 2007b) and discussed in this document, but the work in the examples precedes issue of the EPA guidances. The first two examples (sections 6.2 and 6.3) examine the attenuation of chromium and arsenic, respectively. The third example (section 6.4) highlights how an understanding of the conditions that will exist after the trailing gradient passes fostered development of a treatment approach that will support the long-term stabilization of a contaminant by creating those natural conditions.

Start with What You Know

- Nature of source
- Contaminant distribution
- Geochemical conditions of plume
- Background geochemical conditions
- Geological system
- General contaminant chemistry

Appendix A includes case studies from four sites. Three of the case studies (Monticello Mill Site, Hanford 300 Area, and the Lawrence Livermore Site) discuss investigations and decisions that include MNA as a component of the remedy. The fourth case study (F-Area Seepage Basins Groundwater Unit at the Savannah River Site) discusses an approach to remediation that incorporates the concept of EA through the use of engineered remedies. It should be noted that these sites are in the active stage of their remediation; cleanup goals have not been met. The Lawrence Livermore case study was written from the perspective of the public stakeholders, thus providing insight into some of the issues discussed in Section 5.

This section explores the following topics within the context of the examples and case studies:

- Background conditions—Conditions in the subsurface tend to return to predisturbed (natural) conditions or as close as possible. Metal and radionuclide treatments must work in concert and support this evolution of sites for sustainable attenuation of the contaminants (MNA or EA).
- Eh-pH relationships—The role of these key parameters in the attenuation and long-term sustainability of metals and radionuclides.
- Redox conditions—Their role in the attenuation and long-term sustainability of metals and radionuclides.
- Heterogeneities—Set the stage for the geochemical makeup of the site, which in turn controls the attenuation of the metals and radionuclides or lack thereof. Understanding key heterogeneities is instrumental in providing a representative evaluation of what is occurring on a site and in developing a defensible CSM.

6.1 Mother Nature Rules

If you push the rock uphill, it's likely to roll back down over you.

Whenever foreign material (a waste stream) is added to a system, the existing (natural) conditions are changed. Once that material is removed from the system, the predisturbed (natural) conditions try to reestablish themselves. As discussed in Section 2, the majority of metal species cannot be degraded, and they persist in the environment. The key is to ensure that natural processes have stabilized them or rendered them less toxic. Important in this effort is identifying and understanding the significance of the conditions after the trailing gradient passes through the waste site, as discussed in Section 2.1.6. These conditions define how the system behaves in the long term or until a disturbance occurring upgradient changes conditions.

6.1.1 Why is this important?

In the end, Mother Nature will rule. If the contaminants will be toxic or remain or become mobile once the trailing edge of the plume moves through the system, then attenuation is likely not a viable alternative, and source treatments and/or removal actions will be integral to successful remediation of the waste unit (source, vadose zone, and groundwater).

If the contaminants will be in a stable and/or less toxic form when the trailing gradient passes, then attenuation is a viable alternative. For treatment options that are based on changing subsurface conditions to stabilize contaminants, changing those conditions in opposition to the post-trailing gradient conditions will in many instances result in remobilization of the contaminants, prolonging the time needed to reach remediation goals. If the post-trailing gradient conditions promote stability and/or detoxification then "helping the rock roll downhill" will facilitate attenuation and reaching remediation goals in a timely manner. This is where EA technologies best serve the remediation process. It is feasible that treatment options that violate this idea will be long-lasting, but the burden of proof of longevity is much higher than if treatment options are consistent with the geochemical evolution of the site.

6.1.2 What geochemical information is most useful to begin an assessment?

One of the challenges is that the stabilization mechanisms are reversible for a large percentage of metals and radionuclides. Thus, the conditions after the trailing edge of the contaminant plume moves through the site must provide a stable environment for the contaminants. As described in Section 2.1.6, the trailing edge is created where the contaminant plume and uncontaminated upgradient groundwater come in contact. Easily obtained characteristics of the upgradient groundwater when combined with knowledge of the contaminants present in the plume can begin the process of developing a conceptual model of long-term contaminant stability and strategies to remediate those contaminants. It must be kept in mind that reactions between the contaminant plume and aquifer minerals may alter the aquifer mineralogy. Therefore, upgradient or background parameters controlled by mineralogy may not be representative of those within the post–trailing gradient waste-site compartments.

6.2 A Redox Gradient's Impact on Chromium Attenuation

Chromium is present naturally in groundwater as hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Hexavalent chromium has seen widespread industrial use, including the production of stainless steel, textile dyes, and anticorrosion coatings . While Cr(VI) is relatively mobile in the environment and acutely toxic, Cr(III) has a relatively low toxicity and is immobile at circum-neutral pH. Under this near-neutral pH condition, Cr(III) precipitates as a fairly insoluble hydroxide, making it relatively immobile within the soil column (EPA 1994, 2007b). Thus, successful attenuation of Cr(VI) is predicated on its reduction to Cr(III). There are several potential reductants of Cr(VI), including aqueous species, adsorbed ions, mineral constituents, and organic matter (EPA 1994). While this general information provides a good starting point for the Tier I and II analyses (summarized in Table 2-1 and Sections 3.5 and 3.7), the geochemistry of an aquifer, as discussed in Section 2.1, must be understood to fully evaluate the attenuation rates, stability, capacity, and thus the viability of MNA as a component of a successful remedial strategy. The following is an example of using traditional data types and analyses to support an initial (Tier I and II) evaluation of MNA followed by studies to support a Tier III evaluation.

Hellerich et al. (2003) and Hellerich and Nikolaidis (2005) evaluated the attenuation potential of a hexavalent chromium (Cr(VI)) groundwater plume at a site in southwestern Connecticut. The investigators used direct-push technology (Geoprobe™) to perform continuous water sampling and to collect soil samples along a transect consisting of three locations parallel to groundwater flow from the source to a tidally influenced river (Figure 6-1). The three points along the transect were selected based on results of a larger sampling of the waste site. The analyses provided in Table 6-1 is a subset of all analyses that directly relate to the evaluation of Cr(VI) attenuation. The results of the groundwater sampling indicate sharp redox gradients within the aquifer. The pH is circum-neutral (range 5.9–6.7). The data indicate attenuation of the Cr(VI) within the aquifer along the flowpath. At the time of the initial study the concentrations at point C, approximately 50 m from the receptor (river), are below the Connecticut Remediation Standards Regulations groundwater protection criteria of 50 µg/L and surface water protection criteria of 110 µg/L (Hellerich et al. 2003).

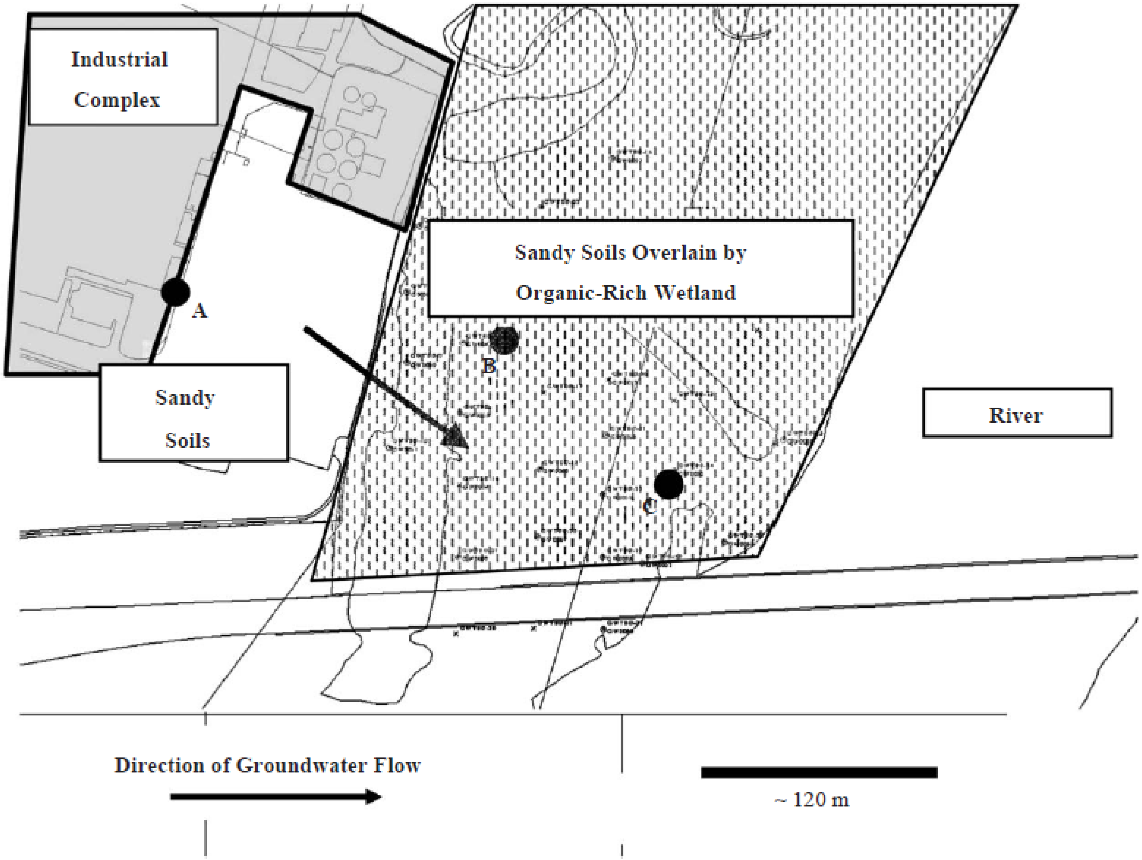

Figure 6-1. Plan view of Cr(VI)-contaminated site in southwestern Connecticut.
(*Source:* Hellerich and Nikolaidis 2005)

Table 6-1. Soil and groundwater chemical parameters used to directly support evaluation of hexavalent chromium attenuation

Aqueous chemical parameters	Soil chemical parameters
Fe(II), Cr(VI), Cr(total), SO_4^{2-}, S^{2-}, SO_3^{2-}, NO_3, CO_2, Eh, DO*, ORP*, pH*	Fraction of organic carbon, Cr(VI), Cr

* Field-measured groundwater quality parameters.

Hellerich et al. (2003) reported sharp redox gradients with respect to depth. In general, the shallower depths, which tended to have greater fractions of organic carbon, were more reducing. Oxidizing conditions became more prevalent with increasing depth. Also, conditions went from oxidizing to reducing along the length of the transect which corresponds with the transition from the sandy soils to the sandy soils overlain by the organic rich wetland sediments, as identified in Figure 6.1. These data support the general principle that, under reducing conditions, Cr(VI) is reduced to the more stable Cr(III) at near-neutral pH conditions. Using the available soil and groundwater data, soil oxidation and reduction capacities and aqueous reduction capacities were calculated for all samples collected along the transect. The aqueous reduction capacity increased by factors of 10 from points A to B to C, a function of the organic matter and ferrous iron. The soil oxidation capacity increased from points A to B but appeared to stabilize from B to C. Yet the soil reduction capacity was ~1.5 to 10 times greater than the soil oxidation capacity at points A and B, and this ratio increased to 3 to 10 times at point C (Hellerich et al. 2003). This information provides an assessment of the aquifer soil's potential reductive capacity, indicating a net potential for reduction exists in the wetland soils. In addition, first-order reduction rates were calculated for Cr(VI), indicating reduction rather than sorption as the likely attenuation process.

A follow-on study (Hellerich and Nikolaidis 2005) involved laboratory experiments to characterize and quantify the kinetics, capacity, and stability of the attenuation processes in the wetland zone. These researchers evaluated attenuation as a combination of sorption, reduction, precipitation, and complexation processes rather than differentiating the individual processes. Table 6-2 summarizes the estimated attenuation capacity of the soils for Cr(VI) with depth and the expected pH range for these soils.

Table 6-2. Estimated attenuation capacity as derived from laboratory Cr(VI) equilibrium attenuation capacity studies (*Source:* Hellerich and Nikolaidis 2005)

Sample location	Sample depth range (m)	pH	Estimated attenuation capacity (µg Cr(VI)/g soil)
Point A	11.0–12.2	4.07	150
		6.40	250
Point B	4.9–5.5	4.50	1000
		6.50	600
	5.5–6.1	4.40	300
		6.66	400
	6.1–7.3	4.50	125
		6.50	50
	7.3–8.5	4.33	120
		6.46	80
	9.8–11.0	4.34	150
		6.52	100
	14.6–15.8	4.40	80
		6.60	20
Point C	4.9–6.1	4.47	600
		6.54	350
	6.1–7.3	4.28	1000
		5.80	750
	7.3–8.5	4.50	400
		6.50	200
	9.811.0	4.72	500
		6.78	450

The trends in this data set are consistent with what would be expected based on organic carbon content of the soils and redox conditions. Data from point A is representative of the sandy source zone which has the highest oxidation reduction potential readings and low fraction organic carbon (Table 6-1). Data from Hellerich et al. (2003) reported high fraction organic carbon and reducing conditions in the upper zones at locations B and C trending at depth to low fraction organic carbon and oxidizing conditions. Within the pH range of this system, reducing conditions with high fraction organic carbon would be most favorable for attenuation of Cr(VI); thus, the higher attenuation capacities at the shallower depths in locations B and C. Table 6-3 provides a summary of the kinetic studies for the attenuation of Cr(VI). The trends in this data set are also consistent with the conditions favorable for Cr(VI) attenuation. The researchers (Hellerich and Nikolaidis 2005) concluded there is potential for chromium to remain immobile in the wetland soils because the high organic carbon content and relatively high distribution coefficients lead to relatively high attenuation capacities and rapid rates of attenuation in the soils. They also postulated that chromium remobilization is unlikely as long as the soil organic carbon provides adequate reducing power.

Lessons Highlighted and Translation to Other Sites

This example highlights the effect of redox gradients on the stabilization of Cr(VI) as controlled by Eh and fraction of organic carbon. Important to the long-term stabilization of the contaminants is maintaining the redox conditions and pH at this site. As described above, the pH is unlikely to change drastically. Factors that may be of importance long-term include stability of the wetland setting to maintain the reducing conditions and supply of organic carbon versus loading of Cr(VI). The first factor impacts the general conditions needed to support the reduction of Cr(VI) to the more stable Cr(III); the second addresses the capacity of the system to attenuate the entire mass of Cr(VI).

Though not presented in this example because it was not a major factor in the attenuation of the Cr(VI), the comingled chlorinated solvent plume is discussed in papers by Hellerich et al. (2003) and Hellerich and Nikolaidis (2005). The impact of competition for sorption sites and/or the impact on precipitation/coprecipitation must be considered for remedial sites with comingled contaminants. When these contaminants are organic in nature, an assessment should be made of the microbiological processes that occur and their impact on the geochemistry of the subsurface.

6.3 Taking Advantage of an Induced Redox Gradient to Evaluate Arsenic Attenuation

The former Ft. Devens military base located west of Boston, Massachusetts was listed as a Superfund site in 1989. Enhanced reductive dechlorination (ERD) was employed in one area (Area of Contamination 50) to degrade the chlorinated solvent contaminants. This demonstration and subsequently implemented remedy (EPA 2004a) produced temporary redox gradients via injection of the molasses as the source of organic carbon to create the reducing zone needed to stimulate microbial dechlorination. A research team led by scientists at the California Institute of Technology (He et al. 2010) investigated the behavior of naturally occurring arsenic (As) in the subsurface as impacted by the ERD. Unlike many metals, As becomes more mobile as it is reduced. Soil cores (gray open circles in Figure 6-2) and groundwater samples (SMW-1 through SMW-4, Figure 6-2) were collected along a transect parallel to groundwater flow that extended from upgradient of the treatment zone to a monitoring well downgradient of the treatment zone, where previously reported data indicated the least As contamination. The resulting data indicate that As, as well as iron (Fe) and manganese (Mn), concentrations were low in background/upgradient groundwater, as is consistent with regional aquifer groundwater quality data as indicated by the Cape Cod aquifer data (Table 6-4). Within the reductive zone, all three contaminants were mobilized.

Table 6-3. Summary of Cr(VI) kinetic attenuation studies (*Source:* Hellerich and Nikolaidis 2005)

Point	Depth range (m)	Soil foc (%)	Average aq. soil ratio (mL/g)	Initial pH	Final pH	Cr(VI) first-order bulk diss. rate k_1 (1/min)	RMSE (µg/L)	AC_{3h}		$AC_{1\ day}$		$AC_{7\ days}$	
								[µg Cr(VI)/ g soil]	%Cr(VI) attenuated	[µg Cr(VI)/ g soil]	%Cr(VI) attenuated	[µg Cr(VI)/ g soil]	%Cr(VI) attenuated
A	11.0–12.2	0.15	2	6.78	8.05	9.30E-06	548	0.02	0.2	0.1	1.2	1.2	11
B	4.9–5.5	4.04	1.7	6.78	6.57	5.60E-02	637	7.9	100	7.9	100	7.9	100
	5.5–6.1	0.38	1.7	6.78	7.91	1.30E-03	532	1.8	22	6.9	82	8.4	100
	6.1–7.3	0.07	1.7	6.78	7.83	1.30E-05	544	0.02	0.2	0.1	1.7	1.3	16
	7.3–8.5	0.11	1.8	6.78	8.07	1.60E-05	614	0.03	0.3	0.2	2.1	1.7	19
	9.8–11.0	0.29	1.0	6.78	0.82	3.20E-05	1366	0.03	0.6	0.2	4.1	1.7	34
	14.6–15.8	0.09	1.9	6.78	7.92	9.30E-05	507	0.02	0.2	0.1	1.2	1.1	11
C	4.9–6.1	0.39	2.3	6.78	7.81	2.20E-03	833	3.9	34	10.8	95	11.5	100
		0.39	5.0	7.24	6.82	8.50E-03	1498	-	-	-	-	-	-
		0.39	5.0	6.92	3.29	1.60E-01	13	-	-	-	-	-	-
	6.1–7.3	0.48	2.3	6.78	7.65	3.50E-03	418	5.6	49	11.4	99	11.5	100
		0.48	5.0	7.21	6.42	4.80E-03	1312	-	-	-	-	-	-
		0.48	5.0	6.83	3.65	1.20E-01	33	-	-	-	-	-	-
	7.3–8.5	0.22	1.0	6.78	7.01	6.90E-02	126	4.9	100	4.9	100	4.9	100
		0.22	5.0	7.29	6.75	6.90E-04	948	-	-	-	-	-	-
	9.8–11.0	0.44	1.7	6.78	7.00	2.80E-01	174	8.6	100	8.6	100	8.6	100

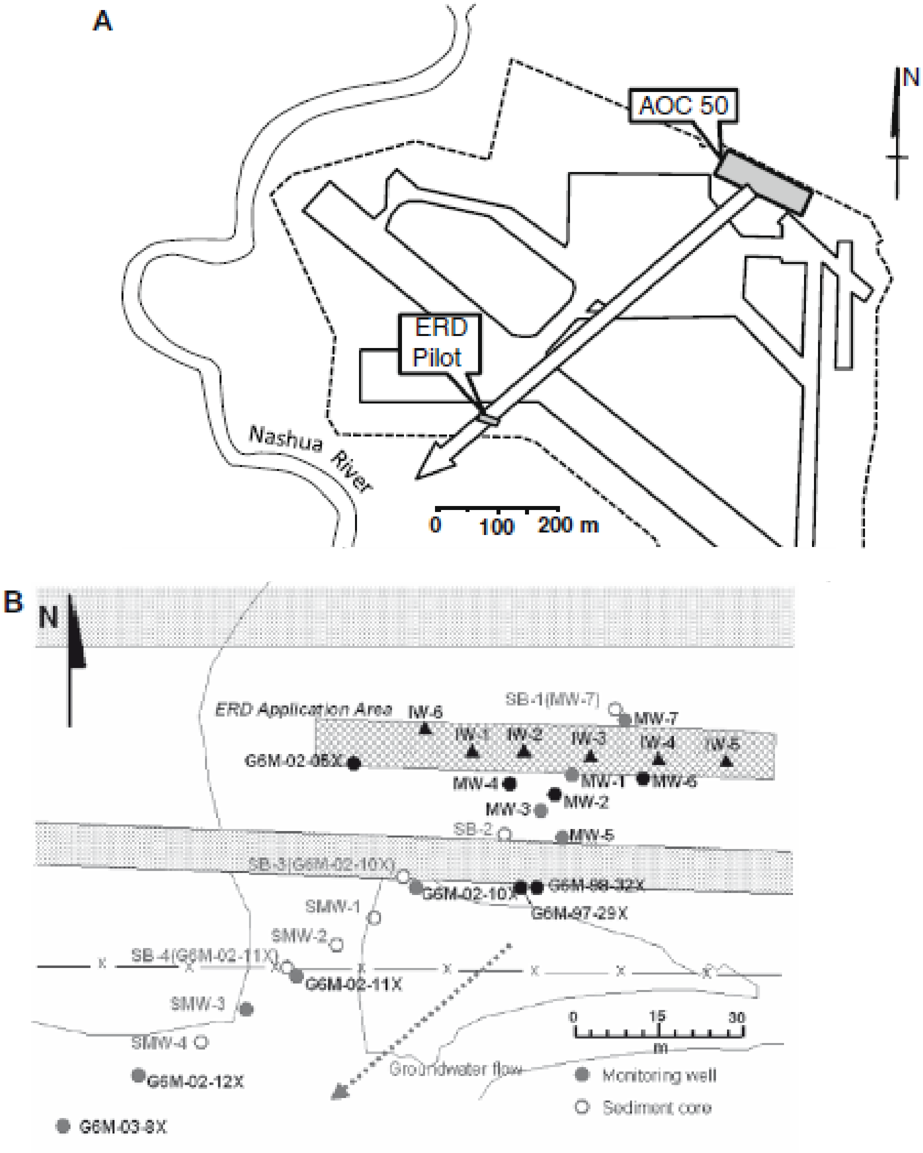

Figure 6-2. Ft. Devens site. (A) Map view showing source of chlorinated solvent contamination (AOC 50) and ERD pilot area. (B) Blowup of ERD pilot area (from A) showing location of injection wells (filled triangles), sediment borings (gray open circles), and sampled monitoring wells (gray filled circles and gray open circles in SMW 1–4) Irregular gray corresponds to surface topography. (*Source:* He et al. 2010)

Table 6-4. Ft. Devens groundwater data (extracted from He et al. 2010)

	Upgradient location	Within treatment zone	Downgradient of treatment zone	Cape Cod aquifer
pH	5.9	NR*	NR	5.7
Eh (mV)	+105	-100	>150	NR
As (µg/L)	<1	~100–~700	2.2	ND
Fe (mg/L)	<0.1	~75–~400	ND	ND
SO_4^{2-} (mg/L)	16.4	ND	17.9	8

*NR = not reported in document, ND = nondetect.

Microorganisms that can reduce As(V) and Fe(III) are ubiquitous in soils and sediments. Numerous laboratory studies have demonstrated that organic substrates will stimulate the microbial reduction of these two compounds. However, multiple factors can influence the rate of these reactions. Batch studies were conducted at this site to assess the potential influence of microbial activity on the mobilization of As, Fe, and Mn from the sediments (He et al. 2010). The results of the studies indicated that these three compounds are present in the sediments in forms that are susceptible to dissolution by microbial activity and that the addition of organic carbon as part of the ERD has the potential to stimulate that activity.

Farther downgradient, where the effects of the molasses injection on the redox state of the groundwater were no longer felt, the concentrations of the constituents were once again low, as reported in Figure 6-3. The soil cores were analyzed to assess the sorption of the contaminants onto the soil. Due to the low levels of As associated with the natural soils, it was not possible to assess the uptake onto the saturated soils. However, analysis of the sediments for Fe uptake indicated enrichment in the saturated soils from location SMW-2, indicating that precipitation and sorption onto aquifer sediments are the most likely mechanisms for sequestering As, Fe, and Mn.

Lessons Highlighted and Translation to Other Sites

At this site, the amendment of organic carbon to the subsurface mobilized solids-associated arsenic into groundwater. Analysis of samples collected downgradient of the amendment injection location, as the redox conditions returned to background, provided insight into factors that may impact attenuation at sites with anthropogenic sources of arsenic or sites with significant levels of natural arsenic and sources of organic carbon that support the reductive dissolution processes.

The research team concluded (He et al. 2010) that while natural attenuation processes appear to be effective in limiting the migration of As, continuing the addition of organic carbon could eventually overwhelm the attenuation capacity of the system. Additional studies to estimate the extent and mechanism of abiotic sorption and oxidation of As(III) that are consistent with Tier III analyses were reported by Choi, O'Day, and Hering (2009) for this site. While not providing a definitive answer, their laboratory studies do provide insight into what may affect the attenuation capacity within this waste site compartment (Section 2.4.1) where the As is being attenuated. This information would be of value in estimating whether sufficient attenuation capacity exists compared to various loadings of organic carbon. The distance to sensitive receptors is also important in the assessment of the viability of MNA. Attenuation capacity will be exhausted by "overloading" from upgradient to downgradient within a waste site compartment. In this case, if the impact of the organic carbon will affect half the length of that waste site compartment and the sensitive receptor is at a distance of three-quarters the length of the compartment, then MNA is still viable. However, if the reverse is true (impact of organic carbon is greater than the distance to the receptor), then MNA is not viable.

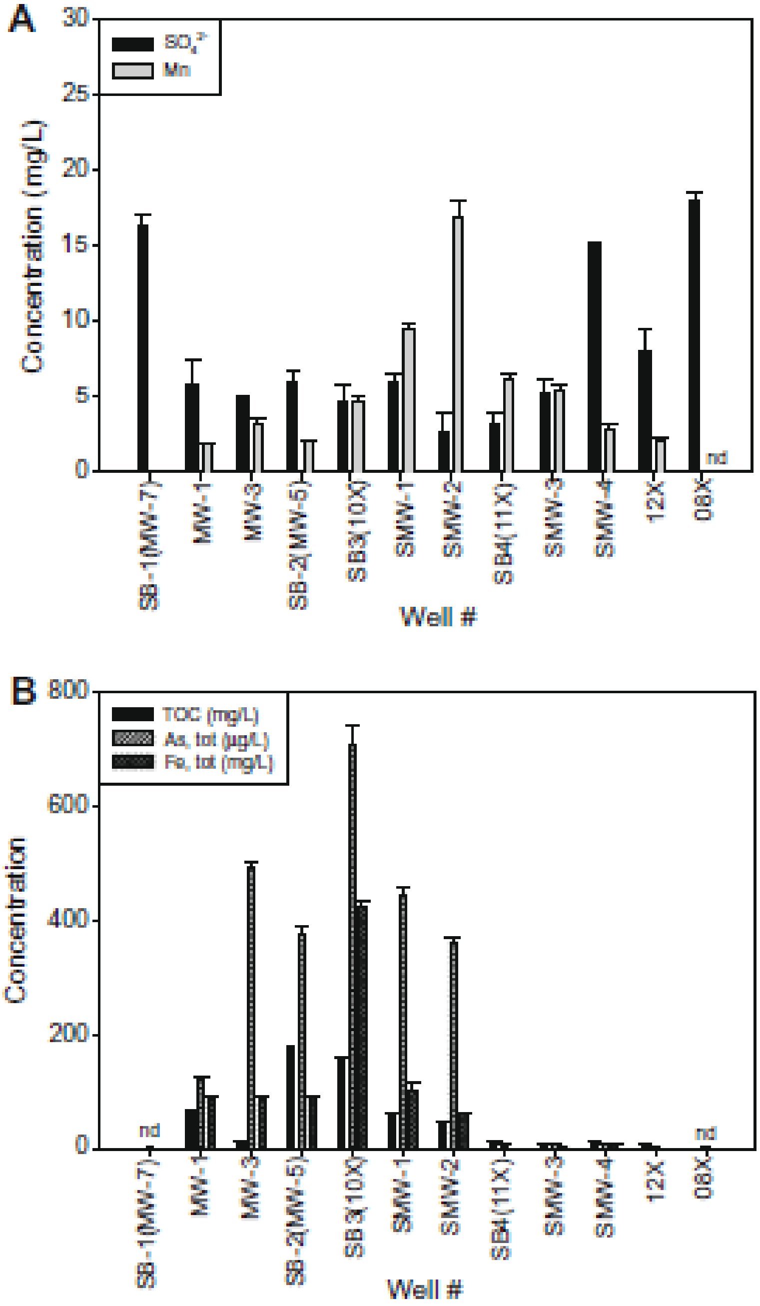

Figure 6-3. Arsenic, iron, and manganese data from groundwater monitoring well samples along a transect beginning upgradient of the ERD treatment area to a downgradient well that does not show signs of arsenic mobility. (*Source:* He et al. 2010)

6.4 Taking Advantage of the Natural pH Gradient

An acidic (pH 2–3) plume at the Savannah River Site in Aiken, South Carolina includes strontium-90, iodine-129, tritium, and uranium. In developing the remediation strategy for this groundwater plume, the project team took advantage of their knowledge of the geochemical conditions of the upgradient groundwater (pH 5.5). Typical site characterization data were used in the decision to investigate the potential of a remediation approach that would be based on pH adjustment. These data included field-based measurements of pH, temperature, dissolved oxygen (DO), ORP, conductivity, turbidity, and concentration data for relevant contaminants and inorganic constituents. Concentration-distance and concentration-time series maps were generated from these data. At pH 5.5, the strontium-90 becomes less mobile. Modeling for this waste unit indicates that at this pH the concentration goals for strontium-90 will be met. The regulators had set a timeframe by which to meet the concentration goal at a selected physical location within the waste site. To meet the timeframe, the remediation team developed an in situ treatment approach that raises the pH of the groundwater to 6, resulting in stabilization of the strontium-90. While the trailing gradient has not reached the area where the treatment is occurring, the engineered treatment is mimicking what will occur when the trailing gradient passes and the influx of upgradient groundwater raises the pH to its precontamination level of approximately 5.5. Appendix A provides additional information on this site.

Lessons Highlighted

This case study illustrates how important knowledge of the natural groundwater geochemistry is in implementing EA technologies. Once the trailing gradient passes, the stability of two of the main contaminants can be inferred by knowing what the permanent groundwater conditions are. Knowledge of the natural groundwater pH was used to create similar conditions within the plume to accelerate stabilization and thus attenuation of these contaminants. The investigations and modeling efforts that have occurred at this site in support of the remediation efforts are consistent with the pre-tier and Tier I analyses, as described in Table 2-4.

Section 2.3.5 discusses the potential complicating effects of multiple contaminants. This example highlights how a treatment that is effective in stabilizing two contaminants, strontium-90 and uranium, has no impact on two other key contaminants, iodine-129 and tritium. As described in Appendix A, development of a treatment to stabilize iodine-129 is under way at this waste site.

6.5 Heterogeneities

If not identified and understood, heterogeneities may lead to unpredicted results. The Hanford example in Appendix A highlights a unique and interesting temporal heterogeneity that had profound effects on the MNA evaluation. Initial modeling assumed a constant head boundary for the Columbia River, where the groundwater from the 300 Area expresses to surface water. The outcome of this initial modeling indicated that attenuation of the uranium would occur before reaching the river and that MNA was thus viable. The data from the site, however, did not support this conclusion. The Columbia River is a dam-controlled river and thus subject to relatively large (up to ~15 feet) variations in river stage. These fluctuations are reported daily, weekly, and seasonally. As reported in the case study in Appendix A, river water has been detected in the aquifer to distances greater than 150 m. This temporal heterogeneity affects the geochemistry over the zone of water table fluctuation. As noted in Section 2.1.2, uranium, the COC at this site, has a complicated aqueous speciation. Recognizing this temporal heterogeneity and its potential impacts to the attenuation have been valuable in the revision of the conceptual model for this unit, as discussed in Appendix A.

Heterogeneities may also be spatial, as represented by the Monticello case study, Appendix A, another site where uranium is the COC. This case study exemplifies the potential pitfalls of oversimplifying a system. In this case, a single K_d value was used, leading to an underprediction of the time to reach the remedial objectives. The presence of carbonate and acid tailings, as well as potentially reducing conditions in the vicinity of the PRB and site wetlands, would indicate the potential for several waste site compartments, as described in Section 2.4.1. Also in Section 2.3.1 there is discussion of how varying plume conditions, as would occur in distinct waste site compartments, may yield distinct distribution coefficients (K_d), as inferred from this case study.

Lessons Highlighted and Translation to Other Sites

These examples highlight the importance of accurately representing those parameters/factors that strongly influence a complex system. Changing water compositions may result in significant changes in subsurface geochemistry setting up gradients that affect the attenuation of the contaminants present in the system. The complex nature of uranium further complicates the Hanford example. While the conditions in this example are promoted by a fluctuating water table, groundwater to surface (fresh/tidal/estuarine) water interfaces that are less variable with time may also impact the mobilization/stabilization of minerals and contaminants in the subsurface. For shallow systems, temporal events that produce large variations in the influx of water from the surface may impact water table elevations, producing changes in geochemical gradients that may impact attenuation of contaminants.

6.6 Summary

The examples selected for presentation in this section, while not exhaustive, are intended to showcase that the traditional data sets collected in many waste site investigations can provide a wealth of information regarding the potential of incorporating MNA into a remedial strategy and support the development of the CSM. In support of the discussion in Section 6.1, incorporating an evaluation of the subsurface conditions prior to the introduction of the waste materials—by evaluating either upflow conditions or conditions beyond the reach of the contaminant plume—is a key component of all MNA and EA evaluations. Information from such data sets aid in the understanding of the conditions once the plume has passed through the waste site compartment and thus the potential attenuation capacity and long-term sustainability of the attenuation mechanisms for the contaminants of interest in that compartment.

7. CONCLUSIONS

MNA can be a viable remedy or component of a remedial alternative for groundwater contaminated with metals and radionuclides and may be capable of satisfying regulatory requirements at many contaminated sites. It may also often result in significant cost savings compared to other, more active remedy choices. MNA is not a "do-nothing" remedy, but rather requires (1) potentially intense characterization to understand the attenuation processes involved and to justify reliance on them and (2) regular, long-term monitoring to ensure the attenuation processes are meeting remedial goals.

MNA of metals and radionuclides does not yet enjoy the same level of acceptance by regulators and stakeholders as natural attenuation of organics, primarily because in many cases the contaminants are not destroyed, but remain in the subsurface. With new guidance and a framework for applying that guidance now available, they will be able to better understand whether attenuation mechanisms can be sustained over time, that is, whether contaminants will be stable under natural background conditions. Greater regulator and stakeholder acceptance is anticipated as these new policies and guidance begin to be applied.

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Appendix A

Case Studies

CASE STUDIES

A.1 HANFORD 300 AREA URANIUM

DOE's Hanford Site is a federal facility located in southeastern Washington along the Columbia River. The site was established during World War II as part of the Manhattan Project to produce plutonium for nuclear weapons. One of the primary waste components from this production effort was uranium. Liquid process wastes generated during these operations were disposed of in unlined surface ponds and trenches. A portion of these liquid wastes are contaminating the vadose zone and underlying unconfined aquifer adjacent to the Columbia River with uranium.

This case study describes the history of waste operations and remedial actions associated with the 300 Area groundwater, CERCLA Operable Unit 300-FF-5 at the Hanford Site. MNA for uranium was selected as a remedial alternative for the 300-FF-5 groundwater. Uranium attenuation has been insufficient for MNA to be successful at this site. Much of the text contained herein is excerpted directly from the original sources.

A.1.1 Setting

The Hanford Site occupies an area of approximately 1,517 km^2 (586 mi^2) in Benton County, north of the confluence of the Yakima River with the Columbia River in south-central Washington State (Figure A-1). The site extends north to south over a distance of about 50 km (30 mi) and 40 km (24 mi) from east to west. The 300 Area, in the southeastern corner, is located north of the city of Richland and covers approximately 1.5 km^2 (0.6 mi^2). Locations of the operable units associated with the 300 Area NPL site are also shown in Figure A-2.

A.1.2 Contamination History

The Hanford Site is divided into several operational areas (e.g., 100, 200, 300, and 400 Areas) associated with specific steps in the plutonium production process (DOE-RL 1998a, 1998b). Plutonium production continued throughout the Cold War and ended in 1988. Presently, the Hanford Site is undergoing cleanup/removal of contaminated facilities and environmental restoration.

Most of the 300 Area was used for industrial activities associated with fabrication of nuclear fuel rods and test materials related to plutonium production processes. The nuclear fuel rods were fabricated from uranium with various degrees of enrichment. The fuel rod manufacturing process included encasing or cladding the uranium within various metal alloys containing aluminum, zirconium, tin, iron, chromium, and nickel. Additionally, laboratories for nuclear fuel research and development and support facilities operated in the 300 Area.

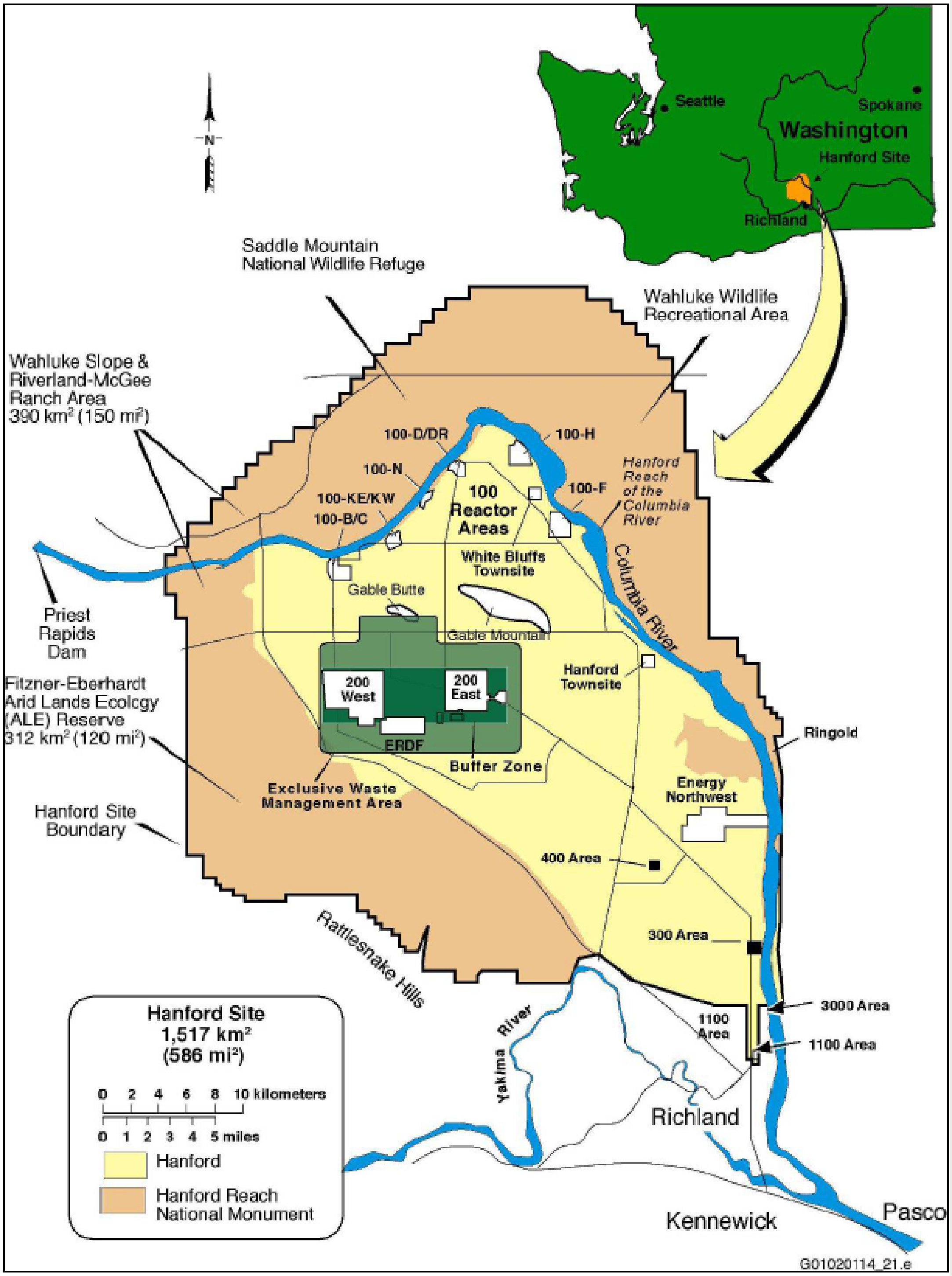


Figure A-1. Location map of the Hanford Site in south-central Washington State.

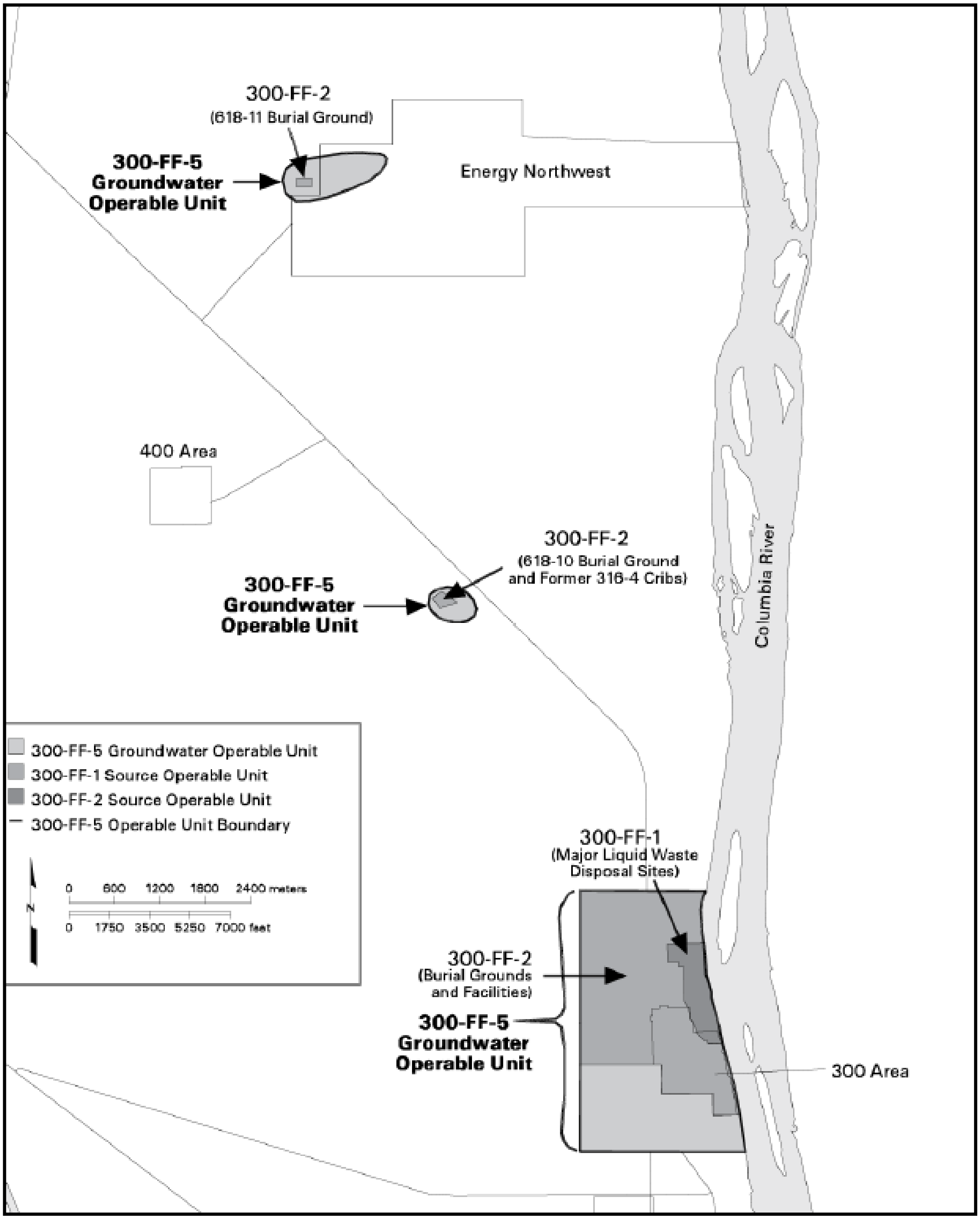


Figure A-2. Map showing operable units of the 300 NPL site.

Wastes generated in the 300 Area resulted from fuel fabrication operations and a variety of support operations, such as electric power generation from coal or oil, laboratory wastes, water treatment residuals, and sanitary waste disposal (DOE-RL 1993). These wastes were disposed in a variety of liquid and/or solid forms to cribs, ponds, and trenches located in the vicinity of the 300 Area. Typical waste streams discharged to the environment through the various ponds and trenches included uranyl nitrate hexhydrate, ammonium nitrate, hexone, neutralized waste acids containing metallic and chemical compounds of the fuel fabrication process, as well as process chemicals and solutions used in the numerous fuel reprocessing and separation technologies employed in the laboratories and test facilities (Gerber 1992). The largest volume of waste was generated from fuel fabrication operations. As a result of these activities, contaminated sediments and groundwater containing significant quantities of uranium exist near and beneath the historic 300 Area disposal facilities (cribs, trenches, and ponds) (Peterson et al. 2008).

Historical operations involving fuel fabrication and research activities at the 300 Area have contaminated engineered liquid waste-disposal facilities, the underlying vadose zone, and the uppermost aquifer with uranium. Principal reports describing historical operations for the purpose of supporting remedial action decisions are Young, Fruland, and Fruchter (1990); Young and Fruchter (1991); and Deford, Carpenter, and Einan (1994). The greatest impact to groundwater from disposal of waste containing uranium probably occurred during the Hanford Site's peak plutonium production period in the 1950s through the mid-1960s. During this period, effluent was directed to the South and North Process Ponds and a lesser amount to the 307 Process Trenches.

Contaminated process wastes continued to be generated during the 1970s and 1980s, with disposal shifting to the 300 Area Process Trenches in the mid-1970s. Table A-1 lists the principal waste-disposal units and chronology of their use. Figure A-3 provides a location map for these waste-receiving facilities. Additional contamination of the 300 Area subsurface occurred because of leakage from the process sewer system, which delivered fuel fabrication and other process/ research waste effluents to the various disposal sites (Lindberg and Bond 1979).

Table A-1. Operating periods for liquid waste disposal facilities

Disposal facility	WIDS[a] code	Period of use for effluent	Comments
South Process Pond	316-1	1943–1975	Removal of contaminated soil completed in 2000; excavation backfilled in 2004.
North Process Pond	316-2	1948–1974	Removal of contaminated soil completed in 1999; excavation backfilled in 2004.
307 Process Trenches	316-3	1953–1963	Backfilled with contaminated soil in 1965; remedial action to be completed by December 2009 (TPA milestone M94-07).
300 Area Process Trenches	316-5	1975–1985, 1985–1994	Received nonhazardous liquid effluent after 1985 through December 1994; expedited response action to remove contaminated soil and infrastructure removal actions in 1997/98; backfilled in 2004.
310 Treated Effluent Disposal Facility		1994 to present	Receives 300 Area effluents via the process sewer system; treated effluent is then discharged to the Columbia River via a National Pollutant Discharge Elimination System permit.

[a] Waste Information Data System (DOE-RL 2005b).

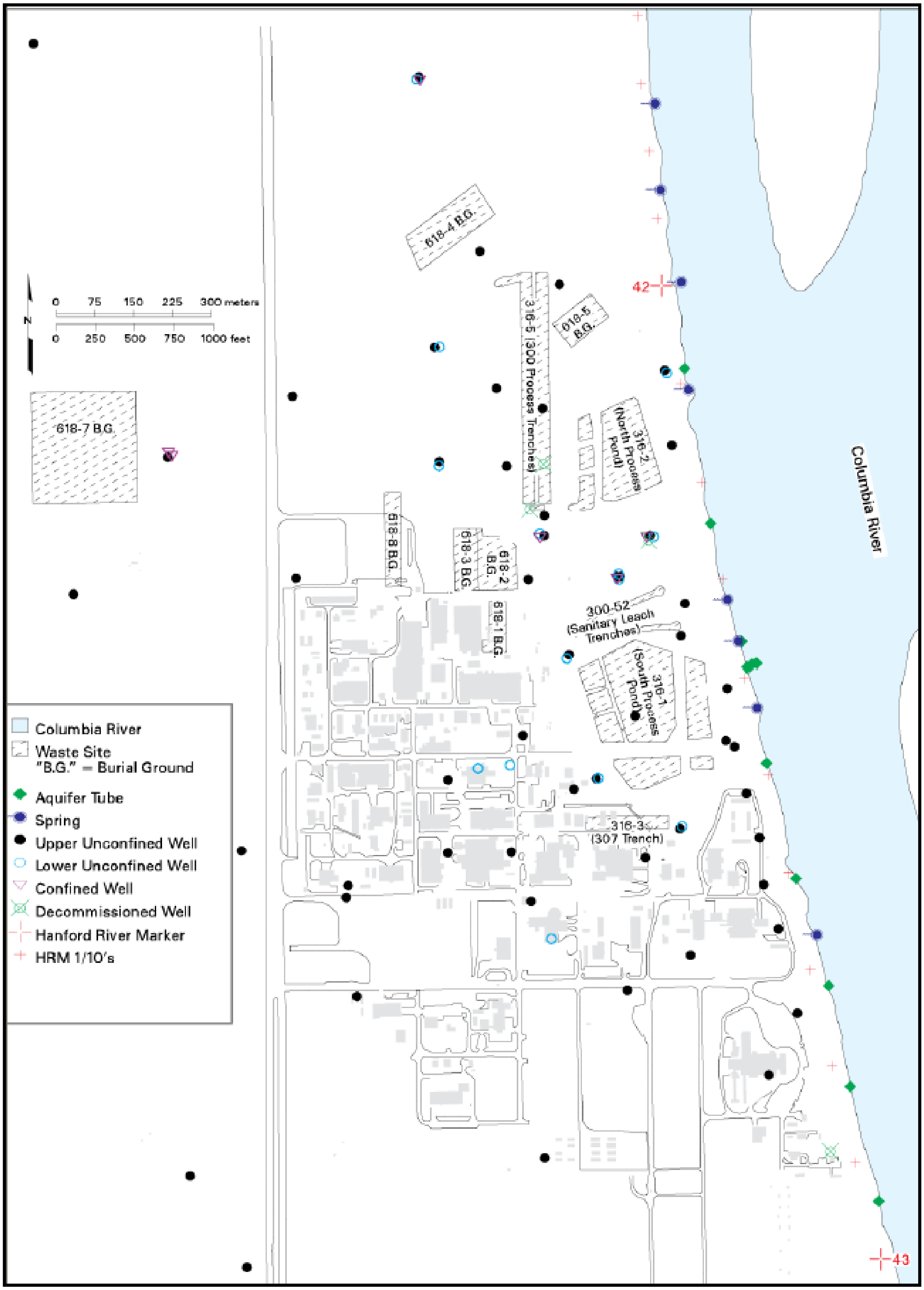


Figure A-3. Map of former waste disposal facilities in the 300 Area. The 310 Treated Effluent Disposal Facility, which is still operating, is located left of center at the top of the map.

Completed source remedial actions have removed significant volumes of uranium-contaminated sediment from the major liquid waste disposal facilities, such as the North and South Process Ponds and the 300 Area Process Trenches (DOE-RL 2005b). The maximum depths for the excavations were a result of predetermined soil cleanup values, and concurrence to backfill excavated areas, by the appropriate regulatory agency. Residual uranium contamination remained at the bottom of some excavations; lesser understood inventories may also remain at greater depths under the vadose zone.

A.1.3 Stakeholders and Remedy Selection

The stakeholders in the CERCLA process governing record of decision (ROD), remedial investigation/feasibility study (RI/FS), and remedial action (RA) activities are EPA, Washington State Department of Ecology (Ecology), and DOE. In November 1989, EPA placed the Hanford Site, including the 300 Area, on the NPL.

The 300 Area has been divided into three operable units. The 300-FF-1 Operable Unit includes the former major liquid waste disposal facilities, such as the North and South Process Ponds, while the 300-FF-2 Operable Unit includes solid waste burial grounds and other facilities. The 300-FF-5 Operable Unit includes groundwater affected by releases from the various waste sites. Because of the probability that residual, mobile uranium in the vadose zone is still contributing to the groundwater plume, portions of the vadose zone are also considered in discussion of 300-FF-5.

Investigations were conducted in the early 1990s under the Hanford Federal Facility Agreement and Consent Order, which was negotiated and approved by stakeholders in May 1989 (Ecology, EPA, and DOE 1989). This agreement, known as the Tri-Party Agreement, governs all CERCLA efforts at the Hanford Site.

MNA was selected as part of an interim action that imposed restrictions on the use of groundwater until natural attenuation processes reduced concentrations for uranium to health-based criteria. The selection of MNA for uranium followed completion of the Phase I and II FS (DOE-RL 1994). The rationale for interim action included an observed, and assumed continuing, decline in groundwater concentrations of uranium to target levels within 10 years of 1993. Source control by excavation and removal actions was in progress and was expected to greatly reduce uranium transport to groundwater.

In November 2001, EPA issued a directive specifying the cleanup level for uranium in groundwater as 30 μg/L. Subsequent groundwater monitoring revealed that uranium concentrations did not decline as anticipated (Figure A-4) and that uranium concentrations persisted above the 30 μg/L target level through 2004. Therefore, a renewed effort to develop and implement groundwater cleanup was initiated in 2005. This renewed effort is outlined in *Work Plan for Phase III Feasibility Study, 300-FF-5 Operable Unit* (DOE-RL 2005a).

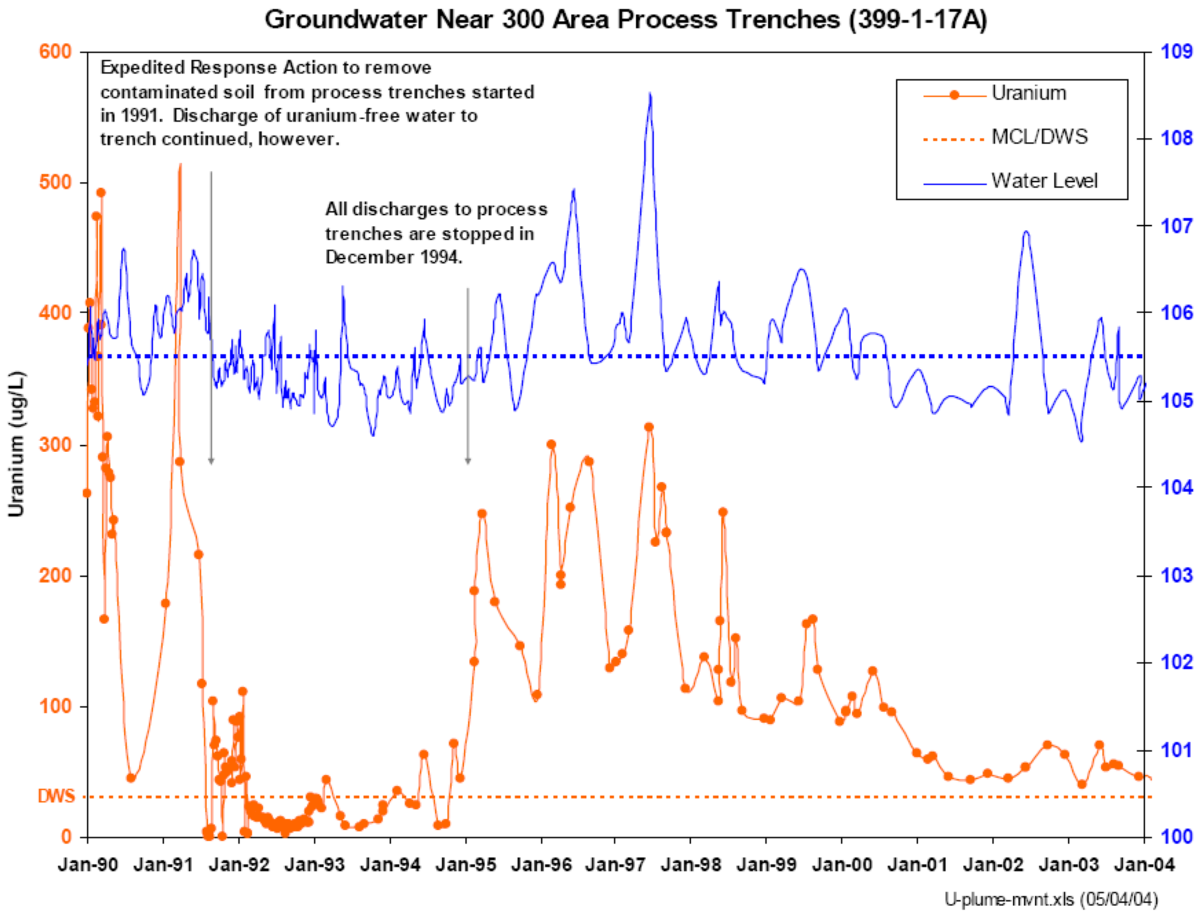


Figure A-4. Groundwater contamination history for uranium in a single well influenced by river stage and uranium-free process discharge. Demonstrates the relationship between river stage and mobilization of uranium from the vadose zone, dilution of uranium by infiltration, and the limited data availability that partially influenced the decision to use MNA as an interim remedy for uranium in groundwater at the Hanford Site 300 Area.

The present remediation strategy report provides updated information resulting from a limited field investigation (Williams et al. 2007), an updated CSM (Peterson et al. 2008), recent hydrologic study and analysis, new remediation technology testing (Wellman et al. 2008), and recent research in the geochemical behavior of uranium (Bond, Davis, and Zachara 2007).

A.1.4 Site Technical Description

A.1.4.1 Climate

The climate of the 300 Area is semiarid, influenced by the rain shadow created by the Cascade Range located approximately 130 km (80 mi) to the west. The resulting climate is characterized by low precipitation, high evapotranspiration, and relatively high winds. Observations at the Hanford Meteorological Station, located approximately 32 km (20 mi) northwest of the 300 Area at an elevation of 223 m (733 ft) above mean sea level, indicate the total annual precipitation averages approximately 16 cm (6 in.). Rain is the usual form of precipitation, but snow also falls in winter. Winter is the wettest season. Summer is the driest season; however, the greatest intensity of precipitation occurs in summer with occasional thunderstorms. Summer is typically hot and dry, and winters are moderately cold. The average temperature in July is 24.7°C (76.4°F), and the average temperature in January is -1.5°C (29.3°F). At the site, most of the water available for recharge to soil comes in winter months during periods of low evaporation (Hulstrom 1992). Based on observations at the 300 Area monitoring station, wind direction at the 300 Area varies over 360 degrees, with a prevailing wind direction from the southwest (11% of the time). Winds from the north, southeast, south-southwest, and north-northwest occur with approximately equal frequency (approximately 8%) (DOE-RL 1989).

A.1.4.2 Topography

The ground surface of the 300 Area has a generally flat surface with an absence of clearly defined drainages. The 300 Area is approximately 119 m (390 ft) above mean sea level, and the eastern boundary is defined by the Columbia River. The river shoreline consists of a steep embankment with an approximate rise of 12 m (40 ft) up to the 300 Area.

A.1.4.3 Hydrogeology

The stratigraphy beneath the 300 Area consists of sedimentary deposits with a total thickness ranging 40–60 m (131–196 ft) overlying basalt bedrock. The principal units of the sedimentary layers consists of (from lower to upper) the fluvial and lacustrine sediments of the Ringold Formation, the glaciofluvial deposits of the Hanford formation, and a relatively thin layer of eolian sand and silt at the surface. However, the surface eolian deposits have been removed by excavation over most of the 300 Area, and up to 10 m (32 ft) of backfill material is at the surface in some places. The Cold Creek Unit, which lies between the Hanford and Ringold Formations in other portions of the Hanford Site, is apparently not present beneath the 300 Area. Figure A-5 is a schematic representation of the hydrologic and stratigraphic units present at the 300 Area. A comprehensive discussion of the hydrogeology is included in the most recent description of the conceptual model for uranium (Peterson et al. 2008).

The water table beneath the 300 Area continuously fluctuates near the Columbia River in response to changing river stage. Nominally, depth to water at the 300 Area ranges 8–17 m (26–56 ft) below the ground surface, depending on the topographical location. The unconfined aquifer beneath the 300 Area, which contains the bulk of groundwater contamination, flows through glacially deposited gravels and sands. Groundwater flow and direction are very dynamic near the river, but generally flow is west to east and toward the river. Groundwater in the unconfined aquifer flows preferentially through the saturated Hanford formation sediment, although the unconfined aquifer system does include sediments of the underlying Ringold Formation. The aquifer solids in the Hanford formation stratum of the aquifer range in size from pebble-cobble gravel to boulders as large as 1 m (3.3 ft) and extend below the water table 1.5–9 m (5–30 ft). The deeper Ringold Formation stratum extends another 12+ m (40+ ft) and consists of interstratified deposits of sand, silt, clay, and gravel. Whereas the upper Hanford formation strata are very permeable with flow velocities as high as 10–15 m (32.8–49.2 ft) per day, the deeper Ringold Formation stratum is moderately permeable with flow velocities 2–3 orders of magnitude less.

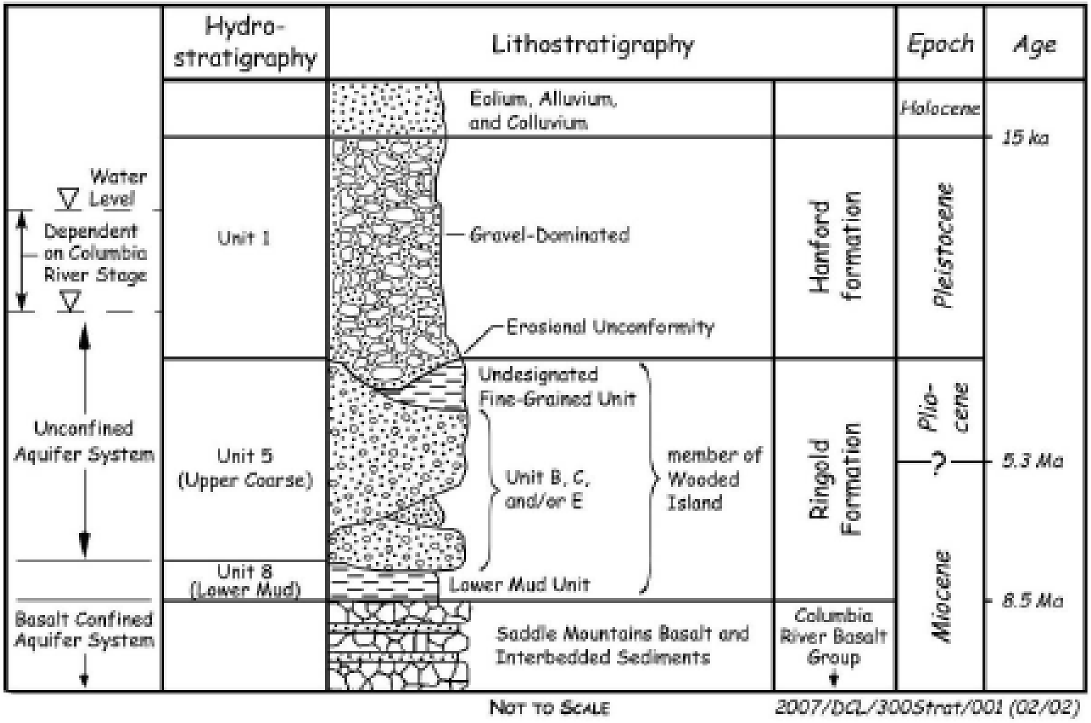


Figure A-5. **Hydrogeologic stratigraphic column for the 300 Area.** (Modified from Reidel, Lindsey, and Fecht [1992]; Lindsey [1995]; Williams et al. [2000]; and DOE-RL [2002].)

Groundwater flow rates and directions in the 300 Area are highly variable because of the high hydraulic conductivities in the saturated Hanford formation portion of the aquifer, along with the large daily, weekly, and seasonal fluctuations in the stage of the Columbia River. Generalized flow directions in the area between the former north and south process ponds are toward the east to south with the directions changing toward the south and west during periods of increases in the river stage (daily and seasonal) exceeds the water table elevation within the aquifer.

Recent studies of the hyporheic zone in the 300 Area have shown the importance of a lower hydraulic conductivity layer (relative to the Hanford formation) in some areas of the riverbed adjacent to the 300 Area. This layer of alluvium dampens the hydraulic head response in wells near the Columbia River to river-stage fluctuations (Fritz et al. 2007). Downhole probe measurements of specific conductance and temperature in wells near the river reveal the extent of the groundwater/river water interaction zone. For example, in 2006 river water was detectable in the aquifer to a distance of more than 188 m (617 ft) inland.

A.1.5 Description of Contamination

The subsurface beneath the 300 Area contains uranium contamination above soil and groundwater background levels as a result of the discharges of liquid wastes containing uranium. The following sections describe the nature and extent of the uranium contamination in the groundwater, vadose zone, and water table interface. Table A-2 provides a summary of earlier estimates for the inventory of uranium sequestered in various subsurface “compartments” beneath the 300 Area, as prepared for an update to the conceptual model.

Table A-2. Summary of uranium inventory estimates for various subsurface repositories in the 300 Area (from Peterson et al. 2008)

Compartment	Description	Uranium inventory (kg)
A	Vadose zone sediment above highest water-table elevation; beneath footprint of former liquid-waste disposal facilities	2,100
B	Vadose zone pore water above highest water-table elevation; beneath footprint of former liquid-waste disposal facilities	75
C	Vadose zone sediment above highest water-table elevation; outside footprint of former liquid-waste disposal facilities	560
D	Vadose zone pore water above highest water-table elevation; outside footprint of former liquid-waste disposal facilities	6
Vadose zone subtotal		***2,700***
E	Sediment in intermittently wetted zone through which water table rises and falls; beneath footprint of disposal facilities	1,050
F	Pore water and intermittently wetted zone through which water table rises and falls; beneath footprint of disposal facilities	38
G	Sediment in intermittently wetted zone through which water table rises and falls; outside footprint of disposal facilities	110
H	Pore water in intermittently wetted zone through which water table rises and falls; outside footprint of disposal facilities	2
Water table zone subtotal		***1,200***
I	Aquifer sediment; within area of greater than 30 mg/L uranium (average concentrations for 2002 to 2007)	120
J	Groundwater; within area of greater than 30 mg/L uranium (average concentrations for 2002 to 2007; total porosity of 26%)	60
Aquifer subtotal		***180***
Total		**4,080**

A.1.5.1 Groundwater Contamination

Monitoring of the plume since the late 1940s has indicated elevated uranium concentrations above background. Concentrations up to several hundred micrograms per liter have been observed at wells within the plume since 2005 (Figure A-3).

As estimated from plume maps and the presumed thickness of the contaminated hydrologic unit, the volume of groundwater contaminated by uranium during the last several years is in the range 1,500,000–2,800,000 m^3, with the mass of uranium dissolved in those volumes in the range 77–105 kg (Peterson et al. 2008, Table 3-3). Groundwater beneath the 300 Area is currently contaminated with a variably shaped plume of uranium extending over approximately 0.5 km^2 (0.19 mi^2). For the portion of the plume that exceeds the drinking water standard, the volume range is 940,000–1,280,000 m^3, and the mass range is 65–78 kg. Other methods for estimating the mass of uranium in groundwater produce similar values, i.e., many tens of kilograms.

The background uranium concentration in groundwater beneath the Hanford Site is estimated to range 0.5–12.8 μg/L, depending on location (DOE-RL 1997). At the 300 Area, natural background is estimated to range 3–8 μg/L. A detailed description of the history, extent, and nature of the groundwater contamination by uranium in the 300 Area is presented in Peterson et al. (2008). The conceptual model summarizes the results of historic groundwater monitoring and includes the results from recent aquifer and sediment characterization activities.

A.1.5.2 Contamination in Vadose Zone

Estimates for the inventory of uranium sequestered in various subregions of the vadose zone were also developed as part of updating the conceptual model (Peterson et al. 2008, Section 6). Sediments and associated pore water beneath the footprints of former liquid waste disposal facilities may contain over half the uranium inventory at the 300 Area, with additional contamination in the zone through which the water table rises and falls. This rough inventory estimate is based on newly acquired but spatially limited data from characterization of subsurface sediments. It appears the quantity of uranium in unsaturated (or periodically wetted) sediments above the always saturated aquifer exceeds the quantity of uranium within the aquifer by a significant factor.

The mobility characteristics of the residual inventories under current hydrologic conditions are only beginning to be understood (Zachara 2005, Zachara et al. 2007), and the relationship between the inventories and the resupply of the groundwater plume is considered a key data gap for any renewed remedial investigation activities. Also, work in progress under DOE’s Integrated Field-Scale Research Challenge program is partially focused on the transport of uranium through the vadose zone at the 300 Area (Freshley 2008). The preponderance of available evidence suggests that the persistence of the uranium plume in groundwater is related to a continuing supply of uranium from the overlying vadose zone, as opposed to the alternatives of release from uranium sequestered in aquifer solids or migrating into the 300 Area from outside sources (Peterson et al. 2008).

The total estimated area of vadose contamination based on the sum of all the disposal unit footprints (ponds and trenches) is approximately 76,000 m^2 (19 acres). Assuming that the contaminating fluid releases extended uniformly downward towards the water table, that acreage represents a minimum area of contaminated sediment source at the groundwater interface. However, sediment characterization southeast of the south end of the 300 Area Process Trenches indicates some lateral spread of uranium contamination in the 1–2 m (3.2–6.5 ft) vertical zone of fluctuating groundwater elevation (“smear zone”). Consequently, the source area of sediment contributing to the groundwater contamination may extend to some unknown distance outside the “footprint” margins of the ponds and trenches that received uranium-bearing waste effluent.

Uranium concentrations in the unsaturated sediments beneath the disposal areas vary according to depth, based on sampling and laboratory work conducted under the limited field investigation (Williams et al. 2007). Uncontaminated Hanford Site sediments contain a range of relatively immobile background of total uranium: approximately 1.5–5 mg/kg of sediment. Contaminated 300 Area sediments may contain 5–25 mg/kg of sediment. However, the geochemical form of the contaminant uranium is variable, which affects the potential for the uranium to be mobilized (i.e., is the form “labile”). For those forms that can be mobilized under geochemical conditions that might exist beneath the 300 Area, a transporting medium such as water is also required for further dispersion along environmental pathways. Currently, a weak nitric-acid leach procedure is used to extract uranium from sediment; the procedure provides a conservative estimate for the amount of labile uranium available. Contact time and the rate of exchange between the sediment and transporting medium are also parameters used in estimating the time it might take to exhaust the inventory of uranium sequestered in a particular subsurface compartment.

Preliminary uranium results for samples of vadose zone sediment at a borehole through the former South Process Pond range 1–5 mg/kg of sediment, and some stratification of the uranium in the vadose zone has been observed. The highest uranium concentrations are associated with samples from the lower portion of the vadose zone and near the water table ("smear zone"). Backfill material at the South Process Pond borehole site revealed a concentration of 3 mg/kg of sediment. Other preliminary results suggest that sediments beneath the former North Process Pond may have slightly higher concentrations of labile uranium.

A.1.5.3 Sediment in the Intermittent Wetted Groundwater Interface Zone

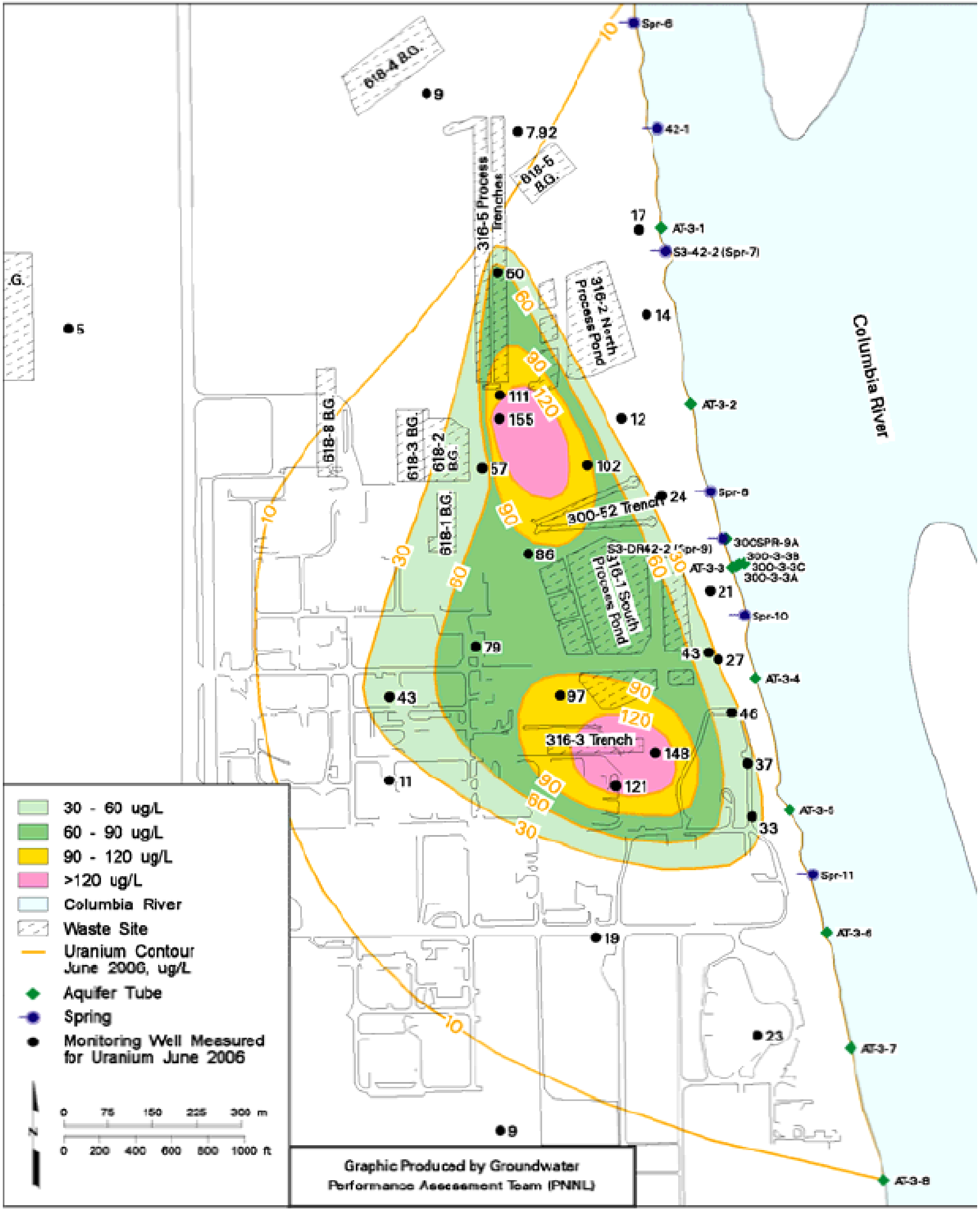
The uranium that maintains the groundwater plume appears to be related to the unsaturated sediment above and immediately in contact with groundwater. Consequently, vadose sediments in the Hanford formation could be important in implementing a remedy for uranium contamination in groundwater. The thickness of the vadose zone varies as the water table moves up and down in response to changes in the Columbia River stage. However, the water table is usually within the Hanford formation throughout most of the 300 Area. The vadose zone is composed predominantly of Hanford formation sand and gravel, recent eolian silt and sand, and, in some places, backfill. The backfill typically consists of reworked sand and gravel of the Hanford formation, or at the former 307 Process Trenches, of scrapings from the former South Process Pond and coal plant fly ash. In summary, the hydrogeologic framework controls the groundwater contact with uranium residuals in the vadose sediment at the dynamic groundwater interface, and determines the convective and diffusive flow path of mobilized uranium in the saturated zone.

The lowermost portion of the vadose zone is of particular significance to the exchange of uranium between the vadose zone and the groundwater system. The sediments in this zone are periodically contacted by groundwater at times when the water table is raised because of elevated Columbia River stages during early summer. This zone, which currently extends as much as 2 m (6.5 ft) above typical low groundwater elevations, is a pathway and possible sequestration region for uranium that contributes to the groundwater plume. Concentrations of labile uranium in this interface zone are generally higher than in the sediments above. Areas extending laterally beyond the "footprints" of the waste sites above are also suspected locations for residual amounts of the contaminant uranium. Sediments and associated pore water in this smear zone may contain an appreciable portion of the uranium inventory in the subsurface, possibly approaching a third of the total. Remedial action that prevents or limits the release of uranium from the interface zone between groundwater and the vadose zone will directly reduce uranium flux into the groundwater.

A.1.6 Conceptual Model of Contaminant Attenuation

The rough estimates for inventories of uranium stored in various subsurface compartments and the relative paths by which the mobile component of that inventory may be transported are shown schematically in Figure A-6. The path arrows suggesting fluxes between the various compartments reflect long-term net conditions. Short-term reversals of flux are possible, particularly in the lower vadose zone, where there are fluctuations in groundwater elevation. This conceptual representation of subsurface inventory and exchange was developed as part of an update to the conceptual model for uranium (Peterson et al. 2008). Numerous uncertainties remain in quantifying this subsurface regime of contamination, although it does provide a qualitative framework that is useful in formulating remediation strategies.

A — 300 Area Uranium, June 2006



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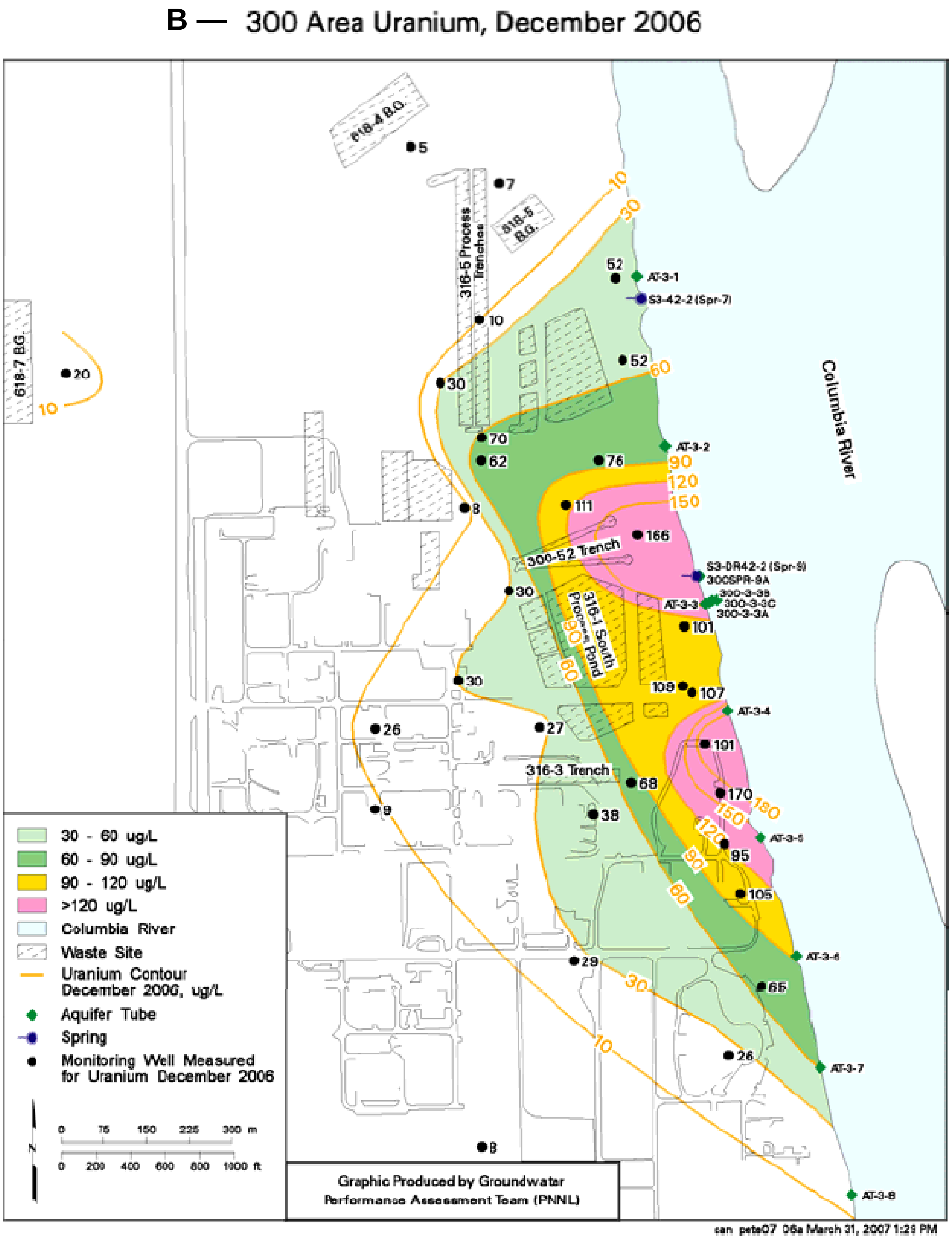

Figure A-6. Uranium plume in groundwater beneath the 300 Area, showing transition from (A) high water table conditions (June 2006) to (B) seasonal average conditions (December 2006).

With currently available information, fluxes between the various subsurface compartments can be discussed only in a semiquantitative manner. Research being conducted as part of the Integrated Field-Scale Research Challenge program (Freshley 2008) will help in quantifying the transfer of uranium among the various compartments. As indicated in Figure A-5, the continuing input of uranium to groundwater involves release from the sediments and pore water in the smear zone, which in turn may be replenished with uranium from the overlying unsaturated zone sediments. Unexcavated sediments directly beneath former liquid waste disposal facilities (compartment A) are a possible source region, assuming the inventory includes labile forms of uranium and that a medium is available to transport the uranium downward.

Recent sediment sampling results conducted after the limited field investigation suggest that the smear zone away from the former disposal site footprints (compartment G) may contain higher amounts of uranium than indicated in Figure A-6, with as-yet unpublished estimates suggesting as much as 10% of the total uranium inventory. If so, such sediments extending beyond the disposal site footprints could be a significant source for supplying uranium to groundwater. The rate of transfer between the individual compartments has a direct influence on the uranium concentrations in the groundwater. Remedial actions that reduce the flux of uranium to groundwater may have a greater effect on groundwater concentrations than actions that reduce concentrations directly in the aquifer.

Under current land-use and meteorological conditions, and in the absence of waste disposal activities, the availability of a transporting medium for labile uranium in the upper portion of the vadose zone appears to be limited. However, uranium in the interface zone between the aquifer and vadose systems may be of sufficient quantity to maintain the uranium plume in the upper aquifer for a future period of time. Remedial treatments that interrupt the transport pathways or reduce the fluxes along these pathways will result in corresponding reductions in groundwater concentrations and the level of contamination. With suitable uranium flux reduction, a new uranium equilibrium may develop under natural processes that would result in attainment of cleanup goals (i.e., groundwater concentrations lower than the 30-µg/L drinking water standard).

A.1.7 Assessment of Plume Stability

Through 1995 a trend of decreasing uranium in 300 Area groundwater suggested that the source removal begun in 1991 had reduced groundwater uranium concentrations. Selection of MNA as the interim remedy for groundwater was supported by contaminant transport model projections. Model predictions for the saturated aquifer indicated that uranium concentrations would decrease by natural attenuation to <20 µg/L over a period of 3–10 years following source removal. This hypothesis later proved to be unsupported by the observations. Tier 1 attenuation was not proven because additional source control was needed to achieve plume stability.

A.1.7.1 Assessment of Attenuation Mechanism and Rate

Determination of attenuation mechanism was made using a distribution coefficient (K_d) approach and numerical modeling of saturated groundwater flow. The assessment did not consider secondary source contributions from the vadose zone, later to be determined to be a significant and continuing source of uranium transport to groundwater, or specific geochemical retardation mechanisms.

A.1.7.2 Assessment of Capacity for Plume Attenuation

The capacity of aquifer sediments ability to sequester uranium was not determined.

A.1.7.3 Assessment of Stability of Immobilized Contaminant

The stability of adsorbed uranium on aquifer sediments, or uranium-bearing solid phases, was not determined. Current plans are to evaluate the potential for vadose zone source stabilization through precipitation of uranium as phosphorous-containing compounds, an evaluation that will result in an assessment of immobilized contaminant stability

A.1.8 Assessment of Remedy Performance

MNA performed poorly as an interim remedy at the Hanford Site 300 Area uranium plume. A four-tiered MNA approach may have resulted in selection of an alternate interim remedy or an MNA pathway different from the one taken.

A.1.9 Lessons Learned

Source control was incorrectly assumed complete after remediation of soils to site-specific criteria. A major secondary source of contamination was not identified during the RI/FS. Had the secondary source (vadose zone uranium released by a fluctuating water table) been known, the four-tier MNA process would have paused at Tier 1, the assessment of plume stability. MNA is not currently successful for the 300 Area groundwater uranium plume; additional source control is required.

The development and implementation of a contaminant transport model for uranium in the unconfined aquifer played a key role in the selection of the interim remedial action for Operable Unit 300-FF-5. It is instructive to evaluate what assumptions were made in constructing the model descriptions of water transport and uranium partitioning to aquifer solids. Waichler and Yabusaki (2005) provide a useful description of the assumptions inherent to the original transport model and the associated limitations for describing uranium transport in the unconfined aquifer. In general, the following assumptions appear to have been critical relative to disparities between model projections and the subsequent observed behavior of the plume: (1) removal of contaminated surface soils eliminated the source of uranium from which the plume developed; (2) groundwater flow was unidirectional towards the Columbia River, which was treated as a constant head boundary; and (3) partitioning of uranium to aquifer solids could be described using a constant equilibrium sorption isotherm (K_d) independent of water chemistry and aquifer mineralogy.

Subsequent investigations to determine the cause of sustained elevated uranium concentrations in the plume have demonstrated that a lack of information on the spatial distribution of uranium within subsurface solids and the chemical speciation of solid-phase uranium were important limitations to the reliability of the contaminant transport model. First, failure to consider that a fraction of the uranium transported through the vadose zone was retained in the subsurface in a range of solid forms led to overly conservative projections of the long-term flux of uranium that could be transported through the saturated aquifer. Characterization of subsurface solids collected from under former waste process areas indicated elevated uranium concentrations bound to the solids in both precipitated (coprecipitated in $CaCO_3$, uranium-phosphate precipitates) and adsorbed (e.g., muscovite in aquifer solids) forms.

As demonstrated by subsequent hydrologic investigations, water level fluctuations induced by periods of recharge from the Columbia River cause a portion of residual uranium solids within the lower vadose zone (i.e., the smear zone in Figures A-7 and A-8) to be cyclically leached into the underlying plume (Qafoku et al. 2005; Zachara 2005; Bond, Davis, and Zachara 2007; Peterson et al. 2008; Yabusaki, Fang, and Waichler 2008). Finally, aquifer recharge by river water with low dissolved carbonate concentrations results in cyclical increases in uranium adsorption to aquifer solids within the plume, which has resulted in slower dissipation of the plume due to flushing from the aquifer.

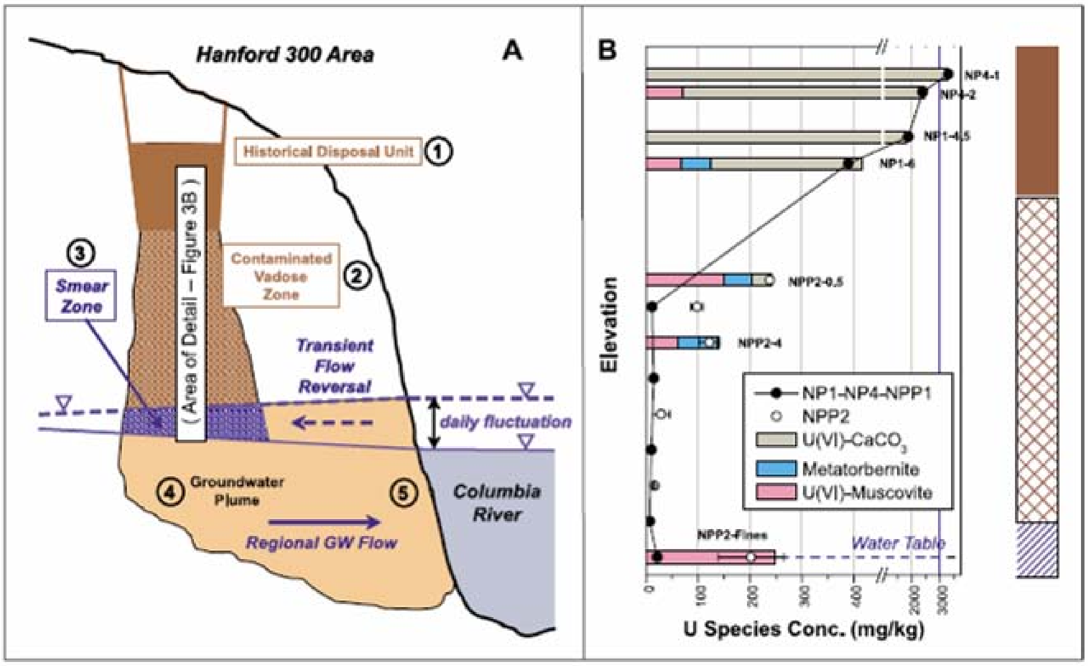

Figure A-7. Subsurface uranium contamination within the Hanford 300 Process Waste Sites area. (A) Primary hydrogeologic features impacting plume migration to the Columbia Region (vertical dimension is exaggerated; CSM zones identified with circled numbers after Nimmons 2007). (B) Concentrations and speciation of solid phase uranium in vadose zone above (North Process Ponds solids and contaminated aquifer solids) and within the influence of ground-water level fluctuations (smear zone).

Tests with contaminated subsurface solids have demonstrated that dissolved carbonate is the most important parameter in site groundwater chemistry with respect to impacting uranium mobility; uranium adsorption to aquifer solids decreases with increasing alkalinity (e.g., Bond, Davis, and Zachara 2007). The revised CSM including identification of the important subsurface zones is provided in Figure A-7A (Peterson et al. 2008, Nimmons 2007), and the solid-phase distribution and chemical speciation of uranium as a function of depth below source areas are shown in Figure A-7B.

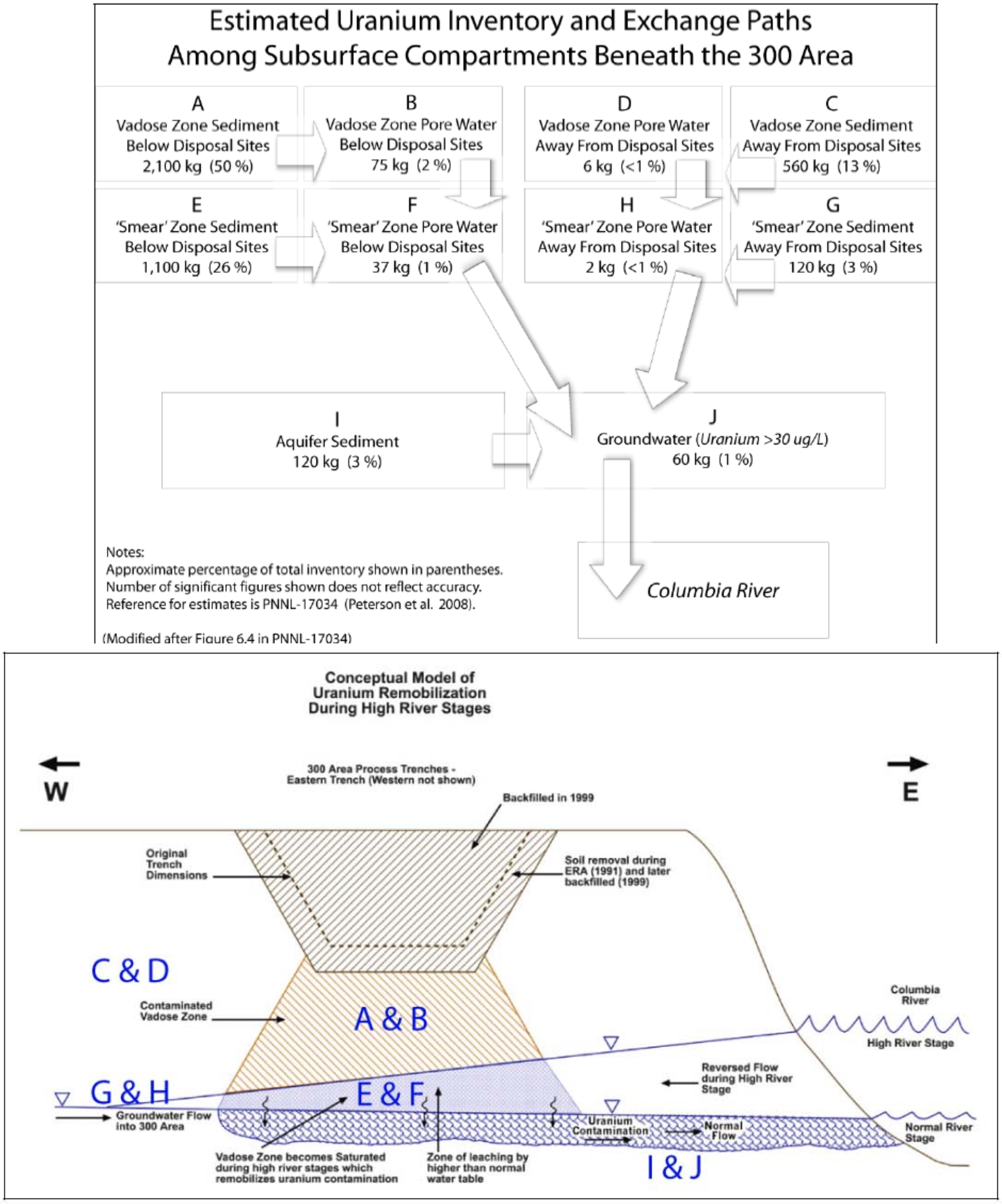

Figure A-8. Estimated inventory of uranium in the subsurface at the 300 Area (top) and schematic cross section beneath waste site, showing locations for compartments defined for uranium inventory and exchange model (bottom). (Modified from Lindberg and Chou [2001].)

Table A-3 summarizes site characterization efforts supporting interim remedy selection under the 1996 ROD and subsequent solid-phase characterization studies for the groundwater system.

Table A-3. Comparison of site characterization efforts during original and revised consideration of MNA as a component of the groundwater remedy for the Hanford 300 Area (OU 300-FF-5)

Data category	Site characterization to support MNA evaluation	
	Original	**Revised**
Hydrology	- Water level measurements in aquifer and stage measurements in Columbia River - Modeled groundwater transport assuming average river stage as downgradient boundary condition	- Higher time frequency measurements of river stage and groundwater level - Modeled groundwater transport to account for time-variant changes in water flux and direction
Reaction process	- Modeled sorption of uranium to aquifer solids assuming fixed K_d independent of groundwater chemistry and aquifer solids mineralogy	- Laboratory tests with aquifer solids from various depths to assess influence of groundwater chemistry on the extent and rate of uranium sorption-desorption - Direct measurement of uranium speciation in vadose zone pore water using fluorescence spectroscopy to identify mobile aqueous species - Direct measurement of uranium speciation in aquifer solids as a function of depth using bulk and microfocused X-ray spectroscopy/diffraction and electron microscopy in combination with chemical extraction methodologies - Determination of uranium distribution as a function of particle size in aquifer solids - Identification of reactive clay minerals in aquifer solids - Modeled contaminant transport to account for rate-limited sorption-desorption processes and influence of groundwater chemistry on uranium sorption to aquifer solids
Attenuation capacity	- Estimated sorption contribution based on K_d and mass of aquifer solids along groundwater flow path - Assumed no additional inputs of uranium from overlying vadose zone into plume	- Laboratory measurements with aquifer solids to estimate mass flux of uranium derived from smear zone
Stability of attenuation	- No measurement of stability of uranium partitioned to aquifer solids	- Laboratory tests to evaluate reversibility of uranium sorption as a function of contact time and/or uranium solid-phase speciation - Geochemical modeling to assess theoretical stability of identified solid-phase uranium species under relevant field geochemical conditions

Comparison of the information collected under the “Original” and “Revised” column listings illustrates the disparity between what was known at the time of the 1996 ROD and at present. The site-specific knowledge of hydrologic dynamics and uranium geochemistry within the vadose zone and groundwater plume gained from the various tests and characterization methods employed using field samples has significantly reduced the level of uncertainty relative to the processes controlling plume dynamics. Based on the current site knowledge, a decision has been made to use active remedial technologies to control the flux of uranium entering into groundwater from the vadose zone and the zone of fluctuating water table (the “smear zone”). It is anticipated that by minimizing the flux of uranium contributing to concentrations in the groundwater plume, natural attenuation processes may be successful in achieving cleanup objectives in more dilute portions of the plume. In general, the revised information on the mass and speciation of uranium in aquifer solids relative to relevant transport pathways has contributed to more realistic expectations of the role that MNA may play as a component of the groundwater remedy.

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A.2 LAWRENCE LIVERMORE SITE 300—PIT 7 COMPLEX

A.2.1 Introduction

This section discusses the application of MNA as a remedy for the tritium plume under Site 300 at the Lawrence Livermore National Laboratory (LLNL).

A.2.1.1 Setting

Site 300 is located in northern California approximately 60 miles east-southeast of San Francisco and 15 miles southeast of the laboratory's main site. It encompasses more than 11 square miles in the Altamont Hills between the cities of Livermore and Tracy. Tracy, 8 miles from the site, has doubled in population in the last 11 years and is expected to keep growing. The Tracy Hills project, adjacent to the site, has a projected population of 28,000. The site is surrounded by open space used primarily for ranching and recreation, but with the rapid growth that is taking place all over the Bay Area, residential development is proposed for some property adjacent to Site 300.

LLNL's Site 300 is a DOE facility operated by the University of California since 1952. This facility is used to ensure the safety and reliability of nuclear weapons by testing components of nuclear weapons. Since 1955, activities at Site 300 have included fabricating high-explosive compounds and weapons components, testing of explosives and mock nuclear bomb cores, and decontaminating high-explosive equipment. During many of the tests, tritium, depleted uranium, and other pollutants were released to the environment.

Solid wastes from these tests were placed in unlined landfills located on site known as "pits." The Pit 7 Complex encompasses over 3,200 acres and operated 1955–1978 for use in explosives experiments on seven outdoor gravel-covered firing tables. Pit 7 Complex was used to dispose of firing table debris. The pits were constructed by excavating material to 15–25 feet deep. Table A-4 lists pits in the Pit 7 Complex along with their years of operation and estimated volume. Most of the tritium was deposited in Pits 3 and 5; Pit 7 is a source of uranium.

Table A-4. Pits in Pit 7 Complex, years of operation, and estimated volume

Pit	Years of operation	Estimated volume (cubic yards)
Pit 3	1958–1967	26,000
Pit 4	1968–1974	2,800
Pit 5	1968–1979	30,000
Pit 7	1978–1988	31,000

A.2.1.2 Contamination History

Past operations involving the processing, testing, and deactivation of explosive materials resulted in soil and groundwater contamination at the site. Primary COCS include volatile organic compounds (especially trichloroethene), tritium, depleted uranium, and high-explosives compounds. LLNL identified 12 release sites within the Pit 7 Complex.

It was reported that 22,670 curies (Ci) of tritium were used at Site 300. Tritium was released from Pits 3 and 5 beginning in the early 1980s due to a rise in the water table that saturated the landfills and washed radioactive tritium into the groundwater aquifer. This area is recontaminated during rainy years. Because of the heavy rainfall in 1993, 1995, and 1996, additional releases of tritium occurred as groundwater temporarily rose in the contaminated pits. In 1997, it was estimated that approximately 4.0 Ci remained in the pits, approximately 12.5 Ci were washed out and remained in the soil, and approximately 7 Ci were in the groundwater. By 1998, total tritium activity in groundwater was approximately 8 Ci, nearly double the activity in 1994. The tritium plume currently stretches almost 2 miles but is contained within the site boundaries.

Concentrations of tritium in groundwater have been measured at up to 1.8 million pCi/L of groundwater. This is 90 times higher than the state and federal maximum contaminant level (20,000 pCi/L) and 4,500 times higher than the State of California Public Health Goal for tritium (400 pCi/L). All downgradient (southeast of Pit 3) tritium sources still exist in and below the pits. Tritium levels are now well below their historic maximum, but every major rainfall event continues to recontaminate groundwater. An example of this phenomenon is a well that measured 412 pCi/L of tritium in 1997. By October 1999, 1.5 years after an El Niño event, levels had risen to 770,000 pCi/L. By 2009, concentrations had declined to 439,000 pCi/L.

Most soil samples (277 of 397) contained tritium. Ten percent of the samples contained soil moisture with tritium in excess of 1×10^6 pCi/L. The highest reading, collected in 1984, was approximately 8×10^6 pCi/L at a depth of 11 feet. Five hundred and eight samples taken from lysimeters (devices that measure water percolating from soil) obtained similar results. Samples taken within Pit 3 were around 1×10^6 and from Pit 5, around 1×10^5. It was estimated in 2003 that 11.7 Ci remain at Pit 3: 2.4 Ci in the pit and 9.3 Ci beneath the pit.

A.2.2 Technical Description

A.2.2.1 Climate

The climate is semiarid, with an average annual rainfall of 10.44 inches, and windy (LLNL 1999). The site generally experiences warm, dry summers and mild, rainy winters with seasonally heavy rainfall.

A.2.2.2 Hydrogeology

The Pit 7 Complex is underlain by weathered and fractured sedimentary rocks. The spatial and temporal distribution of groundwater is influenced by several factors, including episodic heavy rainfall events, hill slope steepness, and geologic structures including bedding orientation, fractures and faults, and the inclined axes of alluvial drainage channels.

There are several hydrostratigraphic units (HSUs), including an uppermost alluvium HSU and a lower regional groundwater aquifer. During heavy rainfalls, which caused most of the tritium to be released in the first place, the groundwater moves in two directions: shallower groundwater in the upper HSU moves to the southeast, and deeper groundwater in the underlying bedrock (lower HSU) moves east-northeast. This latter flow was detected in the past several years. It was estimated through modeling that during heavy rainfall events (El Niño type) 60% of the water infiltrates into the upper HSU and the lower HSU. The remaining 40% flows south. A nearby spring has been contaminated.

A.2.3 Remediation and Regulatory History

In 1981, DOE began investigation and characterization at Site 300. In 1989, EPA issued a Corrective Action Order under RCRA. After several investigations and removal actions, Site 300 was added to Superfund NPL on August 30, 1990 because of contaminants found by LLNL in groundwater at Site 300 and the total tonnage of material deposited in Site 300 landfills. In the early 1990s, to simplify the cleanup process, LLNL divided Site 300 into eight operable units (OUs). Each OU was to undergo the comprehensive investigation and cleanup requirements set forth in CERCLA. In 1992, LLNL placed a RCRA-compliant cap on Pits 7 and 4, including interceptor trenches, vegetative layer, biotic barrier, and a clay layer. This cover overlaps Pit 3 by approximately 25%.

Under the provisions of CERCLA, LLNL performed an RI/FS with oversight by EPA, the California Regional Water Quality Control Board, and the California Department of Toxic Substances Control. The RI addressed such topics as subsurface geology, groundwater flow, contaminant fate and transport, and the nature and extent of contamination. The RI's purpose was to characterize on-site and potential off-site contamination, as well as to evaluate the risks and hazards associated with the contamination. The FS (LLNL 1999) developed and evaluated alternatives for remedial action to address contamination of environmental media at Site 300. In 2001, interim remedies were selected for most contaminated areas of the site in the *Interim Site-Wide Record of Decision* (LLNL 2001).

The original OU that encompassed the Pit 7 Complex was called the East Firing Area/West Firing Area (EFA/WFA). This area encompassed several pits and firing tables. In 1996, LLNL/DOE proposed to prepare an engineering evaluation/cost analysis (EE/CA), an accelerated cleanup approach, for several OUs, including the EFA/WFA. The draft EE/CA for the EFA/WFA proposed MNA for tritium and uranium in groundwater. Not only did stakeholders take issue with the concept of fast-tracking these areas through the EE/CA process; they also objected to an MNA remedy for these contaminants. DOE/LLNL rescinded its draft EE/CA and decided to prepare a site-wide FS for all areas (OUs) that had not yet been completed. The *Site-Wide Feasibility Study* (LLNL 1999) retained the MNA remedy for both tritium and uranium. Again stakeholders objected on the grounds that a 500-year timeframe for remediation of uranium was unreasonable and that the models for tritium contamination were unreliable. Specifically, as supported by independent analysis, stakeholders held that additional characterization of the Pit 7 Complex area was required. At the same time, stakeholders suggested that in addition to MNA for tritium, hydraulic controls could be used to control the source and capture the distal end of the plume, to be reinjected through a groundwater recirculation well system.

EPA also raised questions about the nature of the uranium in the pits. Site reports stated that only depleted uranium (DU) had been used in the firing tables and that any uranium that did not have the isotopic signature of DU was naturally occurring. EPA responded that there was no reason to separate the discussion of depleted (anthropogenic) and naturally occurring uranium, since the same geochemical processes govern mobilization of both forms. It concluded that “landfill-induced geochemical effects” were the cause of elevated bicarbonate concentrations and that inorganic carbon could also be derived from the oxidation of woody material deposited in the pits; i.e., dissolution of natural carbonates is not the only source of inorganic carbon to the groundwater. Thus, it found that the mobilization of uranium, whether natural or depleted, was caused by LLNL and that all uranium would be subject to cleanup. As a result of that finding, the Pit 7 Complex was removed from the interim site-wide proposed plan (LLNL 2000) and the later interim site-wide ROD (LLNL 2001). Work on the remediation studies for the pits started anew. Remediation for uranium was considered (along with perchlorate), and hydraulic control, combined with reinjection, was assessed for the tritium plume. During that process, LLNL developed a new remedial action goal that stated that the remedy should prevent plume migration.

One of the complicating factors in using an MNA remedy is the California State Water Resources Control Board (SWRB) Resolutions 92-49 and 68-16, both of which mandate that potential drinking water sources should not be contaminated. SWRB Resolution 68-16 is known as the nondegradation policy. That is, groundwater quality cannot be degraded, but should be maintained at background levels if it can be shown that it is technically and economical feasible. Resolution 68-16 allows alternatives if the responsible party can show that nondegradation cannot be practically achieved or it is not more protective of human health. The resolution does not apply to existing polluted groundwater; however, if a plume is allowed to migrate, it degrades downstream water quality. Preventing plume migration, therefore, seemed to require the hydraulic control of the distal part of the tritium plume. Instead, the Regional Water Control Board, charged with interpreting these resolutions, suggested that this remedial action objective (RAO) could be modified due to economic and technical issues. The RAO was eventually altered to state that the remedy should "prevent plume migration to the extent technically and economically practicable."

The resolution of the Pit 7 Complex remedy was signed in 2008 and integrated into the site-wide ROD. It has three major components:

- installing an engineered drainage diversion system to isolate contaminant sources
- pumping and treating the uranium and perchlorate plumes, followed by reinjection of the clean water
- MNA for tritium

A.2.4 Stakeholder Concerns

The remedial strategy places an upstream surface water diversion system to prevent groundwater rising in the pits again; however, it does not capture the downstream tritium plume. It relies on natural decay of tritium to meet RAOs. It also does not require excavation of hot spots that remain in the pits. Stakeholders have been critical of LLNL's model for estimating when tritium concentrations will reach the site boundary because there is not enough information or understanding of how the geologic fault lines will affect the water's path. It is not clear how much of the tritium used at the site (22,670 Ci) is dissolved or what the potential for further contamination will be.

The contaminant plume is very large, and without active capture of the plume, it will become larger. Many of the low-permeability confining layers are discontinuous and do not extend throughout the entire site. Additionally, the site is pock-marked with old wells, springs, and geological faults that may act as vertical conduits for contaminant migration.

Stakeholders wanted LLNL to clean up groundwater to the strictest standard achievable. In many cases, this would require the site to achieve background levels of contaminants. Where this is not possible, stakeholders proposed applying Water Quality Objectives (which are more stringent than MCLs). In all cases, stakeholders wanted to hold LLNL to a level that results in no greater than one in one million excess cancer deaths. It should be noted that the California Public Health Goal for tritium in drinking water states that the concentration considered protective at a 10^{-6} risk level is 400 pCi/L (http://oehha.ca.gov/water/phg/pdf/phgtritium030306.pdf).

Stakeholders also felt that hydraulic control must be part of the remedy. After EPA rejected an MNA-based remedy for uranium, stakeholders suggested that additional capture wells be added and that reinjection be part of the remedy. LLNL performed additional analysis, which concluded that complete capture of the plume and subsequent reinjection would run the risk of further spreading the plume. However, stakeholders suggested that the goal of hydraulic control would not have to be complete stabilization of the plume, which was the goal of the model. They argued that the goal of hydraulic control should be to slow the migration of the tritium plume allowing more time for the tritium to decay. In other words, it did not have to be all or nothing. Some of the tritiated water could be pumped and reinjected with the smaller gallery of reinjection wells for the uranium treatment system. At the very least, stakeholders wanted assurance that there would be a contingency plan in case tritium was moving despite upstream diversion. These suggestions, however, were not included in the remedy.

Stakeholders made another related request that LLNL provide an adaptable strategy that could be optimized as the remedy was staged and as data indicated. Specifically, they proposed that DOE adopt a strategy for cleaning up Pit 7 that would be flexible and iterative, a practice known as "remedial process optimization" (RPO). ITRC guidance on RPO notes that, "Optimization should be an inherent element of the remedy evaluation, selection, and design process" (ITRC 2004).

LLNL's response to this concern was that fate and transport modeling of tritium in groundwater indicates that even if all the tritium in the landfills is added to the preexisting groundwater plumes, tritium activities would decrease everywhere to below the federal and state drinking water standard of 20,000 pCi/L after a maximum of 45 years without impacting groundwater off site above background activities. Hydraulic control would not decrease the total tritium activity in the ground. Its only purpose would be to slow movement of the plume to locations where human or environmental exposures might occur. Furthermore, LLNL responded that the storage capacity of the bedrock is limited. Reinjection of tritium-bearing groundwater into bedrock, especially during high rainfall years, would cause lateral spreading of the tritium plume and could exacerbate groundwater rises into the pits, resulting in additional releases of contaminants. Furthermore, to hydraulically control the plume, tritium-bearing water would need to be brought to the surface, which would create a new exposure pathway for workers. There would be no such exposure pathway in allowing the tritium to naturally decay in the subsurface.

Stakeholders countered that they did not believe it appropriate under California regulations to measure the exposure from a hypothetical point at the boundary of the site. In their view, decisions on the remedy should not rely solely on models. Some key modeling assumptions appear to have been dispelled by the last three recent heavy rain years. More tritium is locked up in the vadose zone than had been predicted, as well as a greater mass of tritium in the groundwater and pits. Consequently, stakeholders did not have confidence in the model's conclusion that the contaminants will be below MCLs by the time the plume reaches the site boundary.

A.2.5 Monitoring Plan Development

There is a site-wide monitoring plan; however, there are no specific contingency plans triggered by increasing tritium concentrations as a result of failure of the enhancement (hydraulic manipulation), and there are no specific extra monitoring requirements for tritium.

A.2.6 References

ITRC. 2004. *Remediation Process Optimization: Identifying Opportunities for Enhanced and More Efficient Site Remediation*. RPO-1. Washington, DC: Interstate Technology & Regulatory Council, Remediation Process Optimization Team. www.itrcweb.org.

LLNL (Lawrence Livermore National Laboratory). 1999. *Final Site-Wide Feasibility Study for Lawrence Livermore National Laboratory Site 300*. UCRL-AR-132609.

LLNL. 2001. *Interim Site-Wide Record of Decision for Lawrence Livermore National Laboratory Site 300*. UCRL-AR- 138470.

LLNL. 2002. *Final Proposed Plan for Environmental Cleanup at Lawrence Livermore National Laboratory Site 300*. UCRL-AR-136376.

A.3 F-AREA SEEPAGE BASINS GROUNDWATER UNIT AT THE SAVANNAH RIVER SITE

This case study illustrates how the understanding of the geochemical environment facilitated development and implementation of enhanced attenuation technologies and how site personnel developed a strategy consistent with the framework presented in Section 3 of this document.

Background. The F-Area Seepage Basins are three unlined basins that received approximately 7 billion liters of predominantly acidic aqueous waste from nuclear processing facilities 1955–1988. The basis for this disposal option was the belief that most of the radionuclides would be bound in the soils directly beneath the basins. This was true for many of the radionuclides disposed, including plutonium isotopes and Cs-137, but many, such as Sr-90, uranium isotopes, I-129, Tc-99, and tritium, are now migrating in the groundwater toward a nearby stream (Figure A-9).

The geology of the site is heterogeneous, poorly consolidated quartz sands and clays. The quartz sands contain varying amounts (typically less than 6 wt %) of surface-active minerals consisting mostly of kaolinite and goethite. The plume is stratified within the water-table aquifer, moving mostly within a highly transmissive unit along the top of a clay that confines the aquifer below and cropping out at seeplines along a stream approximately 500 m from the basins.

The main risk drivers in the groundwater are Sr-90, uranium isotopes, I-129, Tc-99, tritium, and nitrate. The pH of the groundwater within the plume is as low as 3.2 near the basins and increases to the background pH of 5.5–6 at the plume fringes and upgradient of the basins. The aquifer sediments underlying the basins and downgradient have been bathed with acidic solutions for over 40 years, with changes to their mineralogy and texture remaining unknown. The dominant attenuation mechanism for all contaminants except tritium is adsorption, though dilution contributes to attenuation at specific locations.

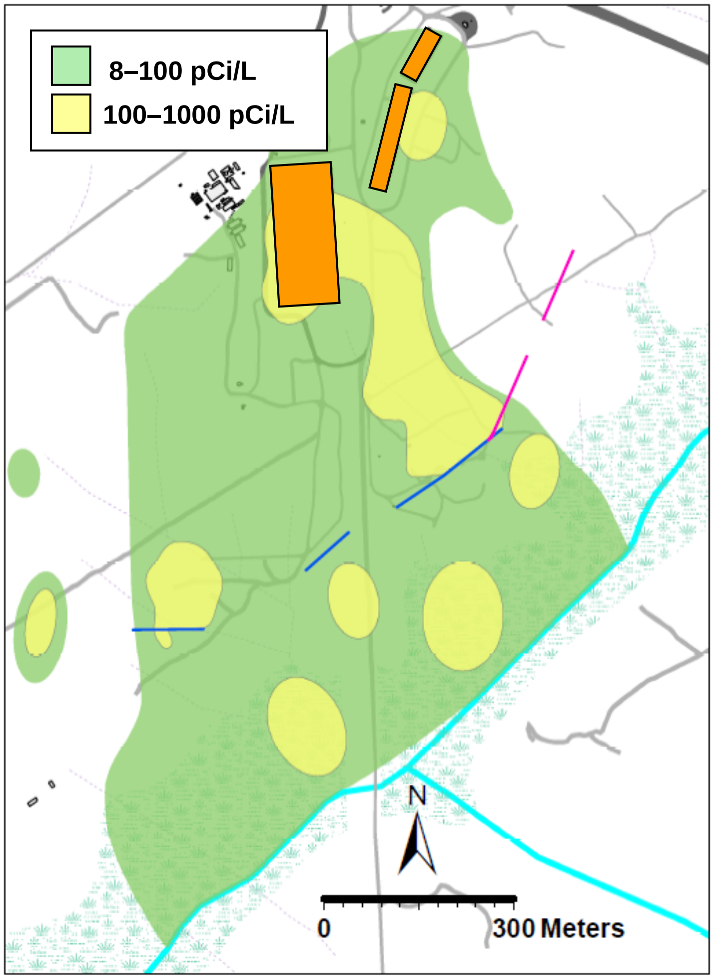

Figure A-9. Extent of strontium-90 plume in water table aquifer.

A.3.1 A Systematic Approach to Selection of Remediation Technologies

As early as 1962 it was known that some contaminants had migrated in groundwater up to 500 ft from the basins. Later, vegetative stress suggested the plume had reached the seepline, and this fact was confirmed by sampling. Extensive sampling and monitoring were done to delineate the plume, which was found to have a footprint of approximately 1 square kilometer.

A lawsuit brought by the Natural Resources Defense Council against the Savannah River Site in 1988 accelerated treatment of this waste unit and associated groundwater under RCRA. The initial action was to address the contamination source, the three basins. So in 1991, the basins were capped after the sediments were stabilized in place using a limestone, blast furnace slag blanket. In 1997, a pump-and-treat remediation system began operation. The system extracted water downgradient of the basins, removed metals and radionuclides in a water treatment unit, and reinjected the water upgradient of the basins in an effort to trap tritium in a hydraulic loop. The water treatment unit was not completely successful at removing all targeted contaminants and was generating large amounts of radioactive solid waste.

A network of monitoring wells is used to measure contaminant concentrations, as well as key indicators that affect the geochemistry within the plume footprint (e.g., pH, redox potential, and specific conductance). Monitoring showed the extent of the plume to be in steady state. It was not expanding downgradient because it had already reached a stream. It was neither expanding nor contracting significantly laterally. Concentrations of contaminants in groundwater from wells adjacent to and downgradient of the capped basins indicated a major flux of contaminants from the vadose zone beneath the basins to the saturated zone. Therefore, MNA was not an option at this point.

Though concentrations were decreasing with time, the trends suggested the pump-and-treat system would have to operate for several decades to meet regulatory goals for stream concentrations. During this time very large amounts of radioactive solid waste would be generated at a very large cost to taxpayers. For these reasons it was decided to identify in situ treatment options that would address the low pH and Sr-90, uranium, and I-129 plumes. This path was consistent with the RCRA permit for this facility. Specific language in the permit that supports development of technologies, as needed, to support cleanup includes "…and develop and test practicable technologies to be employed for the 2b goals (except tritium)…."

A.3.2 Exploiting the Geochemical Evolution of the Waste Site and Evaluating Enhancement Options

A key factor in evaluating a method or methods to attenuate the Sr-90, uranium, and I-129 was to understand the mechanisms controlling their mobility and how to facilitate their stabilization. The low pH (pH 2–4) induced by the codisposed acids were facilitating the mobilization of Sr-90 and uranium. At higher pH (>5) adsorption of these contaminants increases substantially in these aquifer materials, and they become less mobile. The pH of the local uncontaminated groundwater is approximately 5.5; thus returning the pH to its natural value would provide a setting where these contaminants will be stable over the long term.

Laboratory column studies followed by field tests determined that a treatment consisting of injection of alkaline solutions with high buffering capacity would facilitate stabilization. Thus, the enhancement technology would be sustainable. Implementation of this technology began in 2004 with the installation of a modified funnel-and-gate system. The barrier walls of this system direct high concentration lobes of the plume toward the gates. A treatment zone with elevated pH was established extending downgradient from the gates by injecting alkaline solutions. As acidic contaminant-bearing groundwater enters this zone, its pH is neutralized, causing Sr-90 and uranium to adsorb to treatment zone minerals. Monitoring downgradient of the treatment zone indicates that Sr-90 and uranium are being adsorbed in the treatment zone. With time the upgradient portion of the treatment zone loses its buffering capacity and reinjection of alkaline solutions is required. Thus far, reinjection appears to be required every 12–18 months.

While effective, the location of the barrier wall and base injection is midway down the plume, (Figure A-10). In 2009 and 2010, optimization studies are under way to redesign the maintenance injection solution to minimize or eliminate carbonate alkalinity. In addition, it will be determined whether pH neutralization should take place further upgradient or even in the vadose zone to accelerate return of the pH to natural values throughout the plume. A 2009 revision to the facility's Part B RCRA permit includes groundwater remediation by barrier wall and base injection.

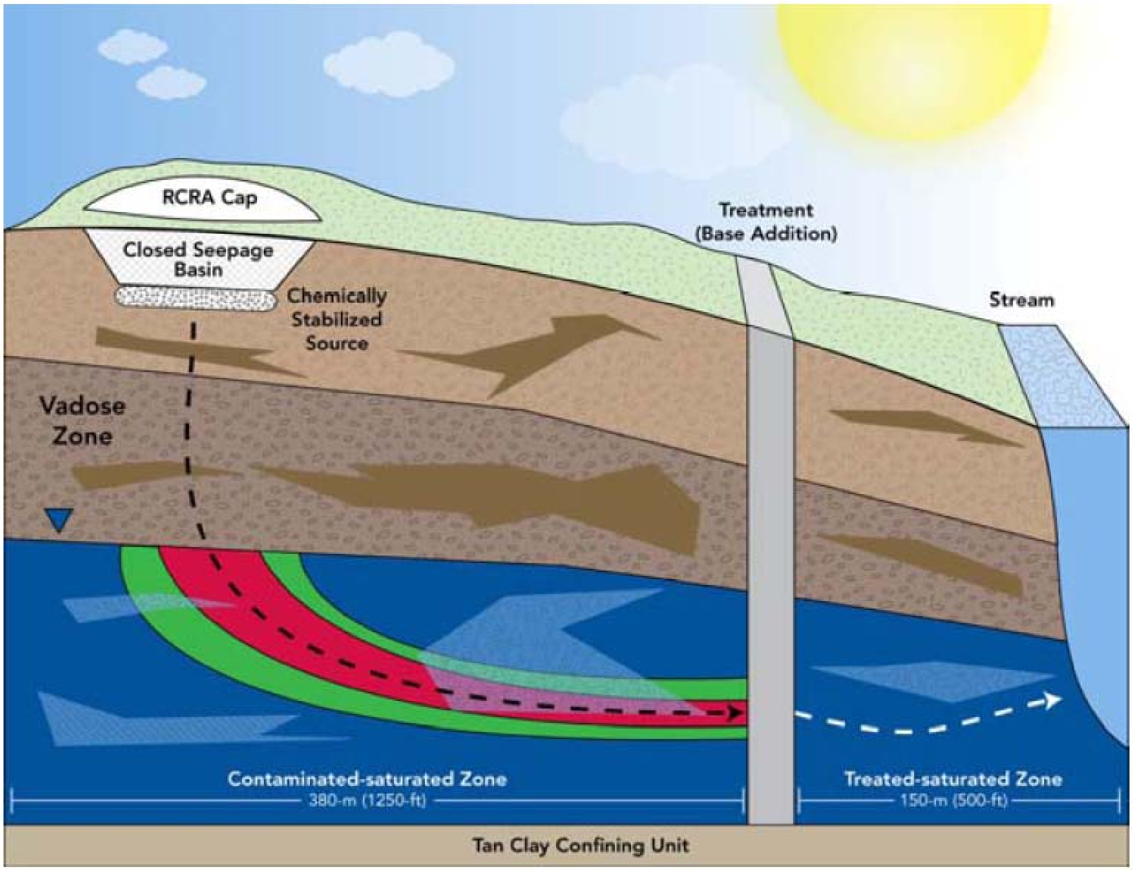

Figure A-10. Example of F-Area seepage base injection remediation. (*Source:* PNNL 2009)

The base injection does not address the I-129, another risk driver at this site. Working through the logic of the decision framework, the answer to “Are enhancement goals achieved?” is a partial “yes.” The base injection is stabilizing Sr-90 and uranium while the barrier wall is reducing tritium concentrations in the stream, but I-129 remains untreated. Returning to the top of the logic chart to address I-129, no additional source/plume treatments were considered. The treatment system that now includes the base injection is not impacting the I-129, and the plume is not stable or shrinking; however, it is not expanding at a rate requiring immediate action. Thus, a second enhancement evaluation to address the I-129 was initiated in 2009 and continued into 2010. The new technology focuses on long-term stabilization of I-129. This technology exploits the very low solubility of silver iodide. Silver chloride particles are injected into the aquifer near the gates. These particles themselves are relatively insoluble but still about six orders of magnitude more soluble than silver iodide. Therefore, as I-129 in the groundwater contacts these particles, it is precipitated as silver iodide, reacting with the silver chloride and releasing chloride ion. Column studies indicated this approach will result in long-term stabilization of the I-129. A field demonstration was initiated in 2009 and will be completed in 2010. As of this date, the final evaluation of the viability of the technology to yield a sustainable enhancement is not complete.

A.3.3 References

PNNL (Pacific Northwest National Laboratory). 2009. *Scientific Opportunities to Reduce Risk in Groundwater and Soil Remediation*. PNNL 18516.

A.4 MONTICELLO MILL TAILINGS SITE

The Monticello Mill, built in 1942, produced uranium and vanadium for military purposes until 1960. The primary sources of contamination from historical operations were mill tailings disposed of in piles along Montezuma Creek (a small stream that ran through the site). Leaching of uranium from the tailings resulted in a groundwater uranium plume within the underlying alluvial aquifer.

Removal of contaminated soil, sediment, and tailings from the facility was completed in 1999, and MNA was selected as the preferred remedy for the groundwater uranium plume in 2004. The decision to implement MNA was based on the presumption that aquifer sediment contained sufficient adsorptive capacity to attenuate uranium once the primary source had been removed.

Although the decision framework discussed in this document was not available when the remedial decisions were made at this site, some elements of the framework were generally followed. However, the groundwater solute transport model used to predict a relatively short remediation timeframe for MNA was based on inadequate soil mineralogy and groundwater geochemistry data. The 42-year timeframe is now considered to be unrealistic, so a pump-and-treat system was implemented in 2009 as a contingency remedy for the groundwater plume.

A.4.1 Introduction

A.4.1.1 Setting

The Monticello Mill Tailings Site (MMTS) is a former uranium and vanadium ore processing mill adjacent to the city of Monticello in southeastern Utah (DOE 2009a, see Figure 4-11). It includes both the 110-acre former uranium and vanadium ore processing mill (millsite) and 1,700 acres of surrounding private and municipal property (DOE 2009b). The mill generated approximately 2.2 million cubic yards of low-level radioactive waste, primarily as tailings, during its years of operation (Table A-5).

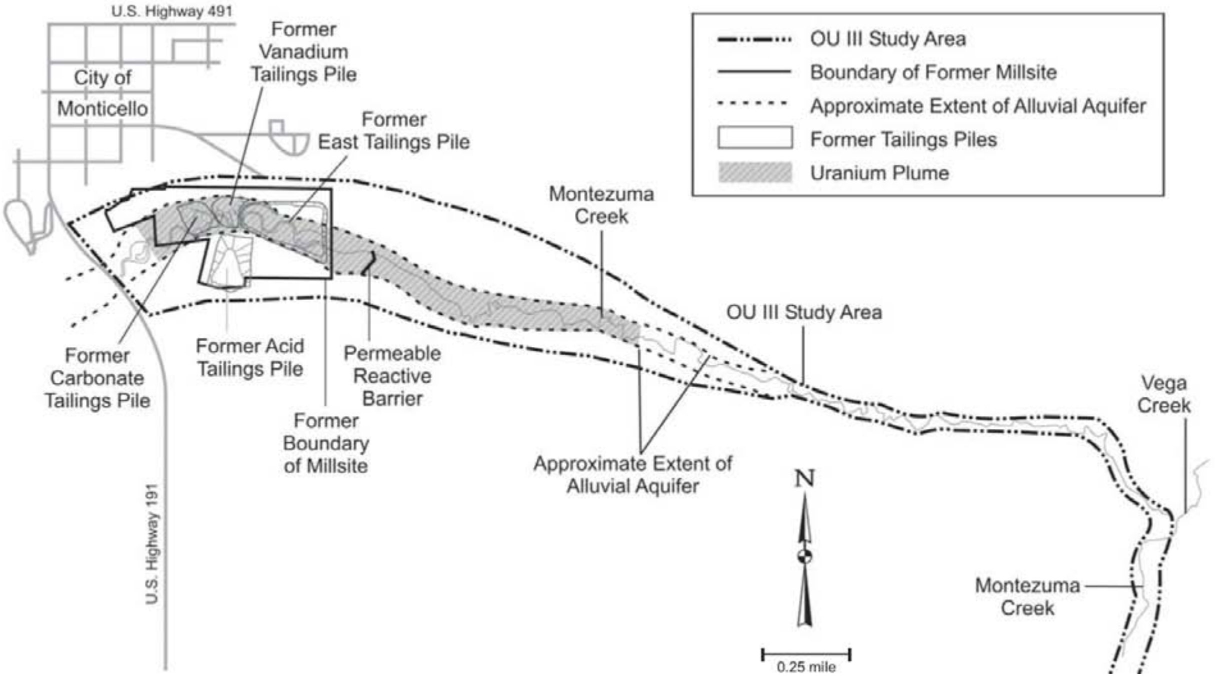

Figure A-11. Monticello Mill Tailings Site.

The elevation at MMTS is approximately 7,000 ft, and the climate is semiarid with four distinct seasons (DOE 2009b). Average annual precipitation is 15 inches, most of which occurs during late summer and early fall storms. MMTS occupies the valley of Montezuma Creek (Figure A-11), a small stream that flows eastward from its origins in the Abajo Mountains, which rise to 11,000 ft about 5 miles west of the site. The valley transitions eastward to an undeveloped, steep-walled canyon of Montezuma Creek. The location of the canyon approximately coincides with the narrowing of the delineated OU III Study Area in Figure A-11.

Table A-5. Chronology of significant MMTS events

Year(s)	Event
1942	Monticello Mill constructed to produce uranium and vanadium for military purposes. Mill tailings locally impounded at four locations along Montezuma Creek.
1960	Milling operations terminated after processing 900,000 tons of ore.
1961–1965	Various measures taken to dismantle mill, bury materials, grade and cover impoundments.
1974–1975	Mill foundation demolished and buried; area graded, revegetated, and fenced.
1979–1991	Environmental investigations of surface and groundwater performed.
1980	Monticello Mill accepted into the Surplus Facilities Management Program to ensure safe caretaking and decommissioning of government facilities.
1989	MMTS placed on the National Priorities List.
1990	ROD approved for OUs I and II (mill tailings and peripheral properties, respectively), requiring that contaminated materials be excavated and placed in an on-site repository.
	ROD for OUs I and II stipulated that a ROD for OU III (Upper and Lower Montezuma Creek) be produced after tailings removed and sufficient data gathered through a focused RI/FS. OU III included soil, sediment, surface water, and groundwater.
1992	OU I and OU II RAs initiated.
	Data collection began for the OU III (groundwater and surface water) RI.
1998	Final RI and Draft FS Reports issued for OU III. Uranium in groundwater identified as the primary human health threat.
	ROD issued for Interim RA (IRA) at OU III that allowed more time to observe the effects of tailings removal before issuing a final cleanup remedy. IRA consisted of institutional controls, millsite dewatering and treatment of contaminated soils and tailings, and evaluation of a PRB.
1998	Soil and sediment removal in OU III completed.
1999	Tailings removal in OU I and construction of zero-valent iron (ZVI) PRB in OU III both completed.
2001	Restoration of OUs I and II completed.
2004	Final RI Addendum/Focused FS Study for OU III completed. Solute transport model calculations performed for RI/Focused FS predict MNA can achieve MCLs for uranium in groundwater in approximately 42 years.
	Final ROD for OU III approved. Selected remedy included MNA, institutional controls, and removal of the PRB. A cleanup time of 42 years was approved, with the condition that contingency remedies would be evaluated and implemented if monitoring showed a lack of progress towards achieving the groundwater MCL for uranium.
2005	Ex situ treatment system installed to supplement PRB in response to excessive mineral precipitation and reduced flow in the PRB.
2009	Explanation of Significant Difference for the MMTS issued, which changed the selected remedy from MNA to a contingency remedy of (1) pump and treat, (2) removal of the PRB, (3) further evaluation of MNA plus pump and treat at the next five-year review, and (4) inclusion of a recently promulgated MCL for uranium of 30 µg/L. Basis for decision was analysis of groundwater uranium trends that showed regulatory criteria for uranium could not be met in 42 years.
	Contingency remedy implemented, which includes an expanded ex situ treatment of groundwater using ZVI.

A.4.1.2 Contamination History

Mill tailings are a sandy by-product of ore milling and were impounded at four locations on the millsite (Figure A-11). These tailings piles were commonly known as the Carbonate Pile, the Vanadium Pile, the Acid Pile, and the East Pile (DOE 2004a). The Carbonate and Vanadium Tailings Piles received wastes from a salt-roast and carbonate-leach milling process. The Acid and East Tailings Piles received wastes from an acid leach and carbonate-leach process.

Prior to their removal in 1999, tailings were dispersed by wind and water erosion, thereby contaminating adjacent properties. Groundwater and surface water contamination also occurred as a result of percolating rainwater leaching the tailings. Based on its relatively wide distribution at high concentrations and its potential risk to human health, uranium was determined to be the primary COC that had been released to groundwater (DOE 1998). The approximate extent of uranium contamination in the underlying alluvial aquifer is shown in Figure A-11.

A.4.1.3 Stakeholders and Remedy Selection

DOE entered into an agreement with EPA and the State of Utah Department of Environmental Quality (UDEQ) to remediate the site under CERCLA. MMTS was added to the NPL in 1989. The MMTS ROD was completed in 1990, and OUs I and II were designated for the remediation of radiologically contaminated soil, sediment, and debris on the millsite (OU I) and peripheral properties (OU II). The removal of contaminated tailings was completed in 1999, and millsite restoration finished in 2001. The 1990 ROD delineated an area known as OU III to address contaminated surface water and groundwater. Figure A-11 shows the extent of OU III in relation to the former mill and other site features.

The RI report for OU III was issued in 1998; however, the companion FS was not completed beyond draft status because it was determined that ongoing OU I and II RAs would significantly and unpredictably impact groundwater and surface water (DOE 2004a). Instead, an IRA was implemented that included institutional controls to restrict use of contaminated groundwater, continuing water quality and hydrologic monitoring, additional study of hydrologic and geochemical factors that affect fate and transport of contaminants at OU III, and implementation of a treatability study using PRB technology with ZVI as the treatment medium.

A Final RI Addendum and Focused FS Report for OU III (DOE 2004b) included a site groundwater model that predicted a restoration period by natural processes of 42 years, beginning in 2002. This prediction, in conjunction with source control measures and institutional controls preventing groundwater use, provided the technical basis for selecting an MNA remedy.

The 2004 ROD for OU III included the following components:

- MNA and comprehensive monitoring to evaluate its effectiveness
- continued implementation and enforcement of the institutional controls that restrict use of the contaminated shallow alluvial aquifer and the restrictive easement that prohibits removal of contaminated sediments from the Montezuma Creek floodplain
- removal of the PRB (which was constructed as a full-scale treatability study during the IRA) after it ceases to be effective in removing contaminants from the groundwater

In 2009, DOE implemented a contingency remedy because trend analyses of monitoring data indicated that groundwater quality standards for uranium could not be achieved in the alluvial aquifer within the 42-year timeframe stipulated in the ROD (DOE 2009b). The contingency remedy, which had been specified in the ROD, included an evaluation of using the pump-and-treat system initially installed in 2005 to supplement the mineral-fouled PRB. Ongoing site monitoring is being performed to evaluate the effectiveness of this contingency remedy.

A.4.2 Site Hydrogeology

The valley of Montezuma Creek is underlain by two groundwater aquifers (DOE 2004b). The upper unit is the alluvial aquifer, consisting of unconsolidated silt, sand, and gravel within the Montezuma Creek paleochannel. Abundant cobbles and up to 15% silt and clay are present in the alluvium. The alluvial aquifer is 200–450 ft wide and is both shallow and thin (with a depth to water and saturated thickness that averages 5–10 ft). The alluvial aquifer has no history of use because of its low yield and the occurrence of alternative sources of water.

The lower aquifer occurs within the Burro Canyon Formation and is used as a secondary source of potable water. It is separated from the alluvial aquifer by sandstones and shales of the Dakota Formation. This aquitard restricts vertical groundwater movement. As a result, beneficial uses of the Burro Canyon aquifer are apparently not impacted.

The alluvial aquifer on the millsite is recharged by underflow from the west and by seeps along the north margin of the valley (DOE 2009b). Total flow of alluvial groundwater at the eastern boundary of the millsite is estimated to be 15–20 gallons per minute. East of the millsite, the alluvial aquifer widens to several hundred feet (north to south), and a losing stream condition prevails. Still farther east (at the head of the canyon), the alluvial aquifer narrows to about 100 ft and remains thin. This constriction forces alluvial groundwater into Montezuma Creek. Also in this reach, the aquitard separating the alluvial and Burro Canyon aquifers has been eroded by the creek, thereby allowing groundwater from the semiconfined Burro Canyon aquifer to discharge. Upward flow (and subsequent dilution) prevents eastward movement of contamination in the alluvial aquifer beyond the location shown in Figure A-11.

A.4.3 Description of Contamination

A.4.3.1 Groundwater Contamination

Groundwater contaminants include arsenic, manganese, molybdenum, nitrate, selenium, uranium, vanadium, and gross alpha and beta activity; however, contamination is generally restricted to the eastern portion of the millsite and the area upgradient of the PRB (DOE 2009b). The most widespread contaminant in OU III is uranium, which forms the groundwater plume shown in Figure A-11. This plume (defined as the area where MCLs are exceeded) extends eastward approximately 1 mile downgradient of the former millsite.

A.4.3.2 Surface Water Contamination

Uranium and selenium are the only COCs to exceed remediation goals in surface water samples (DOE 2009b). Although standards for these contaminants are not exceeded within about 1 mile downstream of the millsite, a relatively constant concentration of uranium and selenium persists through the remainder of OU III. It is hypothesized that residual mill tailings in floodplain and creek bank deposits contribute to the observed rise in contaminant concentrations. An explanation for surface water trends is currently being sought by DOE.

A.4.3.3 Contamination in Soils and Sediment

A remedy was selected to excavate known areas of contaminated soil and sediment in OU III and to backfill with clean material (DOE 1998). This remedy was not implemented, however, in a 0.5-mile reach approximately 1 mile downstream of the millsite, where it was determined that the reduction in the risk could be attained only by causing environmental damage that would be excessive compared to the health benefits. Institutional controls, consisting of long-term surveillance and maintenance and restrictive easements, were included for the canyon.

A.4.4 Conceptual Model of Contaminant Attenuation

Table A-6 shows a sequence of decisions tied to the MNA Decision Framework (Figure 3-1).

Table A-6. Technical Gaps in Monticello Mill Tailings Site MNA Decision Framework

Decision Framework issue	EPA-recommended technical approach	Monticello Mill Site technical approach	Technical gaps
Is the plume stable or shrinking (Tier I)?	Characterize groundwater flow direction and gradients, aquifer hydrostratigraphy	Determined hydraulic units, performed head and flow measurements, and calculated flow directions.	None.
	Determine contaminant concentrations in groundwater and aquifer solids	Time-series groundwater uranium concentration trends show that the plume is either stable or decreasing.	Contaminant concentrations in aquifer solids not adequately characterized (values used in solute transport model inferred from batch sorption studies—see below). Also, groundwater plume concentrations found to be greater than originally understood during selection of MNA remedy.
Do attenuation rates support a reasonable timeframe (Tier II)?	Develop flow model	Flow model calibrated to measured groundwater levels and groundwater discharge flows.	None.
	Perform detailed groundwater chemistry characterization	Analysis performed during 1998 RI.	The variability in groundwater chemistry is important to understanding uranium mobility but was not incorporated into either the CSM or transport model in the Final RI Addendum/Focused FS Study (2004).
	Evaluate aquifer mineralogy, aqueous speciation	Aqueous speciation considered in 1998 RI, but mineralogy not determined.	The effect of mineralogy and speciation not included in the CSM or solute transport model (RI Addendum/Focused FS Study 2004).
	Identify reaction mechanism	Laboratory batch studies identified sorption as an important attenuation mechanism.	The variability in sorption capacity of aquifer solids not adequately determined in experiments.

Decision Framework issue	EPA-recommended technical approach	Monticello Mill Site technical approach	Technical gaps
Is the system capacity sufficient (Tier III)?	Determine contaminant fluxes	Laboratory column leaching studies performed on vadose zone soils. Concentrations used in conjunction with estimated recharge rates as input to transport model.	None.
	Determine mass of available solid phase reactants	Analysis not performed, but capacity assumed sufficient based on removal of primary source and subsequent groundwater uranium trends.	Solute transport model assumes sorption occurs under identical conditions of batch tests.
Is the contaminant stability sufficient (Tier III)?	Test immobilized contaminant stability	Laboratory column leaching studies performed on saturated aquifer material.	Results showed uranium leaching from solids, but results not used to update CSM or solute transport model.
	Perform model analysis to characterize aquifer capacity and contaminant stability	Solute transport model used to predict long-term changes in uranium plume.	Model overestimates contaminant stability due to factors reported above.
Can regulatory criteria be met?	Select monitoring locations and frequency consistent with heterogeneity	Post-remediation monitoring occurring at groundwater monitoring wells in alluvial and bedrock aquifers, as well as surface water seeps and Montezuma Creek.	None.
	Select monitoring parameters	Parameters include COCs (e.g. uranium), major cations, and anions.	None.
	Select conditions that “trigger” reevaluation of monitoring program	Statistical trend analysis of groundwater uranium concentrations used to determine whether remediation goal can be met in a reasonable timeframe.	None. (Note: Trend analysis for major ions would help identify whether there are changes in site geochemistry since tailings removal.)
	Select alternative remedy best suited to site conditions	Remedy includes using a pump-and-treat system.	None.

A.4.4.1 Assessment of Plume Stability

An assessment of plume stability was made following the removal of mill tailings and a subsequent period of evaluation as recommended in Figure 3-1. This assessment included the characterization of groundwater flow directions and hydrostratigraphy, as well as, a determination of contaminant concentrations in groundwater and aquifer solids (DOE 2004a).

Monitoring results have shown that the removal of tailings piles has resulted in a significant decrease in all mill-related contamination in OU III groundwater. Uranium concentrations, in particular, have exhibited large initial effects from source removal in areas near the former millsite. Although trending has been more variable at other locations, the uranium plume has consistently terminated near the location shown in Figure A-11, suggesting plume stability.

A.4.4.2 Assessment of Attenuation Mechanism and Rate

A two-dimensional solute transport numerical model was developed to predict the rate of attenuation of the observed uranium plume within the alluvial aquifer (DOE 2004a). The hydrogeologic component of the model was calibrated to groundwater levels and discharge flowrates by adjusting hydraulic conductivities and model boundary conditions. Uranium attenuation was simulated by the model as an equilibrium partitioning process between groundwater and aquifer materials. Although the solute transport component of the model was not calibrated to monitoring well data, predicted uranium concentrations were compared to observed trends at several OU III locations to evaluate consistency.

The distribution coefficient (or K_d) used in the solute transport model was based on batch sorption tests that included native alluvial deposits from uncontaminated regions of the aquifer and an aqueous solution prepared in the laboratory (this solution was purportedly representative of site groundwater). Six-point variable mass batch tests were conducted following procedures outlined by ASTM, and test results indicated a very narrow range in K_d values (2.8–3.3 kg/L).

The solute transport model, using the lower K_d value of 2.8 kg/L, predicted remediation by MNA would result in groundwater uranium concentrations below MCL values in approximately 42 years. This timeframe was accepted by the EPA, UDEQ, and DOE.

A.4.4.3 Assessment of Capacity for Plume Attenuation

According to documents reviewed for this report, the capacity of the aquifer for attenuating uranium was inadequately characterized. As discussed by EPA (2007), factors that affect sorptive capacity include contaminant fluxes, changes in groundwater chemistry, and insufficient mass of solid reactants. Of these, only the contaminant fluxes were explicitly measured.

Mass fluxes were determined from column leach tests that used residual subpile soils not originally excavated during tailings removal. Because experimental results indicated that uranium was readily mobilized, additional subsoil was excavated at the site. A subpile source term was also included in the solute transport model.

Mass fluxes were not determined for other contaminated soils in the study area, such as soils and sediment in the stream banks and floodplains. In addition, the effect of variable site geochemistry was not captured by the simple batch experiments that used a single, simulated groundwater and alluvial sediment. As a result, the representativeness of the K_d value used in the solute transport model is highly uncertain.

A.4.4.4 Assessment of Stability of Immobilized Contaminant

Column leach tests were also performed on samples of alluvium collected from the saturated zone to determine whether, after mill tailings removal, residual uranium in the aquifer would leach at significant concentrations. Although results indicated that appreciable leaching of uranium from the sediments to groundwater would be expected, these results were not included in the CSM or solute transport model.

A.4.5 Assessment of Remedy Performance

A.4.5.1 Assessment of Monitored Natural Attenuation

The ROD for OU III stipulated that observed concentrations for uranium would be compared to predictions from the solute transport model for OU III as a measure of restoration progress. If the model-predicted average was less than the lower limit of uncertainty for the observed average of uranium for three consecutive sampling events, additional statistical trend analyses would be required, including trends evaluated on a well-by-well basis, as regional averages, and under assumptions of cyclical and noncyclical seasonal variation.

The rate of aquifer restoration was found to be less than model predictions in four out of five regions in OU III between 2004 and 2009 (DOE 2009b). Also, although statistically significant downward trends were recognized at many of the OU III monitoring wells, nontrending uranium concentrations were identified at most. It was concluded that the restoration period would likely be longer than the approved 42-year period. As a result, it was decided to implement the contingency remedy.

A.4.5.2 Contingency Remedy Implementation

A contingency remedy was implemented in 2009 that included the following components (DOE 2009b): (1) a pump-and-treat groundwater system to remove and treat the uranium plume upgradient of the funnel and gate PRB treatment wall; (2) removal of the PRB gate and replacement of the gate with a containment system, which allows for continued treatment of the contaminated plume; (3) further studies to be conducted through 2012 to determine whether the pump-and-treat contingency remedy, together with monitored natural attenuation, is a viable remedy at the surface and groundwater operable unit; and (4) inclusion and evaluation of a new protection standard for uranium in surface water as an RAO.

The ex situ groundwater pump-and-treat system was installed in 2005 (and later expanded in 2007) as an alternative to the in situ PRB. The pump-and-treat system was designed to target the aquifer region between the PRB and former millsite to evaluate the feasibility of this treatment technology in attaining groundwater restoration objectives. The system functions by pumping groundwater through two cylindrical concrete vaults that contain the treatment medium (a ZVI and gravel mixture). Ongoing biannual monitoring includes the collection and analysis of surface water as well as alluvial and bedrock aquifer groundwater samples for COCs and other geochemical parameters.

A.4.6 Lessons Learned

Based on EPA's most recent guidance (EPA 2007a, 2007b), geochemical analyses conducted during site characterization were insufficient. This lack led to the misconception that MNA could achieve groundwater standards for uranium within 42 years. A more-detailed explanation of specific deficiencies for each investigative phase includes the following:

- Underreporting of the nature and extent of contamination (Table A-6) resulted in an inadequate equivalent of a Tier I analysis. This shortcoming was revealed during a subsurface investigation conducted in 2009 to better define the uranium plume and subsurface geology of the alluvial aquifer in OU III. It was found that uranium contamination (particularly south of Montezuma Creek) was much greater in area and magnitude than was determined as the starting condition in the OU III solute transport groundwater model. Concentrations were 2–3 times higher and distributed over a larger area. Furthermore, because the initial uranium mass on aquifer sediments used in the solute transport model was calculated as the product of the assumed K_d value and dissolved uranium concentrations, this value was also likely underestimated.

- The potential variability in K_d values in batch tests was inadequately constrained (Table A-6), making the determination of the mechanism and rate of attenuation (Tier II) difficult. Batch studies performed for MMTS consisted of three uncontaminated soils and one "representative" groundwater. However, according to Davis et al. (2004), K_d values for uranium can vary by five orders of magnitude over the pH range 6–9 and by four orders of magnitude at pH 8 as a function of alkalinity. The presence of carbonate and acid tailings, as well as potentially reducing conditions in the vicinity of the PRB (Morrison, Metzler, and Carpenter 2001) and site wetlands (Figure A-11) suggest the presence of variability in site chemistry that likely affects uranium partitioning (see also Dong and Brooks 2008; Fox, Davis, and Zachara 2006; Hockley, Bowell, and Day 2000; Hyun et al. 2009). In a separate study at the Naturita, CO uranium millsite, Curtis, Davis, and Naftz (2006) found that alkalinity varied by a factor of 10 in site groundwater, leading to site K_d values that varied over a similar range. Consideration of the potential variability in geochemical parameters that affect adsorption at MMTS would have necessitated batch tests using pore water and aquifer materials from the plume. In addition, a series of sensitivity model runs using results from these experiments would likely have predicted considerably longer remediation in many of the simulations.

- Leachate tests that showed considerable solubilization of uranium from aquifer solids indicated that uranium residing on the aquifer matrix was not stable (Table A-6). An analysis of the stability of the immobilized contaminant under Tier III in the decision framework (Figure 3-1) is intended to evaluate this condition. Also, had an analysis of K_d values been performed using aquifer solids and groundwater and/or colocated site aquifer/porewater samples, insight would have been gained concerning the appropriateness of a linear K_d model. In cases where uranium solid-phase concentrations are not linearly related to the dissolved concentrations, then either a Langmuir, Freundlich, or surface complexation model may better predict MNA performance.

MMTS has benefitted from having an adequate monitoring plan to support a remedy performance evaluation methodology, which are elements of Tier IV. It was also advantageous to have a contingency plan in place—another element of Tier IV. The reevaluation triggered by a Five-Year Review has provided an opportunity to identify data or technical gaps in the remedy selection process (Table A-6).

MNA continues to be a part of the remedy at MMTS. Having the guidance provided by the decision framework can provide a basis for future evaluations of the MNA portion of the remedy.

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Appendix B

Links to Additional Resources

LINKS TO ADDITIONAL RESOURCES

Many Internet sites and other references include some useful information on natural attenuation and MNA. The following resources are listed only to provide a starting point for readers to start or continue their own research.

State/agency	Link	Brief description
Air Force Center for Engineering and the Environment	www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/monitorednaturalattenuation/index.asp	An interactive website that explores the topic of natural attenuation, which includes evaluation models, biodegradation calculations, case studies, and sample work plans.
Alaska	www.dec.state.ak.us/spar/csp/guidance/nat_doc.pdf	Provides background information on natural attenuation processes, outlines information which must be collected and considered when evaluating whether natural attenuation is an appropriate remedy at a specific site, and identifies elements which should be addressed in a cleanup operations plan.
Army Corps of Engineers	http://140.194.76.129/publications/eng-regs/er1110-1-8157/a-b.pdf	Engineering and Design–Geotechnical Data Quality Management for Hazardous Waste Remedial Activities, Appendix B.
Center for Public Environmental Oversight	www.cpeo.org/techtree/ttdescript/natatt.htm	A fact sheet overview of MNA. Also provides links to additional resources.
Connecticut	www.ct.gov/dep/cwp/view.asp?a=2715&q=325012&depNav_GID=1626	Provides a gateway page for the Connecticut's Remediation Standard Regulations. The part that applies to groundwater is Section 3, starting on p. 22, especially Section f, which defines compliance criteria.
	www.ct.gov/dep/cwp/view.asp?a=2715&q=325006&depNav_GID=1626	A fact sheet that recognizes MNA sites to be considered differently from those where source control may still be needed.
	http://cga.ct.gov/2010/sup/chap445.htm#Sec22a-134.htm	A statute for property transfer programs in Connecticut.
Delaware	www.dnrec.state.de.us/DNREC2000/Divisions/AWM/sirb/Final_Plans/Final%20Plan%20Reichhold%20Chemical.pdf	Includes a description of a particular site in Delaware, the analytical results of the RI, and the selected remedy as described in the FS, which is sometimes MNA.
Federal Remediation Technologies Roundtable	www.frtr.gov/matrix2/section4/4-32.html	An overview of MNA. Also provides links to additional resources.
	www.frtr.gov/matrix2/section4/4-32/html	Guidance document: *FRTR Remediation Technologies Screening Matrix and Reference Guide*, Vers. 4.0, geared to organics.
Florida	www.dep.state.fl.us/waste/quick_topics/rules/documents/62-780.pdf	Provides guidelines for contaminated site cleanup criteria (see Chapter 62-780).
	www.dep.state.fl.us/waste/quick_topics/rules/documents/62-777/TableVNaturalAttenuationDefaultConcs4-17-05.pdf	Provides a table of default criteria for natural attenuation.
	www.dep.state.fl.us/waste/quick_topics/rules/documents/62-777/TableIVSite-SpecificConditions4-17-05.pdf	Contains site-specific conditions and geochemical parameters for natural attenuation evaluation.
Indiana	www.in.gov/idem/4807.htm	Department of Environmental Management criteria by which sites requesting MNA as a remedial option will be evaluated.

Minnesota	www.pca.state.mn.us/water/groundwater/natural-attenuation.html	Fact sheet/policy on MNA of chlorinated solvents; no information could be found on inorganics.
Missouri	http://dnr.mo.gov/env/hwp/mrbca/mrbca.htm	Chapter 6 (Section 6.8.4) provides an overview on evaluation of occurrence and rate of natural attenuation/biodegradation. Indicators of natural attenuation can be broadly classified into three groups: primary, secondary, and tertiary lines of evidence.
	http://dnr.mo.gov/pubs/pub2110.pdf	This fact sheet, titled "Monitored Natural Attenuation of Groundwater Contamination at Brownfields/Voluntary Cleanup Program Sites," was published by the Missouri Department of Natural Resources.
New Hampshire	http://des.nh.gov/organization/commissioner/pip/publications/wmd/documents/natl_attenuation.pdf	This policy provides guidance for the selection of natural attenuation as a remedial measure to restore groundwater contaminated with volatile organic compounds to Env-Ws 1403 Ambient Groundwater Quality Standards (AGQS).
South Carolina	www.scdhec.gov/environment/lwm/regulatory.htm#hazardous	Laws and regulations relevant to hazardous waste management in South Carolina.
	www.scdhec.gov/environment/lwm/regulatory.htm#radiological	Laws and regulations relevant to radiological waste management in South Carolina.
South Dakota	www.state.sd.us/denr/DES/ground/Spills/Handbook/Chapter4.pdf	Handbook for petroleum from 2000 Federal Register.
Texas	www.tceq.state.tx.us/comm_exec/forms_pubs/pubs/rg/rg-366_trrp_33.html	Describes the elements and development of demonstrations for MNA at affected properties.
U.S. EPA	www.clu-in.org/techfocus/default.focus/sec/Natural%5FAttenuation/cat/Guidance/	The U.S. EPA CLU-IN Technology Innovation Program's "Contaminated Site Clean-Up Information" website provides information with a page solely dedicated to natural attenuation. The page provides an overview on natural attenuation as well as guidance, training, and additional resources.
	www.epa.gov/nrmrl/pubs/600R98128/protocol.pdf	Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water.
	http://clu-in.org/download/citizens/mna.pdf	Fact sheet, "A Citizen's Guide to MNA," provides a brief introduction to basic concepts (pdf, 2 pp.).
	www.clu-in.org/download/techdrct/tdeec01004.pdf	A Science Advisory Board (SAB) review of MNA (pdf, 66 pp.).
U.S. Navy	https://portal.navfac.navy.mil/portal/page/portal/navfac/navfac_ww_pp/navfac_nfesc_pp/environmental/erb/rits_page/tab5390723/nas2.pdf	PowerPoint presentation discussing MNA.
U.S. Geological Survey	http://toxics.usgs.gov/definitions/natural_attenuation.html	This USGS Toxic Substances Hydrology Program page is dedicated to natural attenuation with an overview of other agencies and organizations for natural attenuation policies and guidance. This site also includes related headlines and information on natural attenuation and related topics.
	www.clu-in.org/download/contaminantfocus/dnapl/Treatment_Technologies/NA-Wetlands-Protocol.pdf	Draft Technical Protocol for Characterizing Natural Attenuation of Chlorinated Solvent Ground-Water Plumes Discharging into Wetlands.
Vermont	www.anr.state.vt.us/dec/wastediv/SMS/pubs/capdoc1197.pdf	Provides corrective action guidance which states "Natural attenuation of contamination is an acceptable remedial alternative to evaluate during the review of corrective action technologies."

Wisconsin	http://dnr.wi.gov/org/aw/rr/archives/pubs/RR614.pdf	This document provides technical guidance for evaluating natural attenuation processes in remediating groundwater contaminated with petroleum products. Metals (e.g., lead) are discussed on p. 10.

Appendix C

Survey of State Regulators and Stakeholders

Summary of Survey Findings

Attenuation Processes for Metals and Radionuclides: A Survey of State Regulators and Stakeholders

Internal Final
January 2009

Prepared by
The Interstate Technology & Regulatory Council
Attenuation Processes for Metals and Radionuclides Team

CONTENTS

ATTENUATION PROCESSES FOR METALS AND RADIONUCLIDES: A SURVEY OF STATE REGULATORS AND STAKEHOLDERS

C.1 INTRODUCTION

A number of Department of Energy (DOE) sites, Nuclear Regulatory Commission (NRC) sites, and many Superfund and Department of Defense (DOD) sites are contaminated with radionuclides and/or metals. One of the remedial approaches is to use attenuation-based processes that rely on the immobilization of contaminants as stable, nontoxic species and/or radioactive decay. Until the recent publication of the Environmental Protection Agency's (EPA) three-volume technical report series *Monitored Natural Attenuation of Inorganic Contaminants in Groundwater*, there were no regulatory compliance guidance documents that specifically addressed the use of attenuation-based remedies for metal- and radionuclide-contaminated groundwater. This lack of guidance has contributed to inconsistent approaches and application of attenuation-based remedies and has generally discouraged consideration of such remedies. The net result is that many sites face intractable closure problems. The Interstate Technology & Regulatory Council (ITRC) Attenuation Processes for Metals and Radionuclides Team is in a unique position to develop guidelines that will facilitate the use of this new EPA guidance.

An initial step in deciding on the specific approach of the ITRC product is determining the existing state of regulatory acceptance regarding the concept of the attenuation process and its deployment. To assess this, ITRC developed a Web-based survey of regulators and stakeholders in conjunction with ongoing research at EPA and DOE national laboratories. The findings of the survey are presented in three parts, each with specific objectives.

C.1.1 Survey Structure

The survey contained 29 questions with either multiple choice or text answers. The survey was organized into three parts, each with specific objectives. Part A sought information to assess the extent to which monitored natural attenuation (MNA) and other attenuation-based remedies have been implemented at sites with metals and/or radionuclide contamination. Part B assessed respondents' familiarity and level of comfort with various aspects of MNA and attenuation-based remedies and will be used to direct future research. Part C sought additional details regarding specific contaminants at sites where natural attenuation has been approved.

C.1.2 Data Collection Methods

A Web-based survey was published on the ITRC website on August 3, 2008 for an initial response period of 30 days. This period was later extended to November 24, 2008. Requests to complete the survey were submitted to 53 ITRC state points-of-contact (POCs) across the United States and later to 56 attendees of a three-session training of "Monitored Natural Attenuation of Inorganic Contaminants in Groundwater" presented by personnel from EPA's national research laboratories. The POCs and training attendees were asked to have representatives within their regulatory agencies respond to the survey. Respondents were asked to complete the online survey and were told that the survey would take 10–15 minutes to complete. All survey responses were compiled into an online database. Not all respondents answered all questions.

C.2. EVALUATION OF SURVEY RESULTS

C.2.1 Respondent Demographics and Regulatory Program Jurisdictions

Members of the Attenuation Processes for Metals and Radionuclides Team (the Team) evaluated results from the survey. Twenty-three responses were received from regulators from 16 states, as shown in Figure C-1. In addition to state representatives, two stakeholders, and one tribal representative responded to the survey.

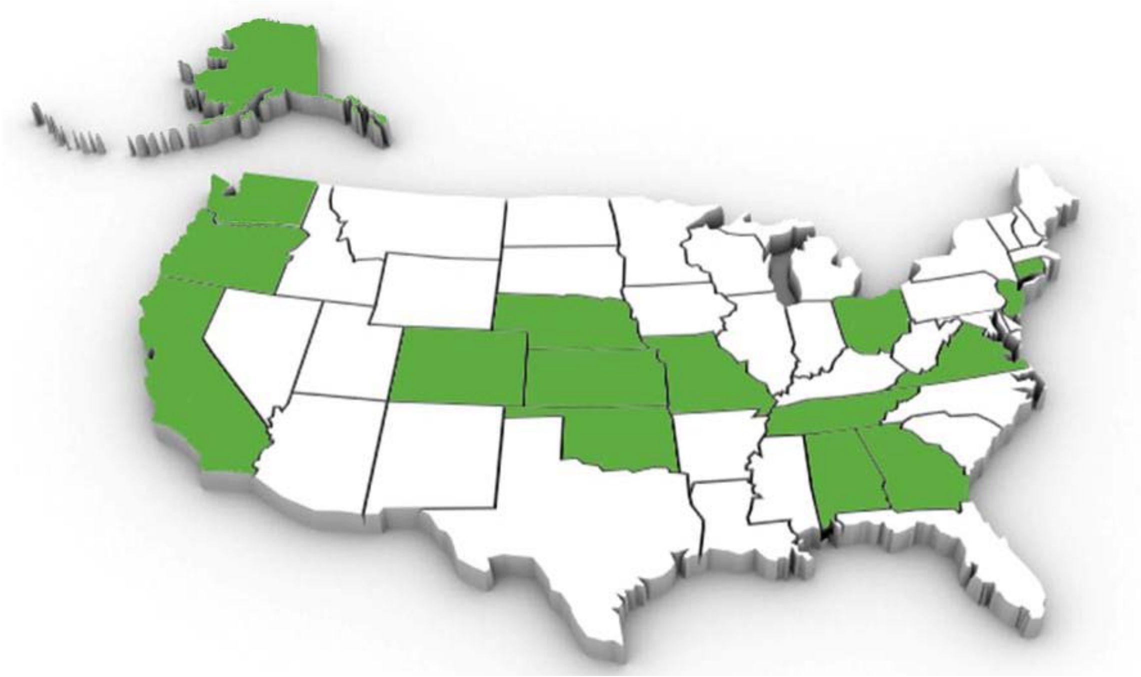


Figure C-1. States represented in this survey.

C.2.2 Part A: Implementation of Remedies

This section provides the findings of each question provided in Part A of the survey. Each question is provided along with the data, which are presented in both a figure and in narrative form when appropriate.

C.2.2.1 Question 3: Familiarity with Technical Aspects of Natural Attenuation for Metals

Q: *How familiar are you with regulatory and technical aspects of natural attenuation for* ***metals****?*

When asked about their level of familiarity with regulatory and technical aspects of natural attenuation for metals, 5 indicated that they were very familiar, 11 replied that they were familiar, 8 said they were somewhat familiar, and 2 were not familiar (see Figure C-2).

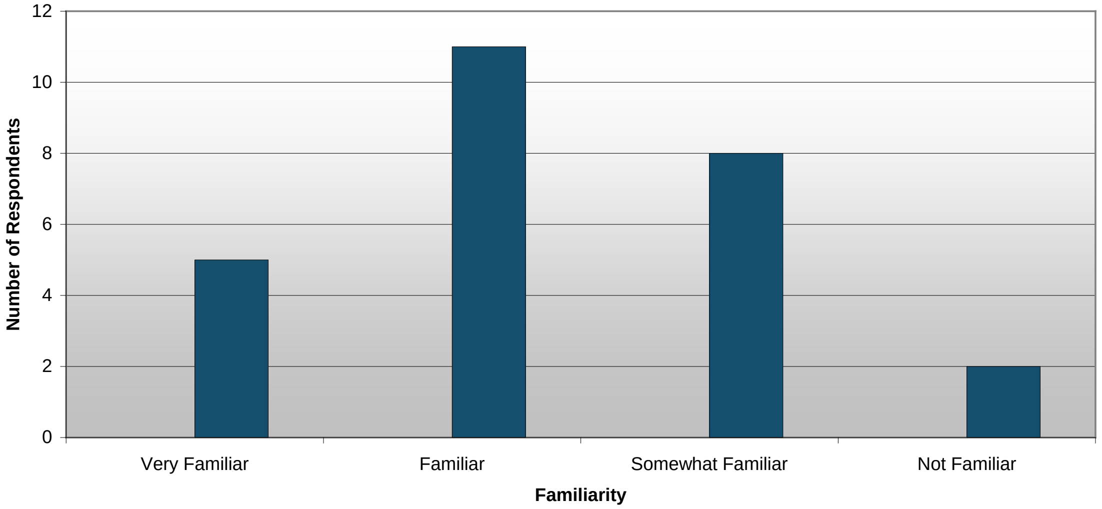


Figure C-2. Respondents' level of familiarity with natural attenuation for metals.
(6 respondents did not answer this question)

C.2.2.2 Question 4: Familiarity with Technical Aspects of Natural Attenuation for Radionuclides

Q: *How familiar are you with regulatory and technical aspects of natural attenuation for **radionuclides**?*

In comparison to the findings of question 3, when asked about their level of familiarity with regulatory and technical aspects of natural attenuation for radionuclides, 4 indicated that they were very familiar, 6 replied that they were familiar, 4 said they were somewhat familiar, and 12 were not familiar (see Figure C-3).

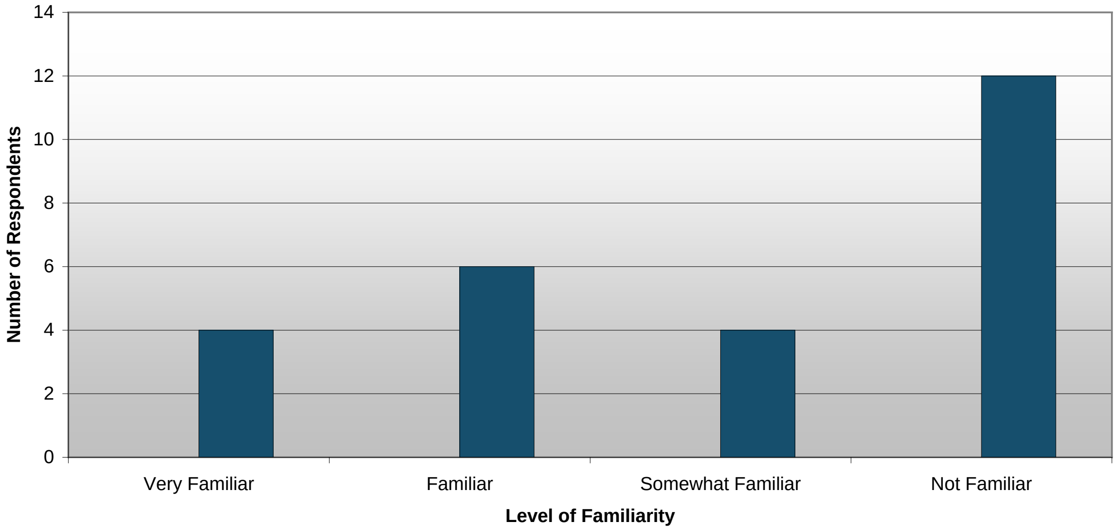


Figure C-3. Respondents' level of familiarity with natural attenuation for radionuclides.
(6 respondents did not answer this question)

C.2.2.3 Question 5: Estimated Number of Known Sites with Metals and/or Radionuclides Contamination in Groundwater

Q: *Within your program jurisdiction, what is the estimated number of known sites with metals and/or radionuclides contamination in **groundwater**?*

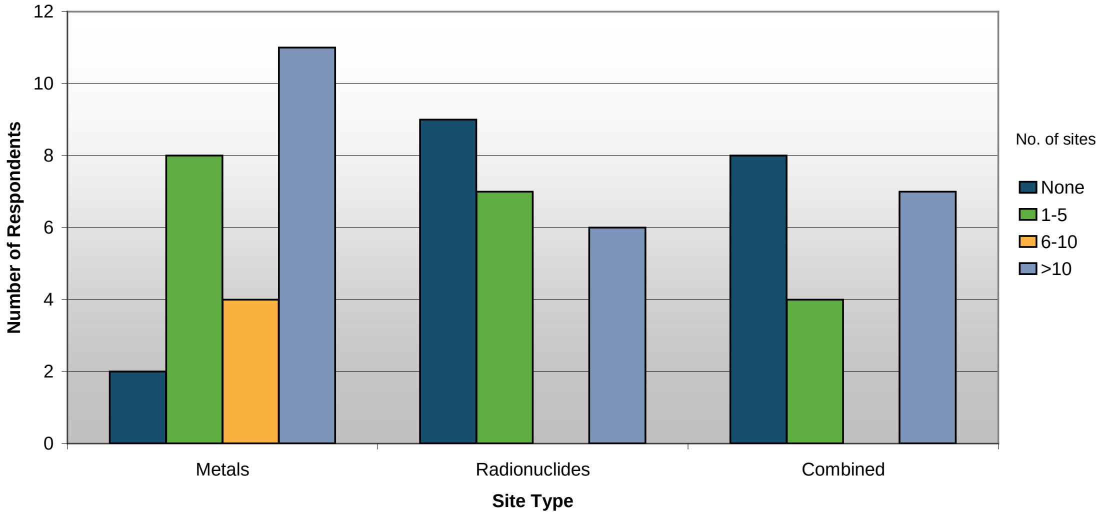


Figure C-4. Respondents' estimated number of known sites with metals and/or radionuclides contamination in groundwater. (1 respondent did not answer this question)

C.2.2.4 Question 6: Estimated Number of Known Sites with Metals and/or Radionuclides Contamination in Soils

Q: *Within your program jurisdiction, what is the estimated number of known sites with metals and/or radionuclides contamination in <u>soils</u>?*

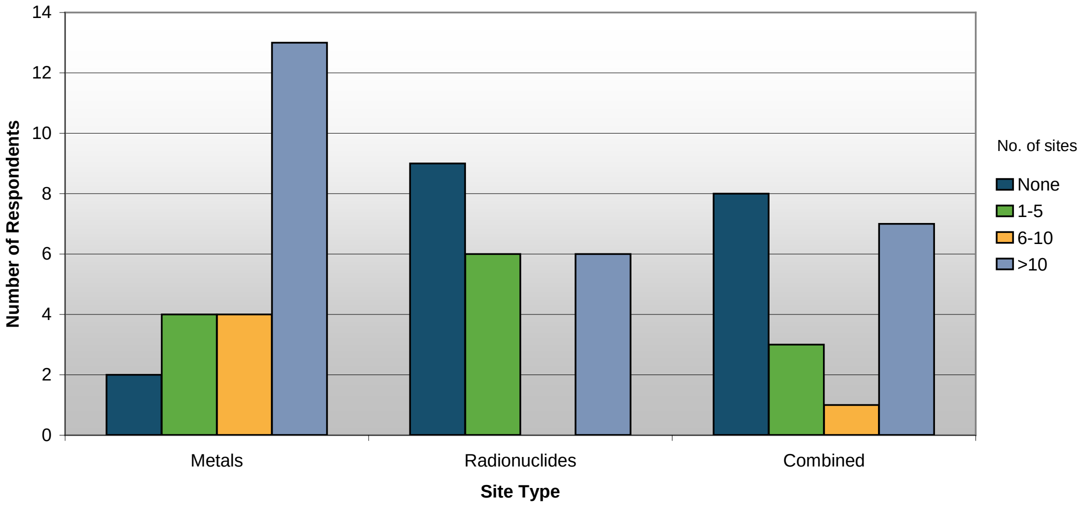


Figure C-5. Respondents' estimate number of known sites with metals contamination in soils. (2 respondents did not answer this question)

C.2.2.5 Question 7: Quantity of MNA Remedies Approved for All or Part of the Remedial Strategy for Sites Contaminated with Metals in Groundwater

Q: *Within your jurisdiction, how many MNA remedies have been approved as all or part of the remedial strategy for sites contaminated with* ***metals*** *in groundwater? (Check all that apply.)*

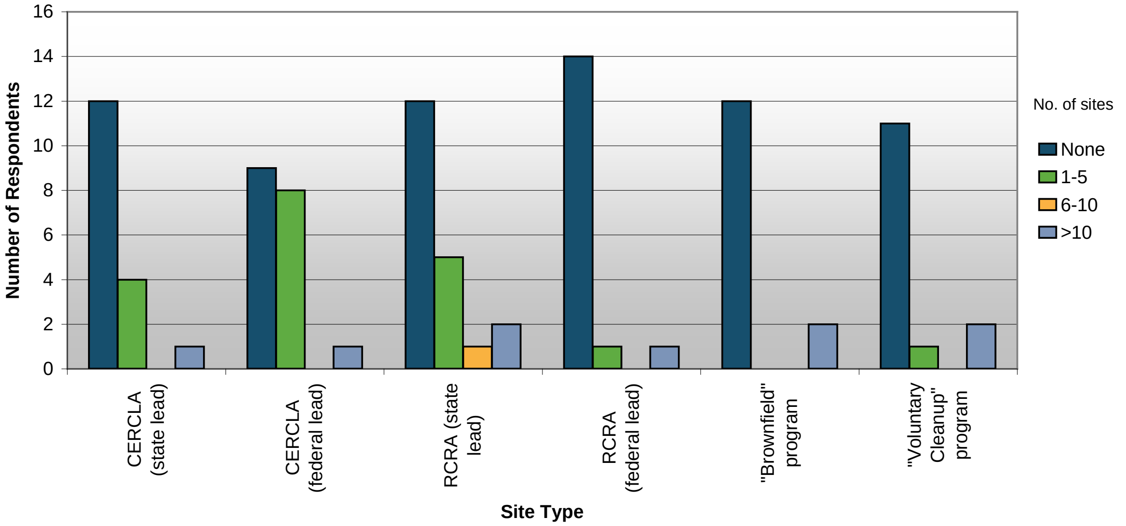


Figure C-6. Respondents' estimated number of known sites with metals contamination in groundwater. (2 respondents did not answer this question)

C.2.2.6 Question 8: Quantity of MNA Remedies Approved for All or Part of the Remedial Strategy for Sites Contaminated with Radionuclides in Groundwater

Q: *Within your jurisdiction, how many MNA remedies have been approved as all or part of the remedial strategy for sites contaminated with* ***radionuclides*** *in groundwater? (Check all that apply.)*

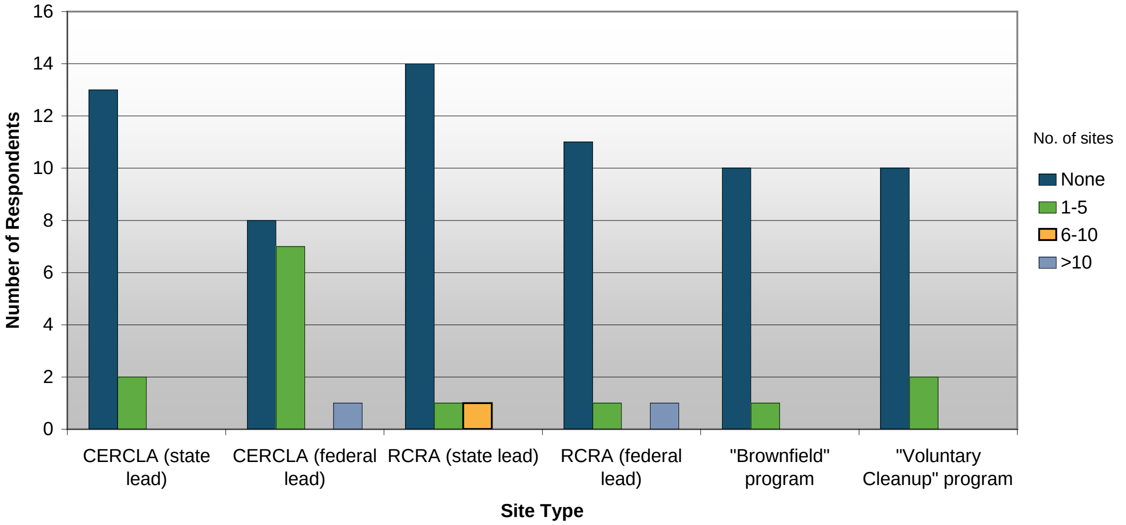
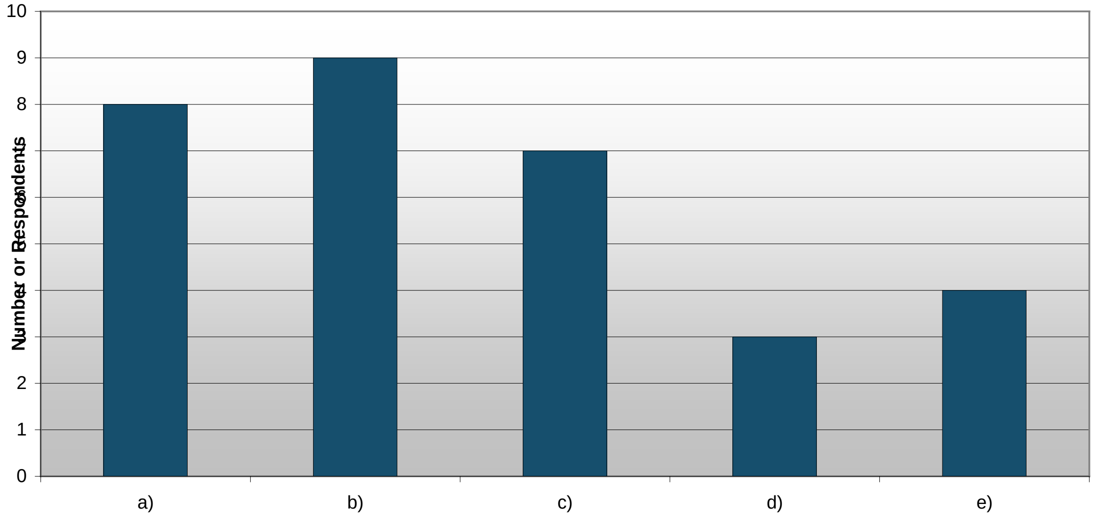


Figure C-7. Respondents' estimated number of MNA remedies that have been approved as all or part of the remedial strategy for sites contaminated with radionuclides in groundwater. (4 respondents did not answer this question)

C.2.2.7 Question 9: Governing Policies or Guidelines for Using MNA to Remediate Sites for Metal and/or Radionuclide Contamination in Groundwater

***Q:** Within your program jurisdiction, what are the **governing policies or guidelines** for using MNA to remediate sites for metal and/or radionuclide contamination in groundwater? (Check all that apply.)*



Legend:

a) No such policies or guidelines currently exist
b) State protocols, policies, regulations, or directives
c) Plan to incorporate new EPA guidance into state protocols, policies, regulations, or directives
d) Site-specific calculations (Alternative Concentration Limits/Mixing Zones, etc.)
e) Other (please specify)
  1. EPA guidance on MNA
  2. EPA MNA guidance combined with state groundwater standards on Superfund sites, UMTRA sites are different
  3. While we have yet to approve MNA (as described in your technical paper), we would evaluate that information if it was provided to use in a corrective action plan
  4. The cleanup standard for naturally occurring elements that exceed risk-based concentrations are background

Figure C-8. Governing policies or guidelines for using MNA to remediate sites with metal and/or radionuclide contamination in groundwater. (1 respondent did not answer this question)

C.2.2.8 Question 10: Summary of Policies, Guidelines, or Issues Related to Implementation of MNA or Other Attenuation-Based Remedies

***Q:** Within your program jurisdiction, please provide a summary of policies, guidelines, or issues related to implementation of MNA or other attenuation-based remedies to remediate sites with metal and/or radionuclides contamination.*

Respondents' replies to this question are detailed below:

1. The Nez Perce Tribe is developing a Hanford Policy as a guidance document for the DOE relative to the value statements in the Nez Perce Tribe Hanford Vision Statement. Within that

policy guidance document, we are addressing MNA. It is not yet publicly available. (Lapwai, ID)

2. Must control the source, provide information that the plume is not migrating, does not provide a human health or environmental risk, and has a downward trend in concentration of pollutants. We use the EPA protocol, California Code of Regulation Titles 23 and 27, CA State Water Resources Control Board Resolutions 92-49 and 68-16. (Rancho Cordova, CA)
3. DOE developed specific policies for use at the Uranium Mill Tailings Remedial Action Sites which in some cases may have pre-dated EPA's MNA guidance. The DOE policies were developed with input from Colorado, so we still use them, even if they may differ slightly from the EPA guidance. (Denver, CO)
4. At this point in time it is on a case-by-case basis typically when there are low levels in soils and ground water, contamination is not leaving the site and three are no receptors nearby. (Trenton, NJ)
5. Program does not "approve" remedies but is based on verification of compliance with numeric goals after remedy selected by licensed professional is implemented. We are currently evaluating how to determine if an MNA timeframe is acceptable as a remedy to allow sites to achieve a interim milestone that all remediation except MNA has been accomplished (i.e., source mitigated and plume stable/declining). (Hartford, CT)
6. No program-related policies or guidance exist at this time. (Lincoln, NE)
7. We use the EPA guidance for MNA, MRBCA guidance, and MNA resources through the Air Force Environmental Center. One issue we have with regard to radionuclides is that state legislation has been passed, referred to as "No Rad Added," where excavated material impacted with radionuclides above background levels cannot be disposed of in the state. (Jefferson City, MO)
8. None. (Richland, WA)
9. Use of bioremediation has been implemented as a remedy for metals contamination at one pond. (Oak Ridge, TN)
10. No policies or guidelines are currently available. Sites with metals as contaminants of concern are approached in a manner similar to MNA for organics: it happens in some cases and the project manager factors it into a remedial decision for the facility, recognizing that site geochemistry plays a major role how effective attenuation will be. (Denver, CO)

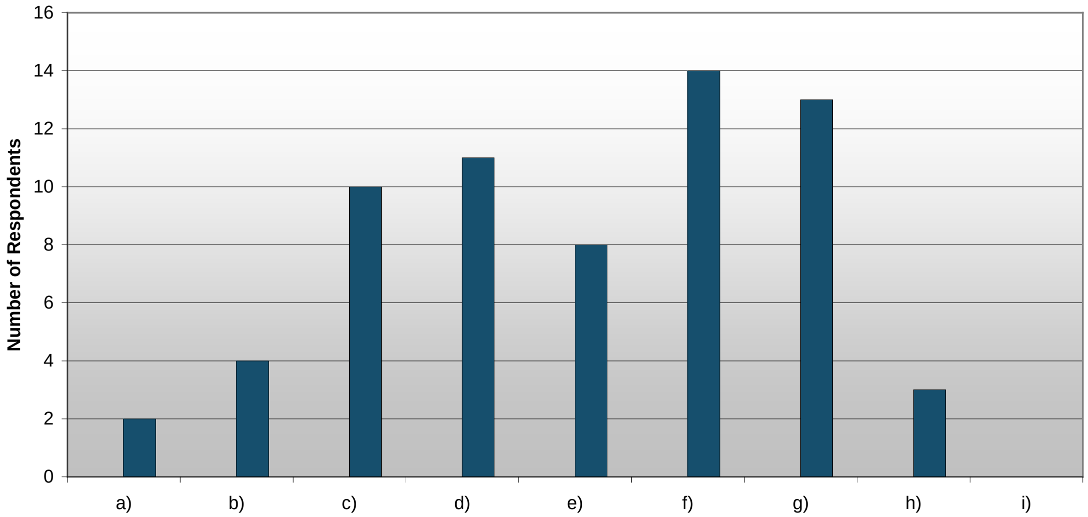
C.2.2.9 Question 11: Respondents Forwarding Documents from Question 10

Q: *Are you able to forward such documents to us?*

Six respondents indicated that they were able to forward documents in response to this question. Thirteen respondents replied that they were not able to forward documents. Seven respondents did not answer this question.

C.2.2.10 Question 12: Governing Policies or Issues that Are Factors in Cases Where MNA or Other Attenuation-Based Remedies Have Been Approved

Q: *Please summarize the governing policies and issues within your program jurisdiction that are factors in cases where* ***MNA or other attenuation-based remedies HAVE been approved*** *as a remediation for sites with metals and/or radionuclides contamination in groundwater. The reason the attenuation-based remedies have been approved is: (Check all that apply.)*



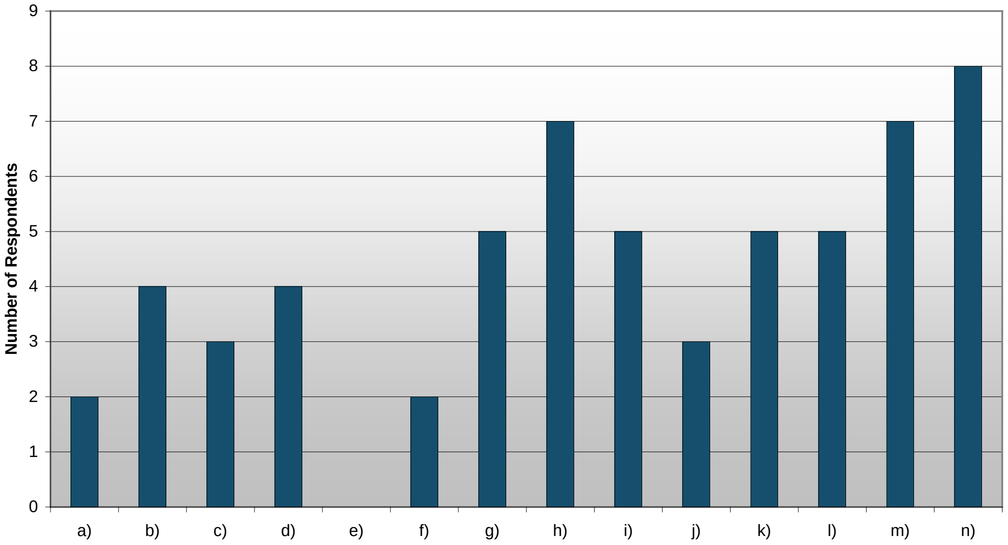
Legend:

- a) No sites with metal and/or radionuclide contamination in groundwater in your jurisdiction
- b) Have not received proposals for MNA remedies at a metal and/or radionuclide contaminated site
- c) Sites with metals and/or radionuclides in groundwater are being included as part of the larger remedy
- d) MNA considered effective for metals and/or radionuclides in groundwater for proposed setting (appropriate geochemistry, geology, hydrology, etc.)
- e) Cost considerations
- f) Metal and/or radionuclide plume is stable and/or shrinking
- g) Metal and/or radionuclide plume is not impacting receptors
- h) Remedy would impact ecosystems less
- i) Remedy would impact cultural resources less

Figure C-9. Governing policies and issues within respondents' program jurisdiction that are factors in cases where MNA or other attenuation-based remedies HAVE been approved as a remediation for sites with metals and/or radionuclides contamination in groundwater.
(1 respondent did not answer this question)

C.2.2.11 Question 13: Governing Policies or Issues that Are Factors in Cases Where MNA or Other Attenuation-Based Remedies Have Not Been Approved

Q: *Please summarize the governing policies and issues within your program jurisdiction that are factors in cases where* ***MNA or other attenuation-based remedies have NOT been approved*** *as a remediation for sites with metal and/or radionuclide contamination in groundwater. The reason the attenuation-based remedies have not been approved is: (Check all that apply.)*



Legend:

a) No sites with metal and /or radionuclide contamination in groundwater in your jurisdiction
b) Have not received proposals for MNA remedies at a metal and/or radionuclide contaminated site
c) MNA of metals and/or radionuclides in groundwater incompatible with existing, overriding state or federal guidance
d) Not enough confidence in (insufficient track record for) MNA of metal and/or radionuclides in groundwater
e) Have not accepted or approved EPA technical guidelines for MNA of inorganics (including metals) and radionuclides as effective or appropriate for your jurisdiction
f) Your agency is in the process of developing or approving guidance/policies for MNA of metals and/or radionuclides in groundwater
g) Sites with metals and/or radionuclides in groundwater are being effectively treated using other remedies
h) MNA remedies considered ineffective for metals and/or radionuclides in groundwater for proposed settings (incorrect geochemistry, geology, hydrology, etc.)
i) Metal and/or radionuclide plume is expanding
j) Metal and/or radionuclide plume is impacting drinking water wells
k) Metals and/or radionuclides plume is impacting surface water
l) Metal and/or radionuclide plume is impacting other receptor
m) Proposal for MNA remedy or other attenuation-based remedy for metals and/or radionuclides did not document effectiveness to address the amount of contaminant and/or to reach regulatory goals in a timely fashion
n) Please provide, if applicable, a brief summary of any additional policies and issues that limit implementation of MNA or other attenuation-based remedies for metals and/or radionuclides contamination in groundwater at sites within your state regulatory program jurisdiction (INSERT RESPONSES)

Figure C-10. Governing policies and issues within respondents' program jurisdiction that are factors in cases where MNA or other attenuation-based remedies have NOT been approved as a remediation for sites with metal and/or radionuclide contamination in groundwater. (14 respondents did not answer this question)

C.2.2.12 Question 14: Percentage of Sites Known to Be Contaminated with Metals and/or Radionuclides That Have Had a Remedy Proposed

Q: *Of the sites within your program jurisdiction known to be contaminated with metals and/or radionuclides in groundwater, approximately what percentage have had a REMEDY PROPOSED for them? NOTE: If you check "None" for BOTH metals and radionuclides, scroll down and skip to the next page (Question 20).*

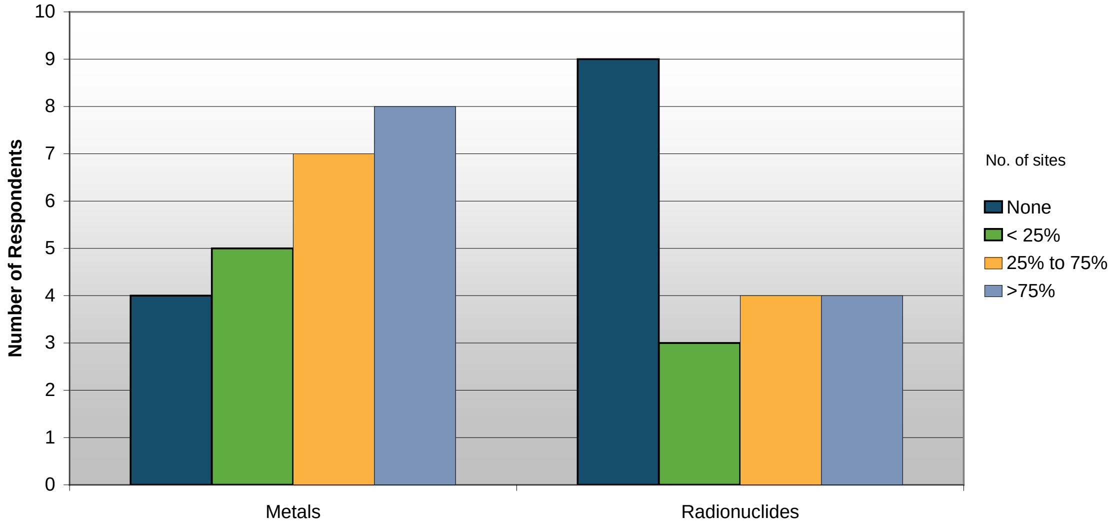


Figure C-11. Sites within respondents' program jurisdictions known to be contaminated with metals and/or radionuclides in groundwater with the approximate percentage that have had a REMEDY PROPOSED for them. (2 respondents did not answer this question)

C.2.2.13 Question 15: Percentage of Sites Within Program Jurisdiction Approved to Use MNA or Other Attenuation-Based Remedy for Metals and/or Radionuclides in Groundwater

Q: *Approximately what percentage of sites within your program jurisdiction* ***have been approved to use MNA or other attenuation-based remedy for metals and/or radionuclides*** *contamination in groundwater? NOTE: If you check "None" for BOTH metals and radionuclides, scroll down and skip to the next page (Question 20).*

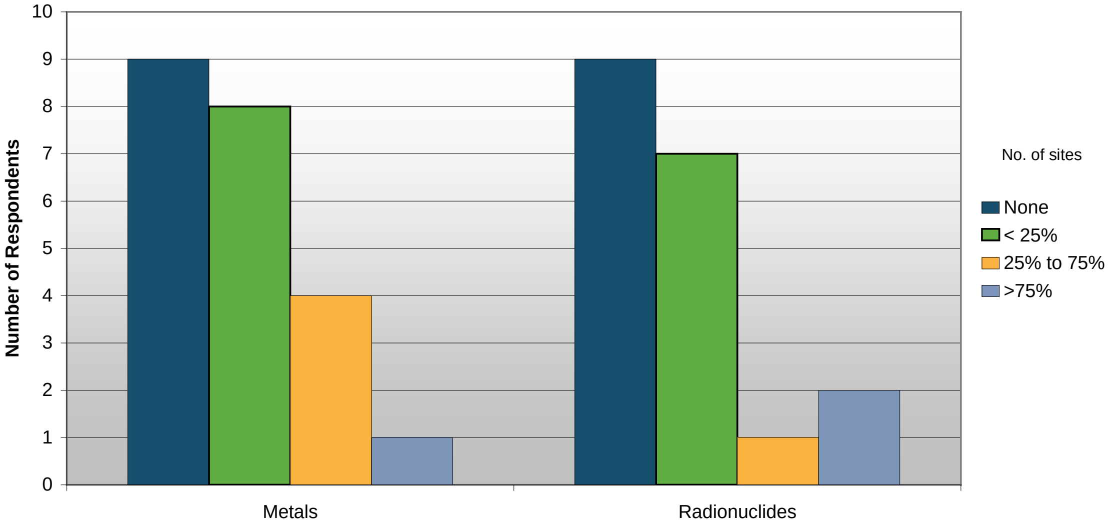


Figure C-12. Percentage of sites within respondents' program jurisdictions that have been approved to use MNA or other attenuation-based remedy for metals and/or radionuclides contamination in groundwater. (3 respondents did not answer this question)

C.2.2.14 Question 16: Percentage of Sites That Still Have Active Treatment System Operating

Q: *For sites within your program jurisdiction where MNA or attenuation-based remedies were approved to treat metals and/or radionuclides contamination in groundwater in combination with an active treatment system, approximately what percentage of the sites still have the* ***active treatment*** *system operating?*

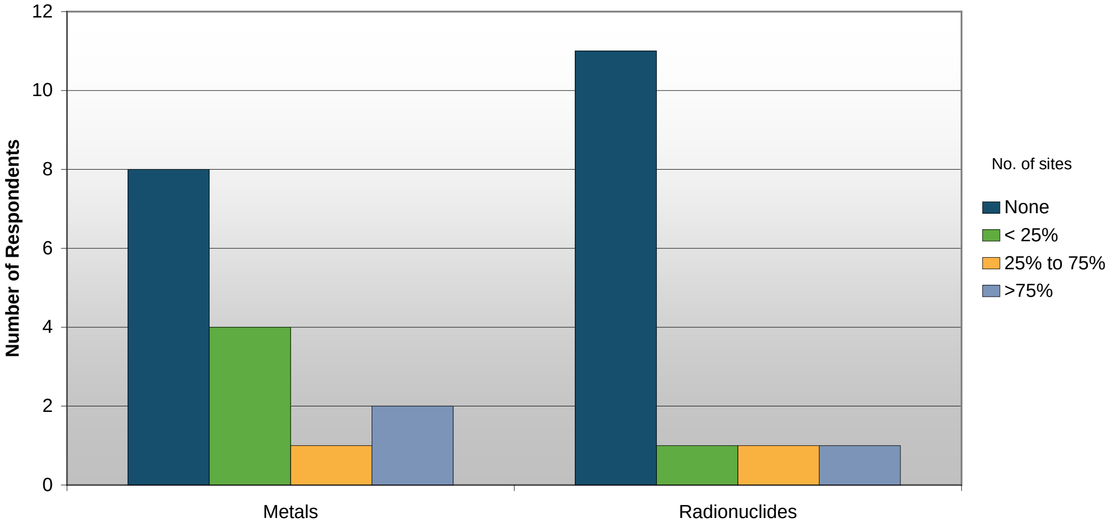


Figure C-13. Percentage of sites within respondents' program jurisdictions where MNA or attenuation-based remedies that were approved to treat metals and/or radionuclides contamination in groundwater in combination with an active treatment system, that still have the active treatment system operating. (9 respondents did not answer this question)

C.2.2.15 Question 17: Percentage of Sites That Still Have Passive Treatment System Operating

Q: *For sites within your program jurisdiction where MNA or attenuation-based remedies were approved to treat metals and/or radionuclides contamination in groundwater in combination with "passive" treatments, such as caps or permeable reactive barriers, approximately what percentage of the sites still have the **"passive" treatment** system operating?*

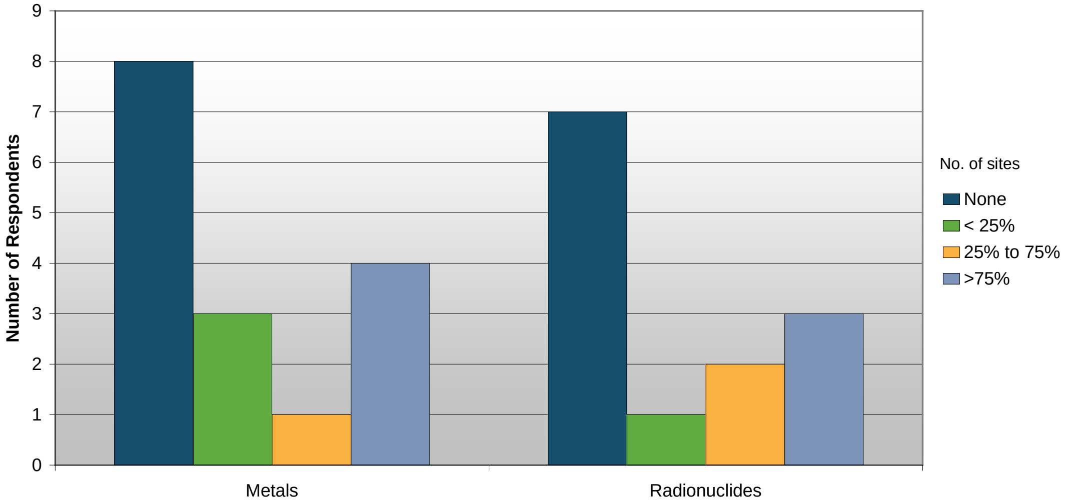


Figure C-14. Percentage of sites within respondents' program jurisdictions where MNA or attenuation-based remedies that were approved to treat metals and/or radionuclides contamination in groundwater in combination with "passive" treatments, such as caps or permeable reactive barriers, that still have the "passive" treatment system operating.
(9 respondents did not answer this question)

C.2.2.16 Question 18: Percentage of Sites Considered "Complete" Where and MNA or Other Attenuation-Based Remedy Was Approved

Q: *For sites within your program jurisdiction where MNA or other attenuation-based remedy was approved as all or part of the remedial strategy for metals and/or radionuclides, approximately what percentage are considered "**complete**" (i.e., "no further action," "certificate of completion," or equivalent)?*

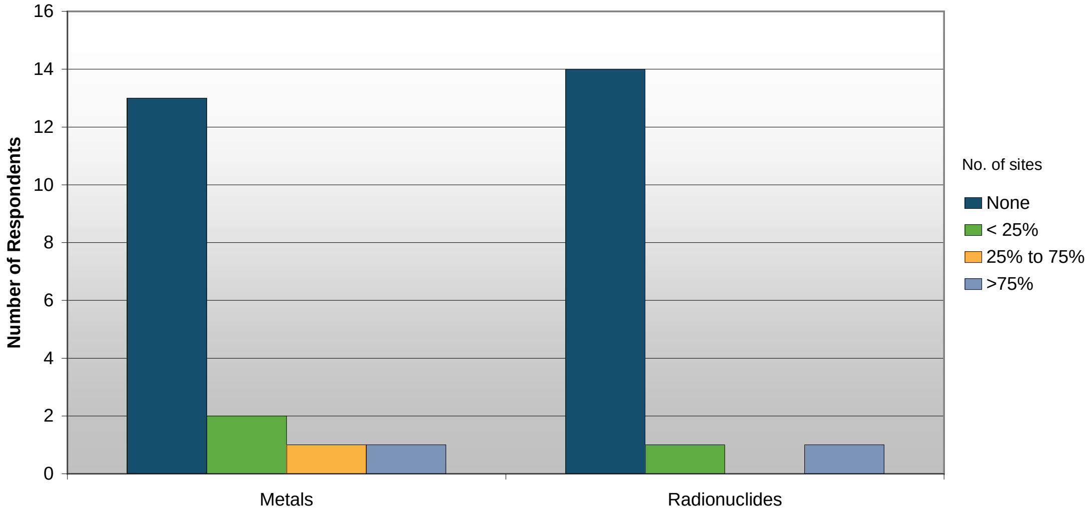


Figure C-15. Percentage of sites within respondents' program jurisdictions where MNA or other attenuation-based remedy was approved as all or part of the remedial strategy for metals and/or radionuclides, that are considered "complete" (i.e., "no further action," "certificate of completion," or equivalent). (7 respondents did not answer this question)

C.2.3 Part B: Data for Future Research and Policy Development

This section provides the findings of each question provided in Part B of the survey. Each question is provided along with the data, which are presented in both a figure and in narrative form when appropriate. The next subsection provides an overall summary of findings of Part B.

C.2.3.1 Question 20: Assessment of the Relative Importance of Mechanisms for a Typical Site Project Where Attenuation-Based Remedies Might Be Proposed as All or Part of the Remedial Strategy for Metal Contamination in Groundwater

Q: *Please provide an assessment of the relative importance of the following mechanisms for a typical site project where attenuation-based remedies (either MNA or Enhanced Attenuation) might be proposed as all or part of the remedial strategy for* ***metal*** *contamination in groundwater.*

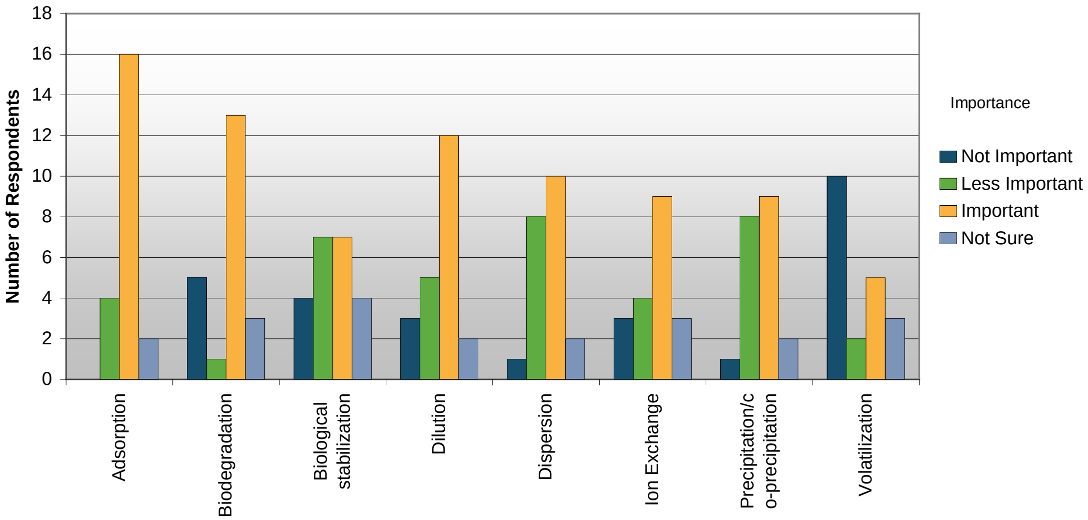


Figure C-16. Respondents' assessment of the relative importance of the following mechanisms for a typical site project where attenuation-based remedies (either MNA or Enhanced Attenuation) might be proposed as all or part of the remedial strategy for metal contamination in groundwater. (9 respondents did not answer this question)

C.2.3.2 Question 21: Assessment of the Relative Importance of Mechanisms for a Typical Site Project Where Attenuation-Based Remedies Might Be Proposed as All or Part of the Remedial Strategy for Radionuclide Contamination in Groundwater

Q: *Please provide an assessment of the relative importance of the following mechanisms* for a typical site project where attenuation-based remedies (either MNA or enhanced attenuation) might be proposed as all or part of the remedial strategy for* ***radionuclide*** *contamination in groundwater. *Processes listed in OSWER Directive 9200.4-17P (EPA 1999)*

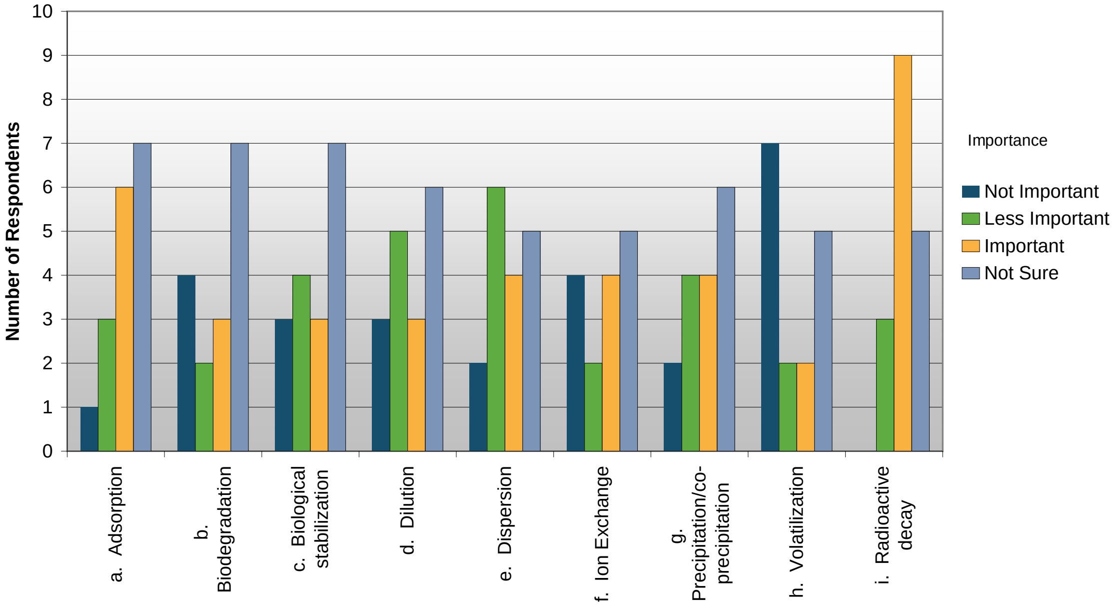
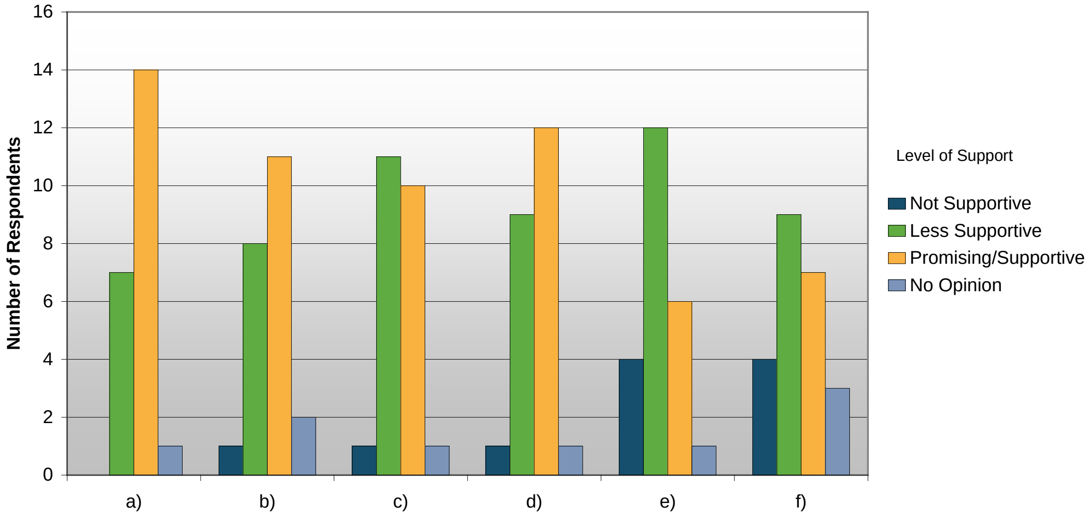


Figure C-17. Respondents' assessment of the relative importance of mechanisms for a typical site project where attenuation-based remedies might be proposed as all or part of the remedial strategy for radionuclide contamination in groundwater.
(9 respondents did not answer this question)

C.2.3.3 Question 22: Level of Support with Possible Means of Evaluating Attenuation-Based Remedy Viability

Q: *This question is designed to assess the level of comfort with possible means of evaluating whether an attenuation-based remedy is viable for a site with metal and/or radionuclide contamination in groundwater. Please provide an opinion on each of the descriptions. Each description should be viewed independent of the other descriptions.*



Legend:

a) Guidebooks or scoring systems based on site-specific factors (climate, geology, biogeochemistry, and hydrology) to support initial site conceptual model development, as well as characterization/ monitoring planning.

b) General protocol and potential scenario development using geological analogs (areas where naturally occurring metals are concentrated and stabilized).

c) Analytical models that estimate concentration or flux versus time and perform mass balance calculations for contaminated sites. These models typically use commonly available data.

d) Analytical numerical models that include the ability to assess the potential impacts of different treatment options. These models typically require sufficient additional input data to model the treatment process.

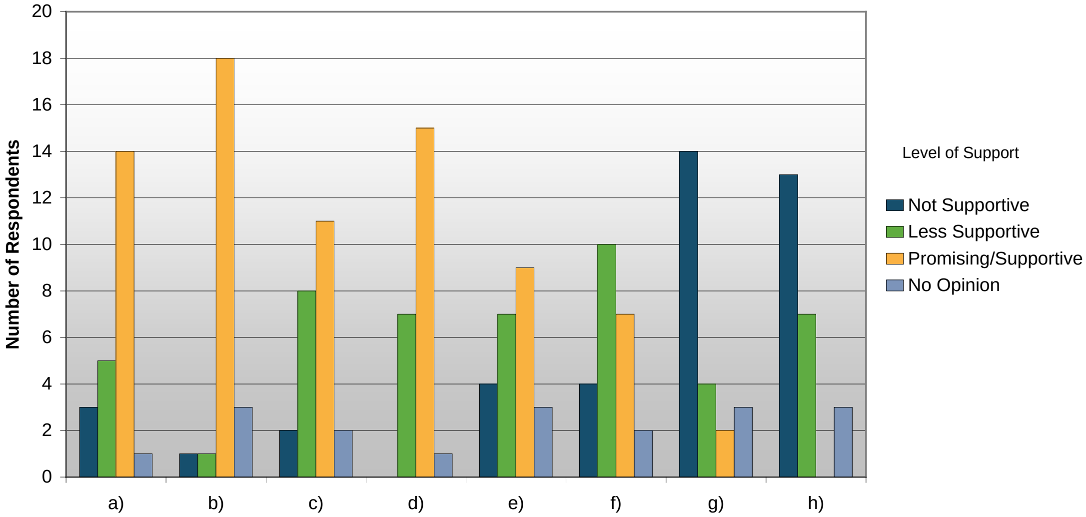
e) Complex numerical models. These models require large amounts of data but provide improved understanding of the contaminant behavior and of potential treatment effectiveness in complicated heterogeneous environments and varied conditions over time.

f) Probabilistic models. These models use distributions of data to generate a range of model results and provide some information on uncertainty. Probabilistic models can be run for either analytical or numerical models.

Figure C-18. Respondents' opinions on means of evaluating remedy viability for a site with metal and/or radionuclide contamination in groundwater.
(4 respondents did not answer this question)

C.2.3.4 Question 23: Level of Support with Possible Technical Solutions for Implementing an Enhanced Attenuation-Based Remedy

Q: *This question is designed to assess the level of comfort with possible technical solutions for implementing an enhanced attenuation-based remedy for a site with metal and/or radionuclide contamination in groundwater. Please provide an opinion on each of the descriptions. Each description should be viewed independent of the other descriptions. Enhanced attenuation technologies are, in many cases, traditional techniques that are designed and implemented to assist a naturally occurring attenuation mechanism(s) so that the mechanism or mechanisms will be sustainable, thus transitioning the site into MNA.*



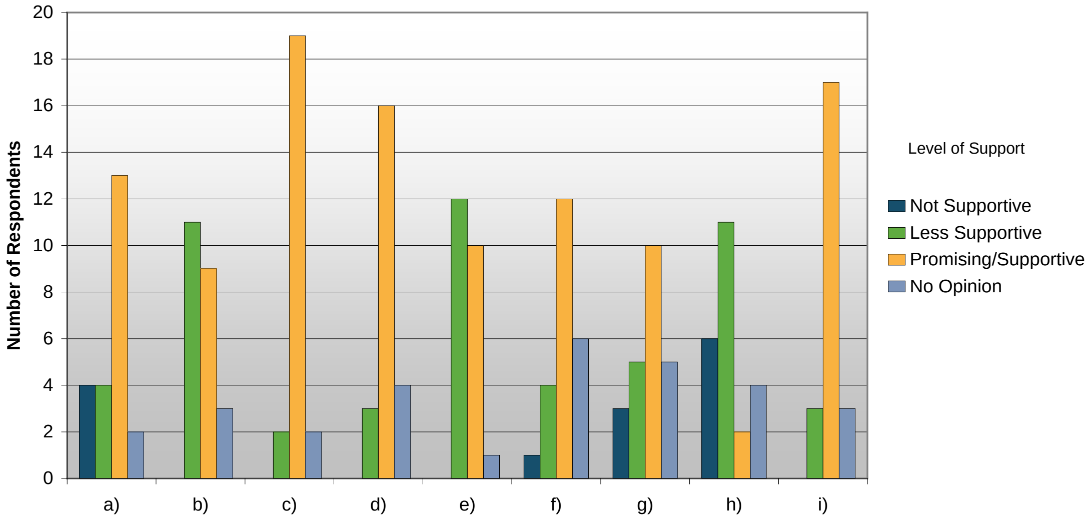
Legend:

a) Methods (e.g., upgradient drains, surface runoff control, caps, walls, floors, etc.) that reduce or divert the flow of water through the source material, thus minimizing the release of contaminants. This does not include chemical or physical stabilization of the source waste.
b) Biological or chemical methods that manipulate geochemistry (such as pH and Eh) of the contaminant plume to create an environment where the contaminant is immobilized and the new conditions are **similar** to the surrounding native groundwater.
c) Biological or chemical methods that manipulate geochemistry (such as pH and Eh) to create an environment where the contaminant is immobilized and the new conditions are **different** than the surrounding native groundwater, for example, creating a reduced zone in a naturally aerobic aquifer.
d) Permeable reactive barriers and other methods that create a treatment zone in which the contaminant is immobilized by sorption, precipitation, or reaction.
e) Stabilization by geochemical conditions in wetland areas adjacent to potential outcrop zones.
f) Uptake into plants and terrestrial ecosystems in the distal portion of the plume.
g) Mixing and dilution in surface water streams or lakes.
h) Precipitation/complexation of contaminants **at the discharge point** into surface waters.

Figure C-19. Respondents' opinions on technical solutions for implementing an enhanced attenuation-based remedy for a site with metal and/or radionuclide contamination in groundwater. (4 respondents did not answer this question)

C.2.3.5 Question 24: Key Issues Associated with Long-Term Monitoring of Attenuation Based-Remedies

Q: *This question is designed to understand key issues associated with long-term monitoring of an attenuation-based remedy at a site with metal and/or radionuclide contamination in groundwater. The attenuation-based remedy may be all or part of the remedial strategy. Please provide an opinion on each of the descriptions. Each description should be viewed independent of the other descriptions.*



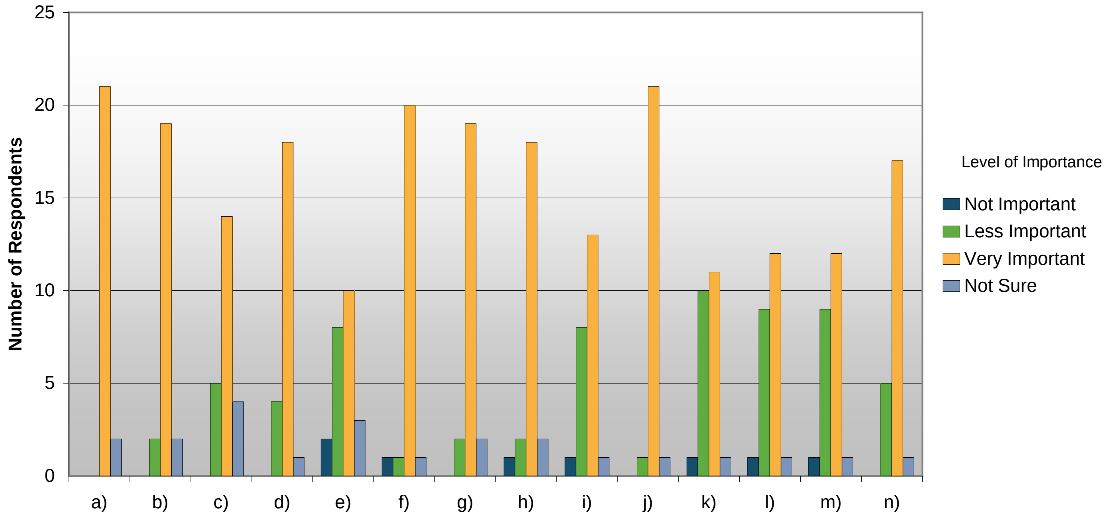
Legend:

a) Long-term monitoring based on the conceptual model that the contaminated site and its surroundings are an ecological system and incorporate ecological monitoring paradigms into protocols and contingency determinations.
b) Monitoring protocols that emphasize geochemical conditions and how they are changing and evolving rather than frequent point samples of contaminant concentration.
c) Monitoring protocols or systems that provide direct assessment of available capacity within the aquifer to attenuate contaminant loading within the required regulatory timeframe.
d) Monitoring protocols or systems that provide assessment on the irreversibility of contaminant immobilization.
e) Monitoring protocols that are based on frequent point sampling.
f) Monitoring systems that reduce the number of sampling locations by identifying or building in failure points. (Failure indicates a negative change in the system. These points may be anywhere in the plume.)
g) Monitoring systems in which more types of data (weather data, evapotranspiration data, remote sensing data, autonomous in situ sensor data etc.) can be incorporated to reduce the number and frequency of well samples.
h) Monitoring systems in which contaminant flux (rate of contaminant mass passing a plane perpendicular to the mean groundwater flow) **rather than** concentration is a key parameter for defining performance and the need for implementing contingencies.
i) Monitoring systems in which contaminant flux **in addition to** concentration is used for defining performance and the need for implementing contingencies.

Figure C-20. Respondents' opinions on key issues associated with long-term monitoring of an attenuation-based remedy at a site with metal and/or radionuclide contamination in groundwater. (4 respondents did not answer this question)

C.2.3.6 Question 25: Assessment of Relative Importance of Attributes and Considerations of Attenuation-Based Remedies

Q: *Research continues to develop a better understanding of the processes that contribute to natural attenuation of metals and/or radionuclides in groundwater. Many of the attributes of these processes influence the acceptability of MNA as a remedy at specific sites. Some of these characteristics may be competing and must be balanced in making remediation choices. The importance of each of these characteristics may be influenced by the specific environmental setting, geochemical factors, hydrogeology, land ownership, regulatory goals, etc. Please provide an assessment of the relative importance of the following attributes or considerations of attenuation-based remedies (either MNA or enhanced attenuation).*



Legend:

a) Immobile end products
b) Potential for hazardous by-products (e.g., methyl mercury) or mobilization of hazardous by-products
c) Potential to reduce long-term operations, surveillance, and monitoring (e.g., radionuclides with shorter half-lives)
d) Complexity of waste and site conditions
e) Existence of a geological analog that is stable under natural conditions
f) Technology has been demonstrated or observed for contaminants of concern
g) Degree to which geochemical environment must be altered to make process viable
h) Technology incorporates contaminant into a chemically stable mineral structure (process more difficult to reverse)
i) Availability of other cost-effective remedies
j) Potential for process failure to result in catastrophe
k) Potential for longer cleanup time using MNA
l) Short-term effectiveness (ability of technology to achieve remediation goals [MCLs, etc.] in a reasonable timeframe)
m) Cost
n) Implementability

Figure 2-21. Respondents' assessment of the relative importance of attributes or considerations of attenuation-based remedies. (4 respondents did not answer this question)

C.2.4 Summary of Part B Findings

In response to questions 20 and 21, there was a larger percentage of respondents that are “not sure” about the relative importance of the mechanisms for a remedial strategy for radionuclides than for metals. For metals, there is much lower number of “not sure” responses and a relatively high number of “important” responses for adsorption and dilution.

In response to question 22, 63.6% of respondents replied that they were supportive of guidebooks or scoring systems. This response is in high contrast to that for complex numerical models, which did not receive nearly the level of support (27%). “Simple” remedies seem to be preferred. In addition, there were very few responses of “no opinion” to this question, indicating a high level of familiarity with these means of evaluation.

In response to question 23, the high number of “supportive” responses for both (1) methods (e.g., upgradient drains, surface runoff control, caps, walls, floors, etc.) that reduce or divert the flow of water through the source material, thus minimizing the release of contaminants, and (2) biological or chemical methods that manipulate geochemistry (such as pH and Eh) of the contaminant plume to create an environment where the contaminant is immobilized and the new conditions are similar to surrounding native groundwater, suggests that the respondents are focusing on the idea that the contaminant will be immobilized. These remedies may be seen as more permanent, reliable remedies and less of an engineering control. “Mixing and dilution in surface water streams or lakes” and “precipitation/complexation of contaminants (at the discharge point) into surface waters” both received few/no responses of “promising/supportive.” PRBs received very few responses of “no opinion” (4.3%) and a high number of responses for “promising supportive” (65.2%), suggesting that this technology is well-known and commonly implemented.

In response to question 24, respondents appeared supportive of remedies that monitored contaminant flux in addition to concentration (73.9%). The reason that respondents did not see option h), monitoring systems in which the contaminant flux rather than concentration is a key parameter for defining performance and the need for implementing contingencies, as supportive may be that the remedy looked at only the flux rather than flux in conjunction with concentration data. There were very few “unsupportive” responses for “long-term monitoring based on the conceptual model that the contaminated site and its surroundings are an ecological system and incorporate ecological monitoring paradigms into protocols and contingency determinations,” “monitoring protocols or systems that provide direct assessment of available capacity within the aquifer to attenuate contaminant loading within the required regulatory timeframe,” or “monitoring protocols that are based on frequent point sampling.” A high percentage of respondents found both c) and i) promising.

Responses to question 25 indicated that all attributes were determined to be generally important. Immobile end products, by far, are deemed by respondents to be very important. Cost effectiveness, long-term operations, and monitoring were not seen to be as important as implementability or permanence of the remedy.

C.2.5 Part C: Additional Detail on Specific Contaminants

Alabama

Site name – Anniston Army depot
  Site location (city, state) – Anniston, AL
  1st major contaminant of concern – Lead
  Maximum concentration (mg/L, pCi/L) – 40 µ/L
  2nd major contaminant of concern – Hexavalent chromium
  Maximum concentration (mg/L, pCi/L) – 91 µ/L
  3rd major contaminant of concern – Thallium
  Maximum concentration (mg/L, pCi/L) – 5 µ/L (estimated)

Site name – Interstate Lead Company (ILCO)
  Site location (city, state) – Leeds, AL
  1st major contaminant of concern – Arsenic
  2nd major contaminant of concern – Nickel
  3rd major contaminant of concern – Manganese

California

Site name – Lawrence Livermore National Laboratory Site 300
  Site location (city, state) – Tracy, CA
  1st major contaminant of concern – Tritium
  Maximum concentration (mg/L, pCi/L) – Was over 1,000,000 pCi/L, now around 200,000
  2nd major contaminant of concern – Uranium
  Maximum concentration (mg/L, pCi/L) – 150 pCi/L
  3rd major contaminant of concern – Trichloroethene
  Maximum concentration (mg/L, pCi/L) – 800,000 µg/L

Colorado

Site name – Shattuck (Denver Radium OU VIII)
  Site location (city, state) – Denver, CO
  1st major contaminant of concern – Molybdenum
  Maximum concentration (mg/L, pCi/L) – approx 18 mg/L
  2nd major contaminant of concern – Uranium
  Maximum concentration (mg/L, pCi/L) – 0.140 mg/L

Site name – Gunnison UMTRA Site
  Site location (city, state) – Gunnison, CO
  1st major contaminant of concern – Uranium
  Maximum concentration (mg/L, pCi/L) – 1.2 mg/L
  2nd major contaminant of concern – Manganese
  Maximum concentration (mg/L, pCi/L) – 6 mg/L

Site name – New Rifle UMTRA Site

- Site location (city, state) – Rifle, CO
- 1st major contaminant of concern – Uranium
- Maximum concentration (mg/L, pCi/L) – 0.250 mg/L
- 2nd major contaminant of concern – Vanadium
- Maximum concentration (mg/L, pCi/L) – 20 mg/L
- 3rd major contaminant of concern – Ammonia/nitrate/nitrite
- Maximum concentration (mg/L, pCi/L) – Nitrate + nitrite 250 mg/L

Missouri

Site name – Weldon Spring Site (WSSRAP)

- Site location (city, state) – St. Charles, MO
- Pertinent geochemical factors – Karstic geology, alkaline soils (pH 8–13)
- 1st major contaminant of concern – Uranium
- Maximum concentration (mg/L, pCi/L) – 270 pCi/L
- 2nd major contaminant of concern – 2,4 DNT
- Maximum concentration (mg/L, pCi/L) – 420 µg/L
- 3rd major contaminant of concern – Trichloroethene
- Maximum concentration (mg/L, pCi/L) – 560 µg/L

Washington

Site name – Hanford Site-200 ZP1 OU

- Site location (city, state) – Richland, WA
- Pertinent geochemical factors – Metals and radionuclides
- 1st major contaminant of concern – Technetium-99
- Maximum concentration (mg/L, pCi/L) – 180,000 pCi/L
- 2nd major contaminant of concern – Carbon tetrachloride
- Maximum concentration (mg/L, pCi/L) – 4500 ppb
- 3rd major contaminant of concern – Chromium
- Maximum concentration (mg/L, pCi/L) – 260 ppb

Site name – Hanford Site, 200 BP-5 OU

- Site location (city, state) – Richland, WA
- Pertinent geochemical factors – Metals and radionuclides
- 1st major contaminant of concern – Uranium
- Maximum concentration (mg/L, pCi/L) – 956 ppb
- 2nd major contaminant of concern – Technetium-99
- Maximum concentration (mg/L, pCi/L) – 73,400 pCi/L
- 3rd major contaminant of concern – Cyanide
- Maximum concentration (mg/L, pCi/L) – 3,990 ppb

Site name – Hanford Site, 100 N Area

- Site location (city, state) – Richland, WA
- Pertinent geochemical factors – Radionuclide

1st major contaminant of concern – Strontium-90
Maximum concentration (mg/L, pCi/L) – 8,000 pCi/L

C.3 SUMMARY AND CONCLUSIONS

There appears to be a lack of knowledge with respect to the technical and regulatory aspects of attenuation for radionuclides. There is a greater level of uncertainty in understanding the importance of the various attenuation mechanisms associated with radionuclides than with metals. The respondents appeared comfortable with their knowledge associated with attenuation of metals and the importance of the various attenuation mechanisms.

A series of questions were asked to evaluate the respondents' level of comfort/interest in a variety of approaches for evaluating, implementing, and monitoring attenuation-based remedies. Each respondent was asked to evaluate each approach identified in a question independent of the other approaches described in that same question.

In regards to the level of interest/comfort associated with approaches for evaluating attenuation-based remedies, the majority of respondents found the simple approaches, such as the scenarios or guidebook, most desirable with the complex, data-rich approaches as least desirable.

A range of implementation approaches/methods were described that addressed areas of contaminant plumes from the source through the discharge zone. Approaches that would be implemented at the discharge areas were negatively viewed. Approaches that reduce mass loading and manipulate the geochemical setting resulting in conditions close to the natural state were looked upon most favorably.

Monitoring approaches that ranged from the traditional, point measurements to a variety of new approaches were described. Respondents liked direct methods that would provide measures of attenuation capacity. They also liked using flux measurements in combination with concentration measurements. The respondents did not like the idea of replacing concentration measurements with flux measurements.

Several key attributes were identified for approaches and tools associated with attenuation-based remedies. The attributes included having immobile end products, identifying the potential for "catastrophic" failure, and ease of implementation. The least desirable attribute was the use of geologic analogs to "show" stability.

C.4. ACKNOWLEDGEMENTS

This work was sponsored by the Interstate Technology & Regulatory Council. The Attenuation Processes for Metals and Radionuclides Team would like to thank the regulators and stakeholders who took the time to complete this survey.

Appendix D

Attenuation Processes for Metals and Radionuclides Team Contacts

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Appendix E

Glossary

GLOSSARY

Bracketed numbers after definitions indicate sources, as listed at the end of the Glossary.

abiotic Occurring without the involvement of microorganisms. [10] Chemical and physical processes occurring without the involvement of living organisms. In some cases, such attenuation processes do not involve microorganisms or plants at all, while in other cases, biological and abiotic processes occur simultaneously and/or serve to enhance each other. [9]

absorption Partitioning of a dissolved species into a solid phase. [12]

actinide(s) A group of elements that are very dense, radioactive metals. The elements are actinium, thorium, protactinium, uranium, neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, and lawrencium.
A radioactive element in the series of elements beginning with actinium (89) and ending with lawrencium (103). [10]

adsorption The adhesion of molecules (in a thin layer) to the surfaces of solid bodies or liquids with which they are in contact. [10] Partitioning of a dissolved species onto a solid surface. [12]

advection The process by which solutes are transported by the bulk motion of flowing groundwater. [10] Transport of a solute by the bulk motion of flowing groundwater. [9]

aerobic Living, active, or occurring in the presence of free oxygen. [10] Conditions for growth or metabolism in which the organism is sufficiently supplied with molecular oxygen. [9]

alpha particle Particle emitted from nucleus of atom during one type of radioactive decay. Particle is positively charged and has two protons and two neutrons. [12]

anaerobic Living, active, or occurring in the absence of free oxygen. [10]

anion A negatively charged ion. [10]

applicable or relevant and appropriate requirement (ARAR) Under the Comprehensive Environmental Responsibility, Cleanup and Liability Act (Superfund), cleanups must follow two kinds of requirements: applicable requirements, meaning those that directly apply to the situation relevant, or appropriate requirements, meaning those that apply to contaminants that are present at the site or apply to a contaminated medium, such as water, at the site. ARARs can be federal, state, or local requirements. [5]

aquifer Stratum of permeable rock, sand, or gravel that can store and supply groundwater to wells and springs. [10]

attenuation capacity Availability within the aquifer to attenuate contaminant mass loading through various mechanisms.

attenuation rate The rate at which a contaminant is removed. This is not a rate constant but a rate, with typical units of µg per L per year. [9]

beta particle A beta is a high-speed particle, identical to an electron, that is emitted from the nucleus of an atom.

bioavailability The accessibility of chemical compounds in the environmental to an organism or organisms. [10]

biodegradation The breakdown of materials into simpler components by microorganisms or their enzymes.
Breakdown of a contaminant by enzymes produced by bacteria. [9]

cation A positively charged ion. [10]

chelate Any of a class of relatively stable coordination compounds consisting of a central metal atom attached to a large molecule, called a ligand, in a cyclic or ring structure. [10]

chelator An agent that causes formation of a chelate. [10]

colloid Microscopic particles suspended in a liquid medium, usually between one nanometer and one micrometer in size. [10] Any fine-grained material, sometimes limited to the particle-size range of <0.00024 mm (i.e., smaller than clay size), that can be easily suspended.
In its original sense, the definition of a colloid included any fine-grained material that does not occur in crystalline form. [12]

complex A type of compound in which a central metal ion is surrounded by a number of ions or molecules, called ligands, that can also exist separately, also known as a coordination compound. A chelate is a type of complex. [10] Any combination of dissolved cations with molecules or anions containing free pairs of electrons. [12]

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 as amended (Pub. L. 99-499, 42 U.S.C. 9601–9657) CERCLA authorizes EPA, consistent with the National Oil and Hazardous Substances Contingency Plan (NCP, 40 CFR 300), to provide for remedial action in response to releases of hazardous substances in to the environment. The act and its amendments created a trust fund, the "Superfund," to finance the investigation and cleanup of abandoned and uncontrolled hazardous waste sites. [3,6]

conceptual site model A three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual model provides the basis for assessing potential remedial technologies at the site. "Conceptual site model" is not synonymous with "computer model"; however, a computer model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions. [8] A hypothesis about how releases occurred, the current state of the source zone, and current plume characteristics (plume stability). [9] A general approach to planning field investigations that is useful for any type of environmental reconnaissance or investigation plan with a primary focus on the surface and subsurface environment. [4]

contamination The deposition of unwanted radioactive material on the surfaces of structures, areas, objects, or people. It may also be airborne, external, or internal (inside components or people). [5] Harmful or hazardous matter introduced into the environment. [10]

contingency plan A document setting out an organized, planned, and coordinated course of action to be followed in case of a fire, explosion, or other accident that releases toxic chemicals, hazardous waste, or radioactive materials that threaten human health or the environment. [13]

contingency remedy A contingency remedy is a cleanup technology or approach specified in the site remedy decision document that functions as a “backup” remedy in the event that the “selected” remedy fails to perform as anticipated. A contingency remedy may specify a technology (or technologies) that is (are) different from the selected remedy, or it may simply call for modification of the selected technology, if needed. [8]

coprecipitation The incorporation of elements into other compounds, such as metal oxide minerals, as they precipitate from solution. [10]

daughter product A compound that results directly from the biodegradation of another. [11]

desorption The converse of sorption, i.e., when a compound slowly releases from a surface(s) that it has previously accumulated upon or within. [9]

diffusion The natural tendency of molecules to move out of areas of high concentration into areas of low concentration until a solution or gas has a uniform concentration of the molecules. [10] The process of (net) transport of solute molecules from a region of high concentration to region of low concentration caused by their molecular motion and not by turbulent mixing. [9] The process whereby molecules move from a region of higher concentration to a region of lower concentration as a result of Brownian motion. [11] Molecular process of transport of matter in the absence of bulk flow. [12]

dilution A reduction in solute concentration caused by mixing with water at a lower solute concentration. [9]

dispersion The distribution of a solute throughout a solvent, as sugar in water. [10] The spreading of a solute from the expected groundwater flow path as a result of mixing of groundwater. [9]

electron A stable atomic particle that has a negative charge. [10] A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions. [9]

electron acceptor Inorganic or organic compound that is reduced in an oxidation/reduction reaction. Chemical substances, such as oxygen, nitrate, sulfate, and iron, that receive the electrons during microbial and chemical reactions. Microorganisms need these compounds to obtain energy. For MNA and EA, these electron acceptors often compete with chlorinated solvents and reduce the attenuation rates. [9] A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, iron(III), manganese(IV), sulfate, and carbon dioxide. [11]

electron donor Inorganic or organic compound that is oxidized in an oxidation/reduction reaction. Chemical substances, such as molecular hydrogen or organic substrate, that yield an electron as they are oxidized, producing energy to sustain life and for the subsequent degradation of other chemicals, in this case, chlorinated solvents. [9] A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon. [11]

element (chemical element) Any substance that cannot be decomposed into simpler substances by ordinary chemical processes.

enhanced attenuation Any type of intervention that might be implemented in a source-plume system to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention. Enhanced attenuation is the result of applying an enhancement that sustainably manipulates a natural attenuation process, leading to an increased reduction in mass flux of contaminants. [9]

exponential notation The following exponential notations are examples of those used in this document.

$1 \times 10^{4} =$ 10,000
$1 \times 10^{2} =$ 100
$1 \times 10^{0} =$ 1
$1 \times 10^{-2} =$ 0.01
$1 \times 10^{-4} =$ 0.0001

flux (including contaminant flux) Rate of flow of fluid, particles, or energy through a given surface. [9]

gamma rays Gamma rays are electromagnetic waves or photons emitted from the nucleus (center) of an atom.

gradient (hydraulic gradient) Slope or elevation difference that influences groundwater velocity. [10] The change in hydraulic head (per unit distance in a given direction) typically in the principal flow direction. [9]

groundwater Water found beneath the earth’s surface that fills pores between materials, such as sand, soil or gravel; supplies wells and springs. [10]

half-life The time required for half of the atoms of a radioactive substance to disintegrate. [10]

heavy metals Metallic elements with high molecular weights. Such metals are often residual in the environment, exhibit biological accumulation, and are generally toxic in low concentrations. Examples include chromium, mercury, and lead. [10]

heterogeneous Consisting of diverse or dissimilar constituents. [10]

hydraulic conductivity A measure of the capability of a medium to transmit water. [9] The relative ability of a unit cube of soil, sediment, or rock to transmit water. [11]

immobilization The precipitation or binding of a substance so that it is no longer able to circulate freely. [10]

inorganic compounds Chemicals that do not contain carbon; for example, metals are inorganic. [10] Compounds that are not based on covalent carbon bonds, including most minerals, nitrate, phosphate, sulfate, and carbon dioxide. [9]

in situ In the original position or place. [10] Literally meaning “in place,” refers to treating a compound where it is rather than first mechanically removing it (by excavation, pumping, venting, etc.) and then treating it. [9]

insoluble Not readily dissolved in a liquid. [10]

institutional controls Refers to nonengineering measures—usually, but not always, legal controls—intended to affect human activities in such a way as to prevent or reduce exposure to hazardous substances. Examples of institutional controls include land and resource (e.g., water) use and deed restrictions, well-drilling prohibitions, building permits, well use advisories, and deed notices. [8]

ion exchange A reversible reaction in which ions are interchanged. This phenomenon is common in soils. [10]

isotope Any of two or more species of atoms of a chemical element with the same atomic number (number of protons) and nearly identical chemical behavior but with a different number of neutrons, hence a difference atomic weight. [10]

ligand A group, ion, or molecule coordinated to a central atom or molecule in a complex. [10]

mass balance Assessment includes a quantitative estimation of the mass loading to the dissolved plume from various sources, as well as the mass attenuation capacity for the dissolved plume. [9]

metabolite The product of chemical reactions in living cells that convert food sources to energy and new cell mass.

methylation Substitution of a methyl group for a hydrogen atom. [10]

microbiology A branch of biology dealing with microscopic forms of life (bacteria, archaea, protozoa, algae, viruses, and fungi). [10]

microorganism Any organism of microscopic or ultra-microscopic size. [10] An organism of microscopic or submicroscopic size, including bacteria. [9]

mineralization The complete breakdown of organic materials by microorganisms into inorganic materials such as carbon dioxide and water. [10] The complete degradation of an organic compound to carbon dioxide and other inorganic compounds, such as water and chloride ions. [9]

monitored natural attenuation Refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a timeframe that is reasonable compared to that offered by other more active methods. 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. These in situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. [8]

National Priorities List The Environmental Protection Agency’s list of the most serious uncontrolled or abandoned hazardous waste sites identified for possible long-term remedial action under the Comprehensive Environmental Response, Compensation, and Liability Act. The list is based primarily on the score a site receives from the Environmental Protection Agency Hazard Ranking System. The Environmental Protection Agency is required to update the National Priorities List at least once a year. [1]

natural attenuation Allowing a variety of natural physical, chemical, and biological processes to reduce the amount, toxicity, mobility, and concentration of contaminants in the environment. These processes include biological degradation, dilution, sorption or soil or aquifer particles, volatilization to the atmosphere, and chemical reactions with natural materials. [10] Naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. [9]

nuclear waste A particular type of radioactive waste that is produced as part of the nuclear fuel cycle (i.e., those activities needed to produce nuclear fission, or splitting of the atom). These include extraction of uranium from ore, concentration of uranium, processing into nuclear fuel, and disposal of by-products. Radioactive waste is a broader term that includes all waste that contains radioactivity. Residues from water treatment, contaminated equipment from oil drilling, and tailings from the processing of metals such as vanadium and copper also contain radioactivity but are not “nuclear waste” because they are produced outside of the nuclear fuel cycle. NRC generally regulates only those wastes produced in the nuclear fuel cycle (uranium mill tailings, depleted uranium, spent fuel rods, etc.). [4]

operable unit Term for each of a number of separate activities undertaken as part of a Superfund site cleanup. A typical operable unit would be removal of drums and tanks from the surface of a site. [13]

organic In chemistry, any compound containing carbon. [13]

oxidant A molecule or atom that accepts electrons in an oxidation-reduction reaction. [10]

oxidation Loss of electrons from a compound. [9]

oxidation/reduction potential (Eh) The relative susceptibility of a substrate to oxidation or reduction. [10]

oxidation-reduction reaction Coupled reactions in which one compound becomes oxidized (releases electrons) while another becomes reduced, gaining the electrons released. [10]

performance monitoring The monitoring program developed for each site should specify the location, frequency, and type of samples and measurements necessary to evaluate whether the remedy is performing as expected and is capable of attaining remediation objectives. In addition, all monitoring programs for natural attenuation should be designed to accomplish the following: demonstrate that natural attenuation is occurring according to expectations; detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes; identify any potentially toxic and/or mobile transformation products; verify that the plume(s) is not expanding (either downgradient, laterally or vertically); verify no unacceptable impact to downgradient receptors; detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy; demonstrate the efficacy of institutional controls that were put in place to protect potential receptors; and verify attainment of remediation objectives. [8] The collection of information which, when analyzed, evaluates the performance of the system on the environmental contamination. [9]

permeable reactive barrier In situ treatment zones that are engineered downgradient from a contaminant plume. As groundwater passes through the treatment zone, contaminants are adsorbed, reduced and precipitated, biodegraded, biotransformed, or chemically degraded. [10] Subsurface walls composed of reactive materials that will either degrade or alter the state of a contaminant when that contaminant in a groundwater plume passes through the wall. [9]

pH Negative logarithm of the effective hydrogen ion concentration or hydrogen ion activity in gram equivalents per liter of solution on a scale of 0–14. Each unit of change (e.g., from 7 to 6) presents a tenfold change in hydrogen ion concentration. A value of 7 represents neutrality; lower numbers indicate acidic conditions and higher numbers alkaline conditions. [modified from 10]

plume An elongated body of fluid, usually mobile and varying in shape. Used to define the contaminated areas of an environment. [10] A zone of dissolved contaminants. A plume usually originates from a source and extends in the direction of groundwater flow. [9]

porosity The volume of aquifer material that is not occupied by solids. [10] The ratio of void volume to total volume of a rock or sediment. [11]

precipitation The process whereby a solid settles out of solution. [10]

radiation Transmission of energy through space or any medium. Also known as radiant energy. [13]

radioactivity Spontaneous emission by radionuclides of energetic particles through the disintegration of their atomic nuclei; the rays emitted. [10]

radioactive waste Radioactive materials at the end of a useful life cycle or in a product that is no longer useful and should be properly disposed of. [4]

radionuclides (radioisotope) An isotope of an element that has an unstable nucleus; it tries to stabilize itself by giving of radioactive particles and undergoes spontaneous decay. [10]

RCRA-authorized state When a state is authorized to administer the RCRA program in lieu of EPA, EPA has made a determination that the state's program is equivalent (in the case of final authorization), or substantially equivalent (in the case of interim authorization), to the federal program and that the state hazardous waste program can thereafter be administered by the state under state law in lieu of the federal program. [16]

reaction A process in which one or more substances are changed chemically into one or more different substances. [10]

receptor Ecological entity exposed to a stressor. [13]

redox reaction Oxidation-reduction reaction in which electrons are transferred between two or more compounds. [10]

reductant A molecule or atom that donates an electron in an oxidation-reduction reaction. [10]

reduction Transfer of electrons to a compound.

reduction potential The inherent tendency of a compound to act as an electron donor or an electron acceptor; measured in volts. [10]

Resource Conservation and Recovery Act (RCRA) A federal law enacted in 1976 to address the treatment, storage, and disposal of solid and hazardous waste. [3]

response action 1. Generic term for actions taken in response to actual or potential health-threatening environmental events such as spills, sudden releases, and asbestos abatement/ management problems. 2. A CERCLA-authorized action involving either a short-term removal action or a long-term removal response. This may include but is not limited to removing hazardous materials from a site to an EPA-approved hazardous waste facility for treatment, containment or treating the waste on site, identifying and removing the sources of groundwater contamination, and halting further migration of contaminants. [13]

risk The quantitative or qualitative expression of possible loss that considers both the probability that a hazard will cause harm and the consequences of that event. [2] The probability of injury, disease, or death under specific circumstances. Risk can be expressed as a value that ranges from zero (no injury or harm will occur) to 100% (harm or injury will definitely occur). Risk-based standards limit the risk that releasing a contaminant to the environment may pose rather than limiting the quantity that may be released. *Absolute risk* is the excess risk attributed to irradiation and usually expressed as the numeric difference between irradiated and nonirradiated populations (e.g., one case of cancer per million people irradiated annually for each rad). Absolute risk may be given on an annual basis or lifetime basis. *Relative risk* is the ratio between the number of cancer cases in the irradiated population to the number of cases expected in the unexposed population. A relative risk of 1.1 indicates a 10% increase in cancer due to radiation, compared to the “normal” incidence. [5]

risk assessment A detailed analysis that provides a numerical probability that a particular kind of injury will occur (for example, the number of additional cases of cancer in a group of 10,000). [5]

saturated zone An underground geologic layer in which all pores and fractures are filled with water. [10] Subsurface environment in which the pore spaces are filled with water. [9]

saturation index (SI) A conventional method for expressing the groundwater saturation state, given by the following:

$$SI = \Delta Gr0/RT + \ln Q = \ln Q/Kr$$

where $\Delta Gr0$ is the standard state free energy change of the reaction, R is the gas constant, T is temperature in degrees Kelvin, Q is the reaction quotient (or ion activity product), and Kr is the temperature- and pressure-dependent equilibrium constant of a reaction. [14]

sediment Material in suspension in water or deposited from suspension or precipitation. [10]

solubility The relative capacity of a substance to serve as a solute, usually in reference to water as the solvent. [10]

sorption The process of being taken up or held by either adsorption or absorption. [10] The uptake of a solute by a solid. [9]

source, source material Source material is material that includes or contains hazardous substances, pollutants or contaminants that act as a reservoir [either stationary or mobile] for migration of contamination to the groundwater, to surface water, to air, [or other environmental media,] or acts as a source for direct exposure. Contaminated groundwater generally is not considered to be a source material although nonaqueous-phase liquids (NAPLS [occurring either as residual- or free-phase]) may be viewed as source materials. [6]

species Actual form in which a dissolved molecule or ion is present in solution. [12]

stability, contaminant Long-term resistance of an immobilized contaminant to remobilization due to changes aquifer chemistry. [15]

stability, plume A groundwater plume that is no longer migrating or increasing in extent. [8]

stakeholder May include people in communities living near contaminated sites, site-specific advisory boards, local governments, and a variety of nongovernmental organizations.

stewardship (long-term stewardship) The physical controls, institutions, information, and other mechanisms needed to ensure protection of people and the environment. [10]

subsurface The geologic zone below the surface of the earth. [10]

Superfund A term commonly used to refer to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). [3]

Superfund Trust Fund A public trust fund created with passage of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) in 1980 to be used to help pay for the cleanup of abandoned hazardous waste sites. This law, nicknamed Superfund, provides the authority through which the federal government can compel people or companies to clean up hazardous waste sites. [10]

sustainability The ability of a system to maintain the important attenuation mechanisms through time. [9]

thermodynamic database A compilation of thermodynamic data for each of the aqueous species, minerals, gases, and adsorbed species in a system for input to a geochemical or reactive transport model.

transport Conveyance of solutes and particles in flow systems. [10]

tribal government Indian nations, tribes, and pueblos that are distinct from stakeholders and enjoy a government to government relationship.

unsaturated zone An underground geologic layer in which pores and fractures are filled with a combination of air and water. [10]

Uranium Mill Tailings Radiation Control Act (UMTRCA) of 1978 (42 U.S.C. 2022) The act that directed DOE to provide for stabilization and control of the uranium mill tailings from inactive sites in a safe and environmentally sound manner to minimize radiation health hazards to the public. It authorized DOE to undertake remedial actions at 24 designated inactive uranium-processing sites and at an estimated 5,048 vicinity properties. Both DOE and NRC implement standards under this act. Additional regulations in 40 CFR Part 192 and 10 CFR 40, Appendix A provide design requirements for closure of mill waste disposal areas. [1, 6]

vadose zone The unsaturated zone above the water table. [10]

valence The property of an element that determines the number of other atoms with which an atom of the element can combine. [10]

volatilization Vaporization. [10] The transfer of a chemical from its liquid phase to the gas phase. [9]

water table The upper limit of a geologic layer wholly saturated with water. [10]

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Appendix F

Acronyms and Abbreviations

ACRONYMS AND ABBREVIATIONS

AEA	Atomic Energy Act
APMR	Attenuation Processes for Metals and Radionuclides
ARAR	applicable or relevant and appropriate requirement
atm	atmosphere (unit)
CDPHE	Colorado Department of Public Health and Environment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CERCLIS	CERCLA Information System
CFR	Code of Federal Regulations
COC	contaminant of concern
CSM	conceptual site model
CWA	Clean Water Act
DEAR	Department of Energy Acquisition Regulation
DEC	Department of Environmental Conservation
DO	dissolved oxygen
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DU	depleted uranium
EA	enhanced attenuation
EE/CA	engineering evaluation/cost analysis
EDTA	ethylenediaminetetraacetic acid
EFA/WFA	East Firing Area/West Firing Area
Eh	measure of oxidation-reduction potential
EMS	Environmental Management System
ERD	enhanced reductive dechlorination
ESTCP	Environmental Security Technology Certification Program
EPA	U.S. Environmental Protection Agency
foc	fraction organic carbon
FS	feasibility study
GCTL	groundwater cleanup target level
GWPP	groundwater protection program
HSU	hydrostratigraphic unit
IAP	ion activity product
IC	ion chromatography
ICP-ES	inductively coupled plasma emission spectrometry
IRA	Interim Remedial Action
ISMS	Integrated Safety Management System
ITRC	Interstate Technology & Regulatory Council
K_d	distribution coefficient
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
LOE	line of evidence
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
MMTS	Monticello Mill Tailings Site

MNA	monitored natural attenuation
MNR	monitored natural recovery
MPN	most probable number
NADC	natural attenuation default criterion
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NOM	natural organic matter
NPL	National Priorities List
NRC	National Research Council
NRC	U.S. Nuclear Regulatory Commission
OLOE	other line of evidence
ORP	oxidation-reduction potential
OSWER	Office of Solid Waste and Emergency Response
OU	operable unit
PLOE	primary line of evidence
POC	point of contact
PRB	permeable reactive barrier
RA	remedial action
RAO	remedial action objective
RCRA	Resource Conservation and Recovery Act
REDOX	reduction-oxidation
RI	remedial investigation
ROD	record of decision
RPM	Remedial Project Manager
RPO	remedial process optimization
SARA	Superfund Amendments and Reauthorization Act of 1986
SDWA	Safe Drinking Water Act
SI	saturation index
SLOE	secondary line of evidence
SWRB	State Water Resources Control Board
TCA	Tennessee Code Annotated
TCEQ	Texas Commission on Environmental Quality
TI	technical impracticability
UDEQ	Utah Department of Environmental Quality
UMTRCA	Uranium Mill Tailing Radiation Control Act of 1978
U.S.C.	United States Code
ZVI	zero-valent iron
µg	microgram
λ	decay constant