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Office of Solid Waste and Emergency Response

USE OF MONITORED NATURAL ATTENUATION FOR INORGANIC CONTAMINANTS IN GROUNDWATER AT SUPERFUND SITES

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
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TABLE OF CONTENTS

Section **Page**

TABLE OF CONTENTS (Continued)

Section **Page**

TABLE OF CONTENTS (Continued)

FIGURES

TABLES

APPENDICES

ACRONYMS AND ABBREVIATIONS

Acronym	**Definition**
α	Alpha
Am	Americium
ARAR	Applicable or relevant and appropriate requirement
As	Arsenic
AVS	Acid volatile sulfide
Bq	Becquerel
Br	Bromine
β	Beta
C	Celsius
Ca	Calcium
Cd	Cadmium
CEC	Cation exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CH_4	Methane
Cl	Chlorine
ClO_4	Perchlorate
C_o	Initial groundwater concentration
CO_2	Carbon dioxide
COC	Contaminant of concern
Cr	Chromium
Cs	Cesium
CSM	Conceptual site model
Cu	Copper
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOE	U.S. Department of Energy
DQO	Data quality objective
EDTA	Ethylenediamine tetraacetic acid
Eh	Redox potential
EPA	U.S. Environmental Protection Agency
ESD	Explanation of significant differences
F	Flourine
Fe	Iron
FR	Federal Register
FS	Feasibility study
γ	Gamma
H_2	Hydrogen
H_2S	Hydrogen sulfide
HS^-	Bisulfide

HTRW	Hazardous, Toxic, and Radioactive Waste
I	Iodine
IC	Institutional control
ITRC	Interstate Technical Regulatory Council
K	Potassium
K_d	Distribution/partition coefficient
kg	Kilogram
K_{oc}	Organic carbon soil-water partition coefficient
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MeV	Megaelectronvolt
Mg	Magnesium
mg	Milligram
µg/L	Micrograms per liter
µs	Microsecond
$\mu S/cm^2$	Microsecond per square centimeter
MNA	Monitored natural attenuation
ms	Millisecond
mV	Megavolt
Na	Sodium
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
Ni	Nickel
NO_2^-	Nitrite
NO_3	Nitrate
Np	Neptunium
NPL	National Priorities List
NRC	Nuclear Regulatory Commission
OE	Ordnance and explosives
ORP	Oxidation-reduction potential
OSWER	Office of Solid Waste and Emergency Response
Pa	Protactinium
Pb	Lead
pCi	Picocurie
pCi/L	Picocurie per liter
PRG	Preliminary remediation goal
Pu	Plutonium
QA	Quality assurance
Ra	Radium
RAO	Remedial action objective
RCRA	Resource Conservation and Recovery Act
RfD	Reference dose
RI	Remedial investigation
Rn	Radon
ROD	Record of decision

SCM	Surface complexation model
SDWA	Safe Drinking Water Act
Se	Selenium
SEM	Simultaneously extracted metals
SEP	Sequential extraction procedure
Sr	Strontium
Tc	Technetium
Th	Thorium
TI	Technical impracticability
TIC	Total inorganic carbon
TOC	Total organic carbon
TPP	Technical project planning
U	Uranium
UMTRCA	Uranium Mill Tailings Radiation Control Act of 1978
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
VOC	Volatile organic compounds
Xe	Xenon

NOTICE/DISCLAIMER

This document was developed through the cooperative efforts of a team of Headquarters and regional staff inside the U.S. Environmental Protection Agency (EPA) and relies on peer-reviewed literature, EPA reports, Web sources, current research, and other pertinent information. This document has been through a thorough internal EPA peer-review process, which included comments from the Office of Solid Waste and Emergency Response (OSWER) and the Office of General Counsel. References and Web links are provided for readers interested in additional information; these Web links, verified as accurate at the time of publication, are subject to change by Web sponsors. Note that the mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This guidance is designed to help promote consistent national approach for implementation of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) response actions at private party and federal facility sites. It does not, however, substitute for CERCLA or EPA's regulations, nor is it a regulation itself. Thus, it does not impose legally binding requirements on EPA, states, tribes or the regulated community, and may not apply to a particular situation based on the circumstances. EPA, state, tribal and local decision-makers retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate. Any decisions regarding a particular facility will be made based on the applicable statutes and regulations.

In working with other federal agencies to make cleanup decisions for groundwater at sites where the other federal agency is lead for cleanup, EPA Regions should use the recommendations in this document to the same extent as at non-federal facility sites. Section 120(a)(2) of CERCLA provides that all guidelines, rules, regulations, and criteria for preliminary assessments, site investigations, National Priorities List (NPL) listing, and remedial actions are applicable to federal facilities to the same extent as they are applicable to other facilities. It states the following: "No department, agency or instrumentality of the United States may adopt or utilize any such guidelines, rules, regulations, or criteria which are inconsistent with the guidelines, rules, regulations, and criteria established by the Administrator under this Act."

EXECUTIVE SUMMARY

This new monitored natural attenuation (MNA) policy document for inorganic contaminants (“2015 MNA guidance”) expands on and is designed to be a companion to the 1999 MNA guidance.[1] The 1999 MNA guidance, which clarified “EPA’s policy regarding the use of monitored natural attenuation (MNA) for the cleanup of contaminated soil and groundwater1 in the Superfund, RCRA Corrective Action, and Underground Storage Tank programs,[2]” focused primarily on *organic contaminants*; however, the 1999 MNA guidance does address inorganic contaminants to some extent (*see for example,* pp. 8-9). Together, these two policy documents provide guidance on the consideration of MNA for a broad range of contaminants at Superfund sites. The two MNA policy documents are supported by a three-volume set of technical reports issued by the U.S. Environmental Protection Agency’s (EPA) Office of Research and Development (2007-2010).[3]

Regions should continue to consider the overall recommendations in the 1999 MNA guidance when evaluating all sites (those with organic and inorganic contaminants). Consistent with the 1999 MNA guidance, the 2015 MNA guidance document discusses in more detail below that MNA for inorganic contaminants: (1) is not intended to constitute a treatment process for inorganic contaminants; (2) when appropriately implemented, can help to restore an aquifer to beneficial uses by immobilizing contaminants onto aquifer solids and providing the primary means for attenuation of contaminants in groundwater; and (3) is not intended to be a “do nothing” response.

Furthermore, as discussed in the 1999 MNA guidance and in more detail below, the Agency’s longstanding policy is that MNA is generally not an appropriate response action if a receptor is currently being exposed to a contaminant or the contaminant plume is expanding. In addition, MNA, whether selected as the sole remedial action or as a finishing step, may be appropriate when it can achieve a site’s remedial action objectives in a reasonable timeframe; thus, MNA remedies should not extend over very long timeframes, and the anticipated timeframes should be reasonable compared with other potential alternatives being considered. However, the document acknowledges that longer timeframes may be needed for some contaminants that degrade or decay over a long time period.

As also discussed in the 1999 MNA guidance and in more detail below, an MNA approach for groundwater may not be appropriate for ensuring protectiveness of human health and the environment at Superfund sites. Regions should evaluate specific site conditions in determining

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[1] *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (OSWER Directive 9200.4-17P, April 21, 1999) (EPA 1999c).

[2] 1999 MNA guidance (page 1).

[3] To the extent it is consistent with CERCLA, the NCP and this and other EPA CERCLA guidance documents, Regions also may find useful information in the Interstate Technical Regulatory Council (ITRC) Guidance on MNA for metals and radionuclides (2010).

whether MNA can be a viable cleanup approach (for example, the groundwater plume should be stable or shrinking, geochemical evidence of attenuation should be documented in the administrative record, there should be no exposure to the contaminated groundwater, and the source of contaminants should be identified and addressed).

This 2015 MNA guidance, consistent with the 1999 MNA guidance, indicates that multiple "lines of evidence" should be obtained to evaluate whether MNA should be considered as part of the site's selected response action. As a related matter, the 1999 MNA guidance also recommends use of a tiered analysis approach for considering MNA, which typically involves a detailed analysis of site characteristics that control and sustain attenuation. The 2015 MNA guidance builds on this tiered approach and recommends a phased analytical approach tailored specifically for inorganic contaminants. Where natural attenuation leads to daughter products that are more toxic than the parent compounds, Regions should ensure protectiveness of human health and the environment by taking steps to make sure that the more toxic compounds do not increase over time or are addressed by changes to the existing remedy.

In conclusion, while the 1999 MNA guidance continues to provide overall recommendations on evaluating MNA, the 2015 MNA guidance (generally) offers more specific recommendations intended to assist the Regions in evaluating whether MNA for *inorganic contaminants* is appropriate. If MNA is considered as an appropriate cleanup approach at Superfund sites, the guidance can assist in identifying steps that can be taken to ensure that the risk to human health and the environment is adequately reduced and managed in a timely manner.

1.0 INTRODUCTION

This guidance document provides recommendations for evaluating monitored natural attenuation (MNA) as a potential component of a remedial action approach for cleaning up inorganic contaminants (including radionuclides) in groundwater at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites. This document uses "inorganic contaminants" as a generic term for metals and metalloids (such as arsenic); the phrase also refers to radioactive as well as non-radioactive isotopes. The purpose of this document is to provide additional guidance, generally consistent with the 1999 MNA guidance, on considering the use of MNA for inorganic contaminants (as well as nitrate and perchlorate) in groundwater as a way to ensure protectiveness of human health and the environment. With regard to inorganic contaminant plumes in groundwater, it describes the primary processes that typically govern MNA and offers a recommended framework for assessing the potential effectiveness of MNA as a cleanup approach.

More detailed discussion of the scientific principles and processes described in this policy may be found in the following three documents, which are referenced frequently in this guidance:

- *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume I – Technical Basis for Assessment,* EPA 600-R-07-139 (EPA 2007a).
- *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume II – Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium,* EPA 600-R-07-140 (EPA 2007b).
- *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume III – Assessment for Radionuclides Including Americium, Cesium, Iodine, Plutonium, Radium, Radon, Strontium, Technetium, Thorium, Tritium, and Uranium,* EPA 600-R-10-093 (EPA 2010a).

As discussed in the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) and in various associated EPA CERCLA guidance documents, "[t]he EPA expects to return usable groundwaters to their beneficial uses whenever practicable, within a timeframe that is reasonable given the particular circumstances of the site" (see 40 Code of Federal Regulations [CFR] §300.430(a)(1)(iii)(F)).

In general, five key principles stem from the overarching expectations for groundwater restoration.[4] As discussed in "Summary of Key Existing EPA CERCLA Policies for Groundwater Restoration" (OSWER Directive Number 9283.1-33, June 26, 2009), these expectations are as follows:

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[4] See "Summary of Key Existing EPA CERCLA Policies for Groundwater Restoration" (OSWER Directive Number 9283.1-33, June 26, 2009) (See pages 3-4.) at www.epa.gov/superfund/health/conmedia/gwdocs/pdfs/9283_1-33.pdf.

(1) "If groundwater that is a current or potential source of drinking water[5] is contaminated above protective levels (that is, for drinking water aquifers, contamination exceeds federal or state maximum contaminant levels [MCLs] or non-zero maximum contaminant level goals [MCLGs]), a remedial action under CERCLA should seek to restore the aquifer to beneficial use (that is, drinking water standards) wherever practicable.

(2) "Groundwater contamination should not be allowed to migrate and further contaminate the aquifer or other media (for example, indoor air via vapor intrusion into buildings; sediment; surface water; or wetland).

(3) "Technical impracticability waivers and other waivers may be considered and, under appropriate circumstances, granted if the statutory criteria are met, when groundwater cleanup is impracticable. The waiver decision should be scientifically supported and clearly documented.

(4) "Early actions[6] (such as source removal, plume containment or provision of an alternative water supply[7]) should be considered as soon as possible. Institutional controls (ICs) related to groundwater use or even surface water use may be useful to protect the public in the short term, as well as in the long term.

(5) "ICs should not be relied on as the only response to contaminated groundwater or as a justification for not taking action under CERCLA.[8] To ensure protective remedies, CERCLA response action cleanup levels for contaminated groundwater should generally address all pathways of exposure that pose an actual or potential risk to human health and the environment."

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[5] The EPA generally considers potential source for drinking water as Class II under EPA's Groundwater Classification System in "Guidelines for Groundwater Classification Under the EPA Groundwater Protection Strategy" (Final Draft, December 1986) and the National Contingency Plan (NCP) where Class I and II generally are considered to be current and potential drinking water aquifers (See 55 FR [Federal Register] 8732 (March 8, 1990).

[6] See "Considerations in Groundwater Remediation at Superfund Sites and RCRA Facilities – Update" (Directive Number 9283.1-06, May 27, 1992) for a more complete discussion of early actions. (See pages 6-8.) at www.epa.gov/superfund/policy/remedy/pdfs/92-83106-s.pdf.

[7] See 55 FR 8865 (March 8, 1990) for a list of potential ways of providing an alternative water supply (Appendix D).

[8] See 40 CFR § 300.430(a)(iii)(D) ("The use of institutional controls shall not substitute for active response measures (for example, treatment and/or containment of source material, restoration of groundwaters to their beneficial uses) as the sole remedy unless such active measures are determined not to be practicable, based on the balancing of trade-offs among alternatives that is conducted during the selection of remedy"). Also see 40 CFR § 300.430(a)(iii)(A) related to the expectation for treatment.

Cleanup levels for response actions under CERCLA generally are developed based on applicable or relevant and appropriate requirements (ARARs) where they are available and sufficiently protective of human health,[9] and on site-specific risk assessments where ARARs do not exist. The determination of whether a requirement is an ARAR, as stated in the NCP, is made on a site-specific basis (see 40 CFR§300.400(g)). In general, drinking water standards provide relevant and appropriate cleanup levels for groundwater that is a current or potential source of drinking water; drinking water standards include federal or state MCLs or non-zero MCLGs established under the Safe Drinking Water Act (SDWA) or more stringent state drinking water standards.[10] Depending on site-specific circumstances, however, drinking water standards may not be relevant and appropriate for groundwater that is not a current or potential source of drinking water (see 55 Federal Register [FR] 8732, March 8, 1990).

Selection of Contaminants

The series of technical resource documents addressing MNA for inorganic contaminants referenced in this policy includes a discussion of a specific list of contaminants. The contaminants addressed in the technical resource documents were selected based on the frequency of occurrence at contaminated sites and to represent the range of contaminant properties that can influence the efficiency of natural attenuation processes to achieve site cleanup goals. The recommendations in this guidance should be considered for all non-radiological or radiological inorganic contaminants in groundwater, regardless of their inclusion in the technical resource documents.

The non-radionuclide contaminants addressed in the technical documents include the following: arsenic, cadmium, chromium, copper, lead, nickel, nitrate, perchlorate and selenium. These contaminants are commonly found at Superfund sites throughout the nation and reflect toxicity, industrial use, and frequency of occurrence at Superfund sites. They represent a broad range of geochemical traits such as the following: ion charge (cation vs. anion), transport behavior (conservative vs. non-conservative) and oxidation-reduction (redox) chemistry (EPA 1999a, 1999b and 2004c). Conservative behavior typically is exhibited by non-reactive contaminants that tend to move readily with groundwater flow, while non-conservative behavior typically is exhibited by contaminants whose transport is retarded by any number of different mechanisms. Finally, the EPA regional staff members were asked to nominate inorganic contaminants that occurred frequently or that were problematic in their Regions. The above list of nine inorganic contaminants reflects this process.

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[9] *See e.g.,* "Clarification of the Role of Applicable, or Relevant and Appropriate Requirements in Establishing Preliminary Remediation Goals under CERCLA," OSWER Directive No. 9200.4-23 (August 22, 1997) ("It remains EPA's policy that ARARs will generally be considered protective absent multiple contaminants or pathways of exposure. However, this Directive clarifies that, in rare situations, EPA regional offices should establish PRGs at levels more protective than required by a given ARAR, even absent multiple pathways or contaminants, where application of the ARAR would not be protective of human health or the environment.").

[10] Other regulations may also be ARARs for purposes of CERCLA §121(d)(2)(B).

A similar process was used to identify the radionuclide contaminants in the technical documents, including the following: americium, cesium, iodine, neptunium, plutonium, radium, radon, technetium, thorium, tritium, strontium and uranium. These radionuclides are daughter and fission products that result from radioactive decay and are commonly found at Superfund sites. The decay of radioisotopes can produce daughter products that may differ both physically and chemically from parent isotopes. The radionuclide contaminants addressed in the technical document also represent a broad range of geochemical traits and environmental characteristics.

1.1 Intended Use of Document

Users of this document may include the EPA and state cleanup program personnel and their contractors, especially those individuals responsible for evaluating alternative cleanup methods for a given site or facility. Depending on site-specific circumstances (for example, which hazardous substances are being addressed), the recommendations in both this 2015 MNA guidance and the 1999 MNA guidance may be useful. For more information on MNA for groundwater cleanups, see www.epa.gov/superfund/health/conmedia/gwdocs/monit.htm. Additional guidance may also be found at www.cluin.org/techfocus/default.focus/sec/Natural_Attenuation/cat/Guidance.

The potential attenuation processes affecting inorganic contaminants generally should be the same for both radioactive and non-radioactive inorganic contaminants contaminant types, except for radioactive decay. As a result, the decision-making approach and process for establishing cleanup levels at CERCLA sites normally should be the same for sites with radioactive and non-radioactive inorganic contaminants, except where there are technical differences between the two types of contaminants (such as external exposure from gamma radiation vs. dermal exposure).

1.2 Tiered Analysis Approach for Developing Multiple Lines of Evidence

As discussed in the 1999 MNA guidance (pp. 15-16):

> Once site characterization data have been collected and a conceptual model developed, the next step is to evaluate the potential efficacy of MNA as a remedial alternative. This involves collection of site-specific data sufficient to estimate with an acceptable level of confidence both the rate of attenuation processes and the anticipated time required to achieve remediation objectives. A three-tiered approach to such an evaluation is becoming more widely practiced and accepted. In this approach, successively more detailed information is collected as necessary to provide a specified level of confidence on the estimates of attenuation rates and remediation timeframe. These three tiers of site-specific information, or “lines of evidence”, are:

(1) Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend [footnote in original deleted] of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a groundwater plume, decreasing concentrations should not be solely the result of plume migration. In the case of inorganic contaminants, the primary attenuating mechanism should also be understood.)

(2) Hydrogeologic and geochemical data that can be used to demonstrate **indirectly** the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.

(3) Data from field or microcosm studies (conducted in or with actual contaminated site media) which **directly** demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).

For inorganic contaminant plumes, the evaluation and selection of MNA as part of a cleanup action in groundwater typically involves a detailed analysis of site-specific data and characteristics that control and sustain attenuation. Developing multiple lines of evidence (as discussed in the 1999 MNA guidance) to support this analysis can require significant resource outlays. Thus, site characterization should be approached in a step-wise manner to collect data for inclusion in the administrative record that support the evaluation of existing natural attenuation processes within the aquifer and the analysis of potential long-term effectiveness. The 2015 MNA guidance builds on the *tiered analysis approach* discussed in the 1999 MNA guidance for inorganic contaminants as a way to provide a cost-effective way to screen sites for MNA because it is designed to prioritize and focus the characterization needs for decision making at each screening step. Conceptually, a tiered analysis approach is designed to progressively reduce uncertainty as more and more site-specific data are collected. The recommended tiered analysis approach is discussed in more detail in Section 3 of this document involves obtaining progressively more information. The recommended approach is designed to acquire lines of evidence that can be used to assess the likely effectiveness of MNA as a remedial action alternative for inorganic contaminants in groundwater. The EPA generally recommends following the tiered approach outlined in this document for inorganic contaminants.

1.3 Conceptual Site Model

As stated in the 1999 MNA guidance (p. 14), “EPA recommends the use of conceptual site models to integrate data and guide both investigative and remedial actions.”

Assessing the suitability of MNA as a component of a groundwater response action for sites with inorganic contaminants is helped by development of a conceptual site model[11] (CSM). Regions should refer to existing EPA guidance on CSMs (see, for example, *Environmental Cleanup Best Management Practices: Effective Use of the Project Life Cycle Conceptual Site Model*, EPA 542-F-11-011, OSWER, July 2011; *Performance Monitoring of MNA Remedies for VOCs in Ground Water,* EPA/600/R-04/027 April 2004; *A Guide To Preparing Superfund Proposed Plans, Records Of Decision, and other Remedy Selection Decision Documents,* OSWER 9200.1-23P, July 1999; *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*. EPA 600-R-98-128, Office of Research and Development, 1998).

Generally, the CSM is a representation (written, graphical or pictorial) of the environmental system at a site and the biological, physical, and chemical processes (and relationships between them) that affect contaminant transport. The CSM is designed to identify potential pathways that may expose receptors to site contaminants. The CSM should also quantify fluxes of contaminants and describe the conditions that may affect or alter the MNA processes. The CSM should include an understanding of the attenuation mechanisms, the geochemical conditions governing these mechanisms, the capacity of the aquifer to sustain attenuation of the contaminant mass and prevent future contaminant migration, and indicators that can be used to monitor MNA performance. Uncertainties and assumptions should be listed with specific strategies to describe and minimize their impact on qualitative and quantitative models. Data collection should be focused on complete or potentially complete exposure pathways, based on both current and reasonably anticipated future land use, to avoid collecting unnecessary data that do not contribute to site closeout. A well-formed CSM can be important in the development of sound data quality objectives (DQOs). DQOs should be developed to ensure that all appropriate data are collected with sufficient quantity, sensitivity, and precision to meet the needs of the project (EPA 2002b and 2006a). Finally, the CSM serves as a planning instrument and data interpretation aid as well as a communication device between and among project staff and the public.[12]

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[11] As stated in the 1999 MNA guidance, A conceptual site model (CSM) is 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. Computer models, which simulate site processes mathematically, should in turn be based on sound conceptual site models to provide meaningful information. Computer models typically require a lot of data, and the quality of the output from computer models is directly related to the quality of the input data. Because of the complexity of natural systems, models necessarily rely on simplifying assumptions that may or may not accurately represent the dynamics of the natural system. Calibration and sensitivity analyses are important steps in appropriate use of models. Even so, the results of computer models should be carefully interpreted and continuously verified with adequate field data.

[12] To the extent it is consistent with CERCLA, the NCP and existing EPA CERCLA guidance documents, Regions may find useful information in documents prepared by the U.S. Army Corps of Engineers (USACE 1998 and 2003) and the Interstate Technical Regulatory Council (ITRC) (ITRC 2003).

Although the focus of this document is on groundwater, the vadose zone often is another source of contaminants to groundwater at CERCLA sites. Thus, both the vadose and saturated zones normally should both be carefully characterized. Regions should consider developing a CSM that adequately characterizes both the saturated and vadose zone.

Initially, the CSM is developed based on existing knowledge of groundwater and vadose zone fate and transport characteristics, as well as known properties of the specific contaminants potentially present at the site. The CSM should be updated in an iterative fashion as progressively more is learned about the site.

1.4 Definition of MNA in Groundwater

The term "monitored natural attenuation," as used in the 1999 MNA guidance and this document, refers to

> " ...[t]he 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 time frame 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." (EPA 1999c, page 3)

1.5 Overview of the 1999 OSWER Directive

The 1999 MNA guidance provides recommendations related to the consideration of MNA generally (for example, for both organic and inorganic contaminants). This 2015 MNA guidance provides additional information and recommendations regarding site characterization, data quality and attenuation processes related specifically to inorganic contaminants.

Although several physical, chemical and biological processes are included in the definition of MNA mentioned above, the 1999 MNA guidance recommends using processes that permanently degrade or destroy contaminants and using MNA only for stable or shrinking plumes, as noted below:

> When relying on natural attenuation processes for site remediation, the EPA prefers those processes that degrade or destroy contaminants. Also, the EPA generally expects that MNA will only be appropriate for sites that have a low potential for contaminant migration. (EPA 1999c, page 3)

> MNA should not be used where such an approach would result in either plume migration[13] or impacts to environmental resources that would be unacceptable to the overseeing regulatory authority. Therefore, sites where the contaminant plumes are no longer increasing in extent, or are shrinking, would be the most appropriate candidates for MNA remedies. (EPA 1999c, page 18)

Control of contaminant sources also is an important aspect of the 1999 MNA guidance:

> 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 1999c, page 22)

The 1999 MNA guidance (*see for example,* pp. 8 – 9) provides a few general recommendations for use of MNA as a remedial approach for inorganic contaminants. For example, these general recommendations include (1) the specific mechanisms responsible for attenuation of inorganic contaminants should be known at a particular site; (2) the stability of the process should be evaluated and shown to be protective under anticipated changes in site conditions; and (3) fate and transport characteristics of any daughter products should be understood. Thus:

> MNA may, under certain conditions (*e.g.,* through sorption or oxidation-reduction reactions), effectively reduce the dissolved concentrations and/or toxic forms of inorganic contaminants in groundwater and soil. Both metals and non-metals (including radionuclides) may be attenuated by sorption[14] reactions such as precipitation, adsorption on the surfaces of soil minerals, absorption into the matrix of soil minerals, or partitioning into organic matter. Oxidation-reduction

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[13] As stated on p. 18 of the 1999 MNA guidance: "In determining whether a plume is stable or migrating, users of this Directive should consider the **uncertainty** associated with defining the limits of contaminant plumes. For example, a plume is typically delineated for each contaminant of concern as a 2- or 3-dimensional feature. Plumes are commonly drawn by computer contouring programs which estimate concentrations between actual data points. The EPA recognizes that a plume boundary is more realistically defined by a zone rather than a line. Fluctuations within this zone are likely to occur as a result of a number of factors (such as analytical, seasonal, or spatial), which may or may not be indicative of a trend in plume migration. Therefore, site characterization activities and performance monitoring should focus on collection of data of sufficient quality to enable decisions to be made with a high level of confidence."

[14] As stated on p. 8 of the 1999 MNA guidance: "When a contaminant is associated with a solid phase, it is usually not known if the contaminant is precipitated as a three-dimensional molecular coating on the surface of the solid, adsorbed onto the surface of the solid, absorbed into the structure of the solid, or partitioned into organic matter. "Sorption" will be used in this Directive to describe, in a generic sense (*i.e.*, without regard to the precise mechanism) the partitioning of aqueous phase constituents to a solid phase."

> (redox) reactions can transform the valence states of some inorganic contaminants to less soluble and thus less mobile forms (*e.g.*, hexavalent uranium to tetravalent uranium) and/or to less toxic forms (*e.g.*, hexavalent chromium to trivalent chromium). Sorption and redox reactions are the dominant mechanisms responsible for the reduction of mobility, toxicity, or bioavailability of inorganic contaminants. It is necessary to know what specific mechanism (type of sorption or redox reaction) is responsible for the attenuation of inorganics so that the stability of the mechanism can be evaluated. For example, precipitation reactions and absorption into a soil's solid structure (*e.g.*, cesium into specific clay minerals) are generally stable, whereas surface adsorption (*e.g.*, uranium on iron-oxide minerals) and organic partitioning (complexation reactions) are more reversible. Complexation of metals or radionuclides with carrier (chelating) agents (*e.g.*, trivalent chromium with EDTA) may increase their concentrations in water and thus enhance their mobility. Changes in a contaminant's concentration, pH, redox potential, and chemical speciation may reduce a contaminant's stability at a site and release it into the environment. Determining the existence and demonstrating the irreversibility, of these mechanisms is important to show that a MNA remedy is sufficiently protective.
>
> In addition to sorption and redox reactions, radionuclides exhibit radioactive decay and, for some, a parent-daughter radioactive decay series. For example, the dominant attenuating mechanism of tritium (a radioactive isotopic form of hydrogen with a short half-life) is radioactive decay rather than sorption. Although tritium does not generate radioactive daughter products, those generated by some radionuclides (*e.g.*, Am-241 and Np-237 from Pu-241) may be more toxic, have longer half-lives, and/or be more mobile than the parent in the decay series. Also, it is important that the near surface or surface soil pathways be carefully evaluated and eliminated as potential sources of external direct radiation exposure.[15] (EPA 1999c, pages 8-9)

The 1999 MNA guidance provides context for the Agency's recommendations regarding the feasibility of employing MNA as part of a cleanup for contaminated groundwater. As indicated by the sections transcribed above, the 1999 MNA guidance also points out some key specific issues associated with what constitutes natural attenuation for inorganic contaminants:

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[15] As stated on p. 9 of the 1999 MNA guidance: "External direct radiation exposure refers to the penetrating radiation (*i.e.,* primarily gamma radiation and x-rays) that may be an important exposure pathway for certain radionuclides in near surface soils. Unlike chemicals, radionuclides can have deleterious effects on humans without being taken into or brought in contact with the body due to high energy particles emitted from near surface soils. Even though the radionuclides that emit penetrating radiation may be immobilized due to sorption or redox reactions, the resulting contaminated near surface soil may not be a candidate for a MNA remedy as a result of this exposure risk."

> Inorganic contaminants persist in the subsurface because, except for radioactive decay, they are not degraded by the other natural attenuation processes. Often, however, they may exist in forms that have low mobility, toxicity or bioavailability such that they pose a relatively low level of risk. Therefore, natural attenuation of inorganic contaminants is most applicable to sites where immobilization or radioactive decay is demonstrated to be in effect and the process/mechanism is irreversible. (EPA 1999c, page 9)

1.6 Relationship of MNA to Remedial Action Objectives

Existing guidance on the development of remedial action objectives (RAOs) and the relationship of MNA to RAOs may be found in the EPA's 1999 record of decision (ROD) guidance titled, *A Guide to Preparing Superfund Proposed Plans, Records of Decision, and Other Remedy Selection Decisions Documents*, OSWER Directive 9200.1-23P, page 6-26 (EPA 1999d).

If the ROD includes an RAO that addresses restoration of groundwater for sites with inorganic contaminants in groundwater it may be appropriate to include MNA as a component of a general remedial approach. However, MNA may not be an appropriate response action to ensure protectiveness at the site if the ROD does not include an RAO addressing restoration of groundwater but rather includes RAOs addressing exposure control and prevention of migration. Where the RAOs include restoring groundwater to beneficial use by meeting ARARs or MCLs and the lines of evidence supporting MNA are documented sufficiently in the administrative record, then MNA may be a viable option used in conjunction with other remedial actions or independently to meet the restoration RAO.

1.7 MNA vs. Treatment as a Response Action for Inorganic Contaminants

As stated in the 1999 MNA guidance on p. 3: "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." Inorganic contaminants can be transferred between solid, liquid or gaseous phases and these phase transfers may reduce the aqueous concentration and mobility of inorganic contaminants in groundwater.

Mass reduction through degradation generally is not a viable process for most of the inorganic contaminants discussed in this document. The exception is radioactive decay, which is a well-understood attenuation process that may result in decreased contaminant mass, as described in Section 5.4. There are also limited examples where degradation of nonradiological inorganic contaminants may reduce contaminant mass (for example, biological degradation of nitrate or perchlorate). Thus, while attenuation can reduce the aqueous concentration and mobility of inorganic contaminants in groundwater, it should not be considered a treatment process for most inorganic contaminants, such as zinc and cadmium.

1.8 Primary Differences between Organic and Inorganic MNA

As discussed in the 1999 MNA guidance (p. 13): "**Decisions to employ MNA as a remedy or remedy component should be thoroughly and adequately supported with site-specific characterization data and analysis**" (emphasis in original).

When the potential use of an MNA approach is evaluated, site characterization for organic contaminants typically is focused on evaluating the mechanism of contaminant degradation, quantifying the risks associated with transformation products[16], and calculating the capacity of site conditions to sustain degradation of contaminant mass to achieve cleanup levels throughout the plume. Much of the emphasis on site characterization for MNA of *organic* contaminants has been directed toward collection and analysis of groundwater samples.

Characterization of the solid substrate within the aquifer normally plays a more significant role during site assessment for *inorganic* contaminants (other than nitrate and tritium), where immobilization onto aquifer solids provides the primary means for attenuation of the groundwater plume. In this case, concentrations in groundwater typically are reduced through sorption of the inorganic contaminant onto aquifer solids in combination with the long-term stability of the immobilized contaminant to resist remobilization because of changes in groundwater chemistry. Precipitation also can be a primary attenuation mechanism for inorganic contaminants, whereas it generally is an insignificant mechanism for organic contaminants. The approach and data and information supporting site characterization for nonradiological inorganic contaminants subject to degradation or reductive transformation processes (for example, nitrate) will likely be consistent with the approach employed to assess MNA for organic contaminant plumes (EPA 1998 and 2001). Figure 1.1 illustrates the conceptual distinction between organic and inorganic plume behavior and the degradation of organic contaminants versus immobilization of inorganic contaminants on aquifer solids. When contaminants of concern (COCs) include radionuclides, it generally is important to identify specific isotopes and associated daughter products present in site groundwater and to include both in the assessment of plume stability.

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[16] As discussed on p. 6 of the 1999 MNA guidance: "The term "transformation products" in the Directive includes intermediate products resulting from biotic or abiotic processes (*e.g.*, TCE, DCE, vinyl chloride), decay chain daughter products from radioactive decay, and inorganic elements that become methylated compounds (*e.g.*, methyl mercury) in soil or sediment. Some transformation products are quickly transformed to other products while others are longer lived."

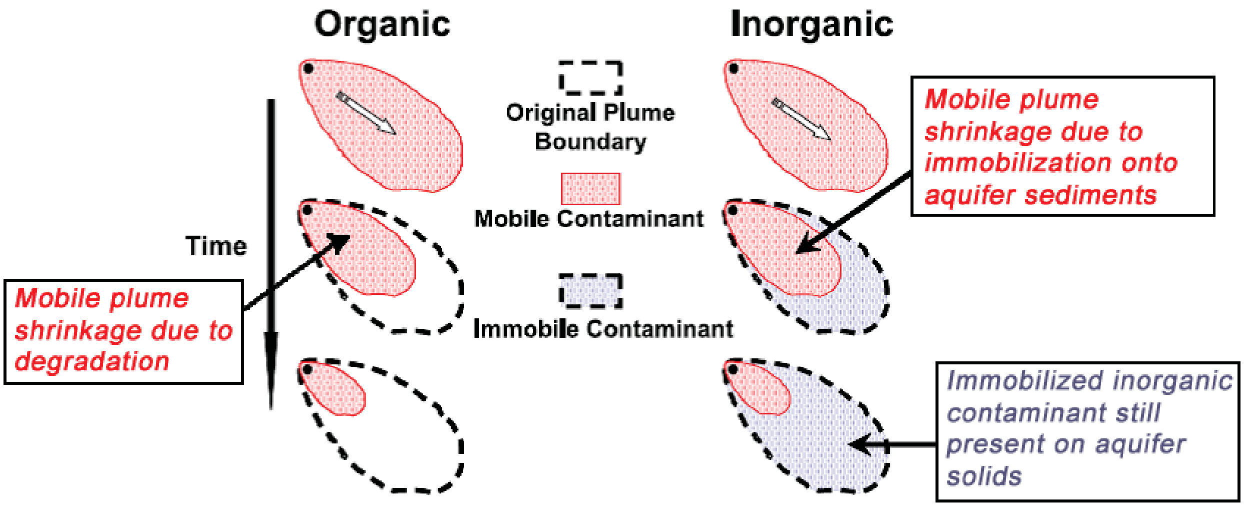

Figure 1.1. Conceptual distinction between organic and inorganic plume behavior illustrating degradation of organic contaminants and immobilization of inorganic contaminants. Immobilization of inorganic contaminants generally may be a viable component of an MNA where the immobilized contaminant remains stable and resistant to remobilization if there are any changes in groundwater chemistry.

2.0 IMPLEMENTATION

Implementation of MNA typically incorporates and balances several factors. It generally is critical to understand the subsurface geologic system and avoid conditions where MNA is not suitable. The Region should obtain data and information to adequately support multiples lines of evidence and a determination of plume stability, which indicate an MNA approach will ensure protectiveness of human health and the environment within a reasonable timeframe.

2.1 Plume Management

As discussed on p. 5 of the 1999 MNA guidance:

> It is common practice in conducting remedial actions to focus on the most obvious contaminants of concern, but other contaminants may also be of significant concern in the context of MNA remedies. In general, since engineering controls are not used to control plume migration in an MNA remedy, decision makers need to ensure that MNA is appropriate to address **all contaminants** that represent an actual or potential threat to human health or the environment (emphasis in original).

Furthermore, as discussed on p. 18 of the 1999 MNA guidance:

> MNA should not be used where such an approach would result in either plume migration[17] or impacts to environmental resources that would be unacceptable to the overseeing regulatory authority. **Therefore, sites where the contaminant plumes are no longer increasing in extent, or are shrinking, would be the most appropriate candidates for MNA remedies** (emphasis in original).

MNA may be implemented in a variety of ways for inorganic contaminants, depending on the nature of the chemical composition of the contaminant plumes, subsurface geology and potential exposures that are addressed. EPA policy allows MNA to be selected as a response action for one plume or comingled plumes; addressing commingled plumes may be significantly more

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[17] "In determining whether a plume is stable or migrating, users of this [1999 MNA guidance] Directive should consider the **uncertainty** associated with defining the limits of contaminant plumes. For example, a plume is typically delineated for each contaminant of concern as a 2- or 3-dimensional feature. Plumes are commonly drawn by computer contouring programs which estimate concentrations between actual data points. The EPA recognizes that a plume boundary is more realistically defined by a zone rather than a line. Fluctuations within this zone are likely to occur due to a number of factors (*e.g*., analytical, seasonal, spatial, etc.) which may or may not be indicative of a trend in plume migration. Therefore, site characterization activities and performance monitoring should focus on collection of data of sufficient quality to enable decisions to be made with a high level of confidence." See USEPA, 1993b, USEPA, 1993c, USEPA, 1994b and USEPA, 1998b, for additional guidance (citations in original).

complex than addressing similar separate plumes and may involve additional risk management considerations and expertise.

It may also be appropriate to select MNA for a particular contaminant while another response action is selected for other contaminants within the same plume. Likewise, it may be appropriate to select MNA for a particular contaminant in a portion of the plume and another remedy for the same contaminant in another portion of the plume. For example, enhanced bioremediation of a plume containing petroleum hydrocarbons can produce reducing conditions if bioremediation results in consumption of dissolved oxygen and other electron acceptors in the aquifer. These reducing conditions may result in the increased mobilization or solubility of redox-sensitive inorganic contaminants such as iron or manganese, which may also be associated with arsenic.

MNA may be an appropriate response action for the inorganic plume where it can be shown that the geochemistry downgradient of the hydrocarbon plume reverts to oxidizing conditions that would immobilize the inorganic contaminants. Similarly, an active remedy may be selected for one portion of a plume (for example, near a source area) while MNA may be selected for the same contaminant at the lower-concentration portion of the same plume farther downgradient.

2.2 Dispersion and Dilution

As discussed on p. 18 of the 1999 MNA guidance:

> An example of a situation where MNA may be appropriate is a remedy that includes source control, a pump-and-treat system to mitigate the highly-contaminated plume areas, and MNA in the lower concentration portions of the plume. In combination, these methods would maximize groundwater restored to beneficial use in a timeframe consistent with future demand on the aquifer, while utilizing natural attenuation processes to reduce the reliance on active remediation methods and reduce remedy cost. If, at such a site, the plume was either expanding or threatening downgradient wells or other environmental resources, then MNA would **not** be an appropriate remedy (emphasis in original).

Dispersion and dilution resulting from mixing with influent precipitation, up- or cross-gradient groundwater or leakage from overlying surface water bodies may be elements of an MNA response action for inorganic contaminants. **However, dilution and dispersion generally are not appropriate as primary MNA mechanisms because they reduce concentrations through dispersal of contaminant mass rather than destruction or immobilization of contaminant mass.** Dilution and dispersion may be appropriate as a "polishing step" for distal portions of a plume when an active remedy is being used at a site, source control is complete and appropriate land use and ground water use controls are in place. Results of conservative tracer studies can be used to estimate the contribution of dilution and dispersion to contaminant attenuation rates.

2.3 Site Monitoring

As discussed on p. 20 of the 1999 MNA guidance:

> It should be noted that the timeframe required for MNA remedies is often longer than that required for more active remedies. **As a consequence, the uncertainty associated with the above factors increases dramatically. Adequate performance monitoring and contingency remedies (both discussed in later sections of this Directive) should be utilized because of this higher level of uncertainty** (emphasis in original).

Furthermore, as discussed in the 1999 MNA guidance (pp. 22-23):

> Performance monitoring to evaluate remedy effectiveness and to ensure protection of human health and the environment is a critical element of all response actions. Performance monitoring is of even greater importance for MNA than for other types of remedies due to the potentially longer remediation timeframes, potential for ongoing contaminant migration, and other uncertainties associated with using MNA. This emphasis is underscored by EPA's reference to "monitored natural attenuation."
>
> 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 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 [footnote in original deleted];
> - 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.

In addition to the 1999 MNA guidance, other existing EPA CERCLA guidance discusses development of a performance monitoring framework and monitoring plan (see *Performance Monitoring of MNA Remedies for VOCs* [volatile organic compounds] *in Ground Water* [EPA 2004b]). Although that guidance focuses on attenuation of common organic contaminants, the recommended framework and many of the recommendations regarding plan development also may be useful at sites with inorganic constituents.

The performance of an MNA response action should be monitored to determine whether site-specific RAOs identified in remedy decision documents are achieved.[18] Where the time horizons for successful implementation of an MNA response action are expected to be long, Regions should pay particular attention to long-term monitoring plans. Monitoring trends in groundwater COCs through time and space in a carefully designed monitoring network typically is a key part of informed decision making for both (1) selecting MNA as an appropriate response action for a site, and (2) assessing the effectiveness of MNA over time.

Initial assessments of whether the aquifer is generally oxidizing or reducing, shallow or deep, and whether it is influenced by external hydrologic forces (for example, interactions between groundwater and surface water, recharge from meteoric precipitation or episodic regional withdrawals from the aquifer) should be considered in designing the dimensions of the monitoring network and the frequency of data collection to characterize site chemistry and hydrology (EPA 2008).

With the exception of nitrate, perchlorate and radioactive decay, inorganic contaminant mass generally is not reduced with most attenuation mechanisms. Therefore, performance monitoring for these chemicals typically is designed to demonstrate geochemical alteration of COCs to lower-risk or lower-mobility compounds or species (for example, Fe^{2+} to Fe^{3+}). A determination that cleanup levels have been achieved should be based on data and information contained in the administrative record that demonstrate degradation and immobilization, in addition to showing that decreasing concentrations are within the risk level or in compliance with ARARs specified in the remedy decision (for example, MCLs attained throughout the plume). The data and information collected by the Region also should demonstrate that site conditions and contaminant concentrations have long-term stability (so that there will be no remobilization of contamination in the future).

Much of the monitoring to evaluate performance of MNA usually falls into three basic categories: (1) ambient monitoring to assess background contaminant levels and the status of relevant ambient geochemical indicators (for example, redox potential [Eh] and pH); (2) monitoring to assure the viability and efficacy of attenuation processes; and (3) monitoring to

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[18] As stated on p. 23 of the 1999 MNA guidance: "**Performance monitoring should continue until remediation objectives have been achieved, and longer if necessary to verify that the site no longer poses a threat to human health or the environment**" (emphasis in original).

detect any plume expansion (EPA 2007a). Identifying the solid phase components' contribution to attenuation of the contaminant plume often can be critical to reducing the level of uncertainty in selecting MNA for sites where immobilization is the dominant attenuation process. These solid-phase components can be grouped into the following three categories: (1) components that serve as a source of contaminants within the plume; (2) components (biotic and abiotic) that participate directly or indirectly during the attenuation process; and (3) the chemical form of the immobilized contaminant and its long-term stability considering future changes in groundwater chemistry.

The specific recommended objectives for an MNA performance monitoring program discussed in the 1999 MNA guidance usually can be met by implementing a performance monitoring program that measures contaminant concentrations, geochemical parameters and hydrologic parameters (for example, hydraulic gradients). Much of the monitoring typically focuses on groundwater and should be used to evaluate changes in plume distribution in three dimensions as well as changes in redox state that may affect the rate and extent of natural attenuation. Data on groundwater can often be used to evaluate mobile contaminant mass and concentration reductions that would indicate progress toward RAOs (EPA 2007a). However, periodic sampling of aquifer solids, through soil coring, generally will be warranted in most situations to evaluate potential reduction in the capacity of aquifer materials to immobilize contaminants.

Ultimately, monitoring programs should be designed to demonstrate continued stability of the plume over time and to identify changes in groundwater chemistry that may lead to decreases in rates or capacity of the aquifer to attenuate the contaminant of concern or changes that may lead to re-mobilization of attenuated compounds. Changes in indicator parameters or compounds such as pH, dissolved iron, or sulfate may indicate dissolution of important sorptive phases within the aquifer. These changes may be detected before observed changes in concentrations of COCs and thus often serve as indicators of potential MNA failure.

Demonstrating that the inorganic contaminant immobilized onto aquifer solids will not remobilize typically depends on identifying the chemical speciation of the inorganic contaminant partitioned to the solid phase. This information often is critical for identifying the mechanism controlling attenuation and evaluating the long-term stability of the immobilized contaminant in light of observed or anticipated changes in groundwater chemistry.

2.4 Plume Stability

As stated on p. 18 of the 1999 MNA guidance:

> Of the above factors, the most important considerations regarding the suitability of MNA as a remedy include: whether the contaminants are likely to be effectively addressed by natural attenuation processes, the stability of the groundwater contaminant plume and its potential for migration, and the potential for unacceptable risks to human health or environmental resources by the contamination. MNA should not be used where such an approach would result in

> either plume migration[19] or impacts to environmental resources that would be unacceptable to the overseeing regulatory authority. **Therefore, sites where the contaminant plumes are no longer increasing in extent, or are shrinking, would be the most appropriate candidates for MNA remedies** (emphasis in original).

Demonstration of plume stability generally is a critical factor for selecting MNA and typically involves delineating a plume in all three dimensions and designing a monitoring network to assess the plume over time. In general, a plume may be considered stable if the monitoring network shows that groundwater contaminant concentrations (in unfiltered samples) do not increase in space or time. The demonstration of plume stability normally should consider both the aqueous mobile and the enhanced colloid transport phases, if present, throughout the plume.

If the attenuation rate is less than the rate of concentration increase within the plume, then the plume could expand. MNA normally would not be considered suitable for an expanding plume. It is possible that expanding plume conditions could develop over time because of formation of daughter products or unforeseen geochemical or other site changes. (See Section 5 for additional information on conditions that affect plume stability.) Such a situation would warrant further or additional sampling and analysis to determine if MNA is still a suitable action. Therefore, MNA remedies for stable plumes should be evaluated systematically (that is, quarterly to yearly), and an appropriate contingency remedy should be identified if conditions no longer conform to those defined as necessary for MNA.

As discussed on p. 22 of the 1999 MNA guidance:

> 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 (emphasis in original).

Although source control will likely reduce contaminant mass flux, the plume may still continue to expand or migrate. It is therefore generally not appropriate to demonstrate plume stability after source control has been accomplished only by showing a decrease in contaminant mass flux. Instead, plume stability generally should be demonstrated by showing decreasing concentration trends at all wells and static or contracting plume boundaries. See Sections 3 and 4 of this document for further discussion of mass flux.

MNA is generally not appropriate for plumes that are considered stable, yet there is confirmed discharge to surface water bodies or potential human or ecological receptor exposure.

2.5 Complex Geologic Regimes

As discussed on p. 15 of the 1999 MNA guidance:

> MNA may not be appropriate as a remedial option at many sites for technological or economic reasons. For example, in some complex geologic systems, technological limitations may preclude adequate monitoring of a natural attenuation remedy to ensure with a high degree of confidence that potential receptors will not be impacted. This situation typically occurs in many karstic, structured, and/or fractured rock aquifers where groundwater moves preferentially through discrete pathways (*e.g.*, solution channels, fractures, joints, foliations). The direction of groundwater flow through such heterogeneous (and often anisotropic) materials cannot be predicted directly from the hydraulic gradient, and existing techniques may not be capable of identifying the pathway along which contaminated groundwater moves through the subsurface. MNA will not generally be appropriate where site complexities preclude adequate monitoring. In some other situations where it may be technically feasible to monitor the progress of natural attenuation, the cost of site characterization and long-term monitoring required for the implementation of MNA may be higher than the cost of other remedial alternatives. Under such circumstances, MNA may not be less costly than other alternatives

MNA generally should not be considered at sites with zones where groundwater flow is rapid or overwhelms biotic and abiotic attenuation mechanisms. The particular situation may be problematic in specific fractured rock and karst environments because of high flow regimes and inadequate reaction times. Sites with these conditions generally are characterized by very rapid groundwater transport and, thus, attenuation mechanisms are unlikely to occur at a rate commensurate with or exceeding the rate of contaminant transport. MNA generally will not be effective or protective under these conditions. In addition, technological limitations in such complex geologic systems may preclude adequate monitoring of MNA to ensure with a high degree of confidence that potential receptors will not be affected.

2.6 Reasonable Timeframe

The 1999 MNA guidance (p. 2) states that natural attenuation should “achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods” (EPA 1999c). In the “Reasonable Timeframe for Remediation” section, the 1999 MNA guidance (p. 19) goes on to state that “determination of the most appropriate timeframe is achieved through a comparison of estimates of remediation timeframe for all appropriate remedy alternatives.”

Furthermore, the 1999 MNA guidance states (on pp. 19 – 20) states:

> Whether a particular remediation timeframe is appropriate and reasonable for a given site is determined by balancing tradeoffs among many factors which include:
>
> - Classification of the affected resource (*e.g.*, drinking water source, agricultural water source) and value of the resource[19];
> - Relative timeframe in which the affected portions of the aquifer might be needed for future water supply (including the availability of alternate supplies);
> - Subsurface conditions and plume stability which can change over an extended timeframe;
> - Whether the contamination, either by itself or as an accumulation with other nearby sources (on-site or off-site), will exert a long-term detrimental impact on available water supplies or other environmental resources;
> - **Uncertainties** regarding the mass of contaminants in the subsurface and predictive analyses (*e.g.*, remediation timeframe, timing of future demand, and travel time for contaminants to reach points of exposure appropriate for the site);
> - Reliability of monitoring and of institutional controls over long time periods;
> - Public acceptance of the timeframe required to reach remediation objectives; and
> - Provisions by the responsible party for adequate funding of monitoring and performance evaluation over the time period required for remediation (emphasis in original).

In evaluating what is a "reasonable timeframe" for achieving RAOs at a site with inorganic contaminants in groundwater, Regions should consider a number of factors that may affect the timeframe. The EPA recommends that Regions also consider additional factors, including contaminant properties, exposure risk, classification of the protected resource (for example, a source of drinking water), the potential for plume stability and the relative timeframe for active remediation methods to achieve RAOs.

Some radionuclides have long decay half-lives, and substantially longer timeframes generally will be required that may exceed both the remediation timeframe and active treatment if radioactive decay is used as the primary natural attenuation mechanism. In these situations,

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[19] "In determining whether an extended remediation timeframe may be appropriate for the site, the EPA and other regulatory authorities should consider state groundwater resource classifications, priorities and/or valuations where available, in addition to relevant federal guidelines. Individual states may provide information and guidance relevant to groundwater classifications or use designations as part of a Comprehensive State Groundwater Protection Program (CSGWPP)." (See USEPA, 1992a and USEPA, 1997b) (citations in original).

MNA may not be reasonable for radionuclides that have a long half-life and decay daughters that are long lived, have other properties affecting mobility or that emit other particles that increase risk.

While remediation timeframes for organic plumes may be on the order of a few tens of years to more than a hundred years, remediation timeframes for inorganic plumes may be substantially longer. Ultimately, the timeframe for remediation will be based on site-specific conditions and chemical characteristics. The longer timeframes for inorganic plumes may be reasonable if the source term has already been addressed, the plume is stable or shrinking, the exposure risks for the source term and daughter products are acceptable, and when active measures have similar timeframes. Multiple lines of evidence are recommended for demonstrating “reasonable timeframe” considering the above factors in conjunction with the following: source control or removal is complete; there is high confidence in the attenuation mechanisms, rates and capacity identified; and contingency plans are included for both the monitoring program and containment or treatment approaches. Ultimately, consistent with CERCLA and the NCP, an MNA remedial action must be protective of human health and the environment over the selected timeframe of the site cleanup (until RAOs are met).

MNA may be particularly useful for radionuclides that have a short half-life (that is, less than 50 years), depending on the total timeframe required for MNA to achieve RAOs and reach cleanup levels. The initial concentrations of the radionuclides and daughter products should be considered and reflected in the Region’s evaluation of MNA as a potential response action. Using the equation below normally should be useful in evaluating the reasonableness of the time required to reach the MCL (or, in the absence of an MCL, the risk-based number) using the total radionuclide contaminant concentration from groundwater (or selected media). Depending on the initial groundwater concentration (C_o), many half-lives may be required to reach the MCL (or risk-based cleanup level). Failure to account for this potential lag may lead to inappropriate consideration of MNA as a potential response action (that is, a longer response action timeframe than is reasonable or the groundwater plume migrates and contaminates a larger area).

The time required to reach the cleanup concentration for radionuclides in groundwater generally may be calculated as follows:

$$t = 3.323 * t_{1/2} * \log \frac{C_o}{C} \qquad \text{Eq. 1}$$

where $t_{1/2}$ is the half-life of the radionuclide, C represents the target cleanup level, and C_o represents the initial chemical concentration in groundwater (Smith and Smith 1971). For example, if the initial concentration of uranium-234 ($t_{1/2}$=2.4x10^5 yrs) in groundwater was 700 micrograms per liter (µg/L), the time required to reach the 30 µg/L MCL for uranium-234 would be more than 1 million years, clearly not generally considered a reasonable timeframe. This example was calculated using mass concentration units but may be calculated using activity units (picocuries per liter, for example). This recommended simple equation can allow time required to reach a desired concentration C to be estimated; it also may be rearranged to determine the final concentration at a specified time t. Note that additional calculations would be needed to quantify concentrations of daughter products generated and their associated decay timeframes.

In the event of long-duration MNA remediation timeframes, ICs may be needed to help ensure protectiveness of human health as a short-term tool to supplement MNA, consistent with CERCLA and the NCP (40 CFR 300.430(a)(1)(iii)). ICs generally should remain in place and be maintained and enforced effectively until the groundwater concentrations allow for an acceptable level of risk for all resources uses (EPA 2012).

2.7 Cleanup Levels for MNA

As discussed in the 1999 MNA guidance (p. 12):

> The NCP Preamble also specifies that cleanup levels appropriate for the expected beneficial use (*e.g.*, MCLs for drinking water) "should generally be attained throughout the contaminated plume, or at and beyond the edge of the waste management area when waste is left in place" (USEPA, 1990a, p.8713) (citation in original).

An MNA remedial action should attain the same cleanup levels that would be defined for active remedies and be consistent with the NCP's expectation for achieving restoration of groundwater to beneficial use;[20] site-specific decision documents typically include RAOs, preliminary remediation goals (PRGs), and cleanup levels that reflect groundwater restoration when that is the selected remedy.[21] MCLs defined in the Safe Drinking Water Act are typically used as ARARs and cleanup levels for groundwater. The groundwater standards for uranium-234 and 238 under the Uranium Mill Tailings Radiation Control Act of 1978 (UMTRCA) generally are potential ARARs (see Table 1 of Subpart A, 40 CFR 192). If promulgated ARARs do not exist for the inorganic compound being remediated, risk-based cleanup levels should be established such that exposure to the contaminant will not result in unacceptable risk to human health or the environment at the calculated cleanup level.[22]

To help evaluate the performance of an MNA remedial action, a site-specific groundwater exit strategy should be developed early in the cleanup process.[23]

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[20] *See* "Summary of Key Existing EPA CERCLA Policies for Groundwater Restoration" (OSWER Directive Number 9283.1-33, June 26, 2009).

[21] *See* "A Guide to Preparing Superfund Proposed Plans, Records of Decision, and Other Remedy Selection Decision Documents," OSWER Directive 9200.1-23P, 1999).

[22] *See* "Clarification of the Role of Applicable, or Relevant and Appropriate Requirements in Establishing Preliminary Remediation Goals under CERCLA," OSWER Directive No. 9200.4-23 (August 22, 1997).

[23] More detailed OSWER guidance regarding development of an exit strategy at CERCLA sites is currently under development.

2.8 Relationship to Technical Impracticability (TI) Waiver

The 1999 MNA guidance discusses TI waivers on p. 13 as follows:

> It also should be emphasized that the selection of MNA as a remedy does **not** imply that active remediation measures are infeasible, or are "technically impracticable" from an engineering perspective. Technical impracticability (TI) determinations are used to justify a departure from cleanup levels that would otherwise be required at a Superfund site or RCRA facility based on the inability to achieve such cleanup levels using available remedial technologies (USEPA, 1993a) (citation in original). Such a TI determination does not imply that there will be no active remediation at the site, nor that MNA will be used at the site. Rather, such a TI determination simply indicates that the cleanup levels and objectives which would otherwise be required cannot practicably be attained using available remediation technologies. In such cases, an alternative cleanup strategy that is fully protective of human health and the environment must be identified. Such an alternative strategy may still include engineered remediation components, such as recovery of free phase NAPLs and containment of residual contaminants, in addition to approaches intended to restore some portion of the contaminated groundwater to beneficial uses. Several remedial approaches could be appropriate to address the dissolved plume, one of which could be MNA under suitable conditions. However, the evaluation of natural attenuation processes and the decision to rely upon MNA for the dissolved plume should be distinct from the recognition that restoration of a portion of the plume is technically impracticable (*i.e.*, MNA should **not** be viewed as a direct or presumptive outcome of a technical impracticability determination.) (emphasis in original).

The EPA's response actions may be designed to achieve several objectives, including to remove or treat source materials, contain non-restorable source areas, and restore contaminated groundwater to beneficial uses at CERCLA sites with inorganic contaminants in the groundwater. Complete restoration of the contaminated groundwater (for example, achieving MCLs throughout the plume) may not be technically practicable at some sites, however. Depending on site conditions, groundwater restoration may be impractical because of a combination of hydrogeologic factors (such as fractured rock or karst conditions, or matrix diffusion) and contaminant-related factors (such as low solubility).

Under CERCLA and the NCP, one of the potentially available ARAR waivers in such circumstances is a technical impracticability (TI) waiver. EPA's TI guidance[24] discusses the circumstances where it may be appropriate for Regions to consider a TI waiver, as well as the data and information that should be collected to ensure the administrative record contains sufficient information and data to support the Agency's determination.

The utilization of a TI waiver for a portion of the site does not preclude the use of MNA at the site where MNA would potentially being appropriate outside of the TI zone. Data collected as part of the overall site characterization for contaminant and hydrogeologic factors may be helpful in evaluating whether MNA may be an appropriate approach at another area of the site. Both TI waiver and MNA decisions should be supported by sufficient data and information in the administrative record (multiple lines of evidence).

2.9 Documentation

As discussed in the 1999 MNA guidance (pp. 13-14):

> **Decisions to employ MNA as a remedy or remedy component should be thoroughly and adequately supported with site-specific characterization data and analysis.** In general, the level of site characterization necessary to support a comprehensive evaluation of MNA is more detailed than that needed to support active remediation. Site characterizations for natural attenuation generally warrant a quantitative understanding of source mass; groundwater flow (including preferential pathways); contaminant phase distribution and partitioning between soil, groundwater, and soil gas; rates of biological and non-biological transformation; and an understanding of how all of these factors are likely to vary with time. This information is generally necessary since contaminant behavior is governed by dynamic processes which must be well understood before MNA can be appropriately applied at a site. Demonstrating the efficacy of MNA may require analytical or numerical simulation of complex attenuation processes. Such analyses, which are critical to demonstrate natural attenuation's ability to meet remediation objectives, generally require a detailed conceptual site model as a foundation (emphasis in original).

Consideration of MNA in the remedy selection process at a site where inorganic contaminants are present in the groundwater should be documented and supported like any other CERCLA response action, consistent with the statute, NCP and existing guidance (such as the 1999 ROD guidance). Thus, for example, data and information to support evaluation and selection of MNA

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[24] *Guidance for evaluating the technical impracticability of ground-water restoration*, OSWER Directive 9234.2-25, EPA/540-R-93-080 (1993). *See also A Guide To Preparing Superfund Proposed Planned, Records Of Decision, and other Remedy Selection Decision Documents,* OSWER 9200.1-23P July 1999 (section 9.5).

should be collected and documented in the administrative record, starting with the remedial investigation (RI) phase of a project and continuing throughout the remedy selection and remedy implementation phases of the cleanup.[25] MNA typically should be identified as a potential response action in the feasibility study (FS) and included as a free-standing alternative or as a component of an alternative that involves other technologies (for example, source removal via excavation, in situ chemical oxidation in high concentration areas, or ICs). Supporting rationale for selecting MNA, if it is part of the preferred alternative, should be included in the proposed plan, and final selection should be documented in the ROD for a site. In general, when MNA is selected, contingency ROD language may be appropriate (see 1999 MNA guidance, p. 24).

2.10 Five Year Reviews

Consistent with CERCLA § 121(c), the NCP at 40 CFR § 300.430(f)(4)(ii), states:

> If a remedial action is selected that results in hazardous substances, pollutants, or contaminants remaining at the site above levels that allow for unlimited use and unrestricted exposure, the lead agency shall review such action no less often than every five years after the initiation of the selected remedial action.

At sites where MNA is selected in the ROD, five-year reviews evaluate the continued protectiveness of the remedy until cleanup levels are met because MNA does not immediately allow for unlimited use and unrestricted exposure of groundwater. In general, it is important to understand the attenuation mechanisms so that the risk for contaminant mobilization or remobilization can be anticipated, incorporated into the long-term monitoring plan, and addressed in a manner that ensures protectiveness of human health and the environment.

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[25] Refer to Subpart I of the NCP and the EPA guidance (EPA 2010b) regarding preparation of the administrative record.

3.0 RECOMMENDED TIERED ANALYSIS APPROACH TO DEVELOP MULTIPLE LINES OF EVIDENCE

As discussed earlier, the 1999 MNA guidance recommends a three- tiered evaluation approach. A tiered analysis approach to site characterization to develop multiple lines of evidence for evaluation of MNA may have the advantage of potentially saving significant resources because it is designed to prioritize and focus the data used for decision making at each screening step. Uncertainty typically also is reduced as site-specific data are collected. Information and data collection and evaluation within the tiered analysis approach typically should be developed in the following four phases:

- Phase I: Demonstration that the groundwater plume is *not expanding*.[26]
- Phase II: Determination that the *mechanism and rate* of the attenuation process are sufficient.[27]
- Phase III: Determination that the *capacity* of the aquifer is sufficient to attenuate the mass of contaminant within the plume and the *stability* of the immobilized contaminant is sufficient to resist re-mobilization.[28]
- Phase IV: Design of a *performance monitoring program* based on an understanding of the mechanism of the attenuation process, and establishment of contingency remedies tailored to site-specific characteristics. This phase in effect reflects recommendations in the 1999 MNA guidance, but consolidated into a single, additional phase.[29]

Obtaining data and information for inclusion in the administrative record to support a demonstration that a groundwater plume is *not expanding* (Phase I) and determination that the *mechanism and rate* of attenuation are sufficient (Phase II) are the recommended initial steps in evaluating MNA. Successful demonstration of Phase III generally involves predicting future MNA performance, which may be difficult to accomplish with confidence at sites with complex hydrogeology and contaminant geochemistry. Developing multiple lines of evidence reflecting

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[26] In the 1999 MNA guidance, this tier is described as: “Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points.”

[27] In the 1999 MNA guidance, this tier is described as: “Hydrogeologic and geochemical data that can be used to demonstrate **indirectly** the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels.” (emphasis in original).

[28] In the 1999 MNA guidance, this tier is described as: “Data from field or microcosm studies (conducted in or with actual contaminated site media) which **directly** demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only)” (emphasis in original).

[29] Refer to Table 1.1 in *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume I – Technical Basis for Assessment,* EPA 600-R-07-139 (EPA 2007a).

these three phases should be considered at any site with inorganic contaminants in the groundwater where MNA is evaluated as a component of the groundwater remedy. The technical knowledge obtained through the first three phases generally may be useful in designing a monitoring program (Phase IV) that tracks MNA performance.

In discussing the three tiers, the 1999 MNA guidance (p. 16) states:

> **Unless the EPA or the overseeing regulatory authority determines that historical data (Number 1 above) are of sufficient quality and duration to support a decision to use MNA, data characterizing the nature and rates of natural attenuation processes at the site (Number 2 above) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (Number 3 above) may also be necessary.**[30] In general, more supporting information may be required to demonstrate the efficacy of MNA at those sites with contaminants which do not readily degrade through biological processes (*e.g.*, most non-petroleum compounds, inorganics), or that transform into more toxic and/or mobile forms than the parent contaminant, or where monitoring has been performed for a relatively short period of time. The amount and type of information needed for such a demonstration will depend upon a number of site-specific factors, such as the size and nature of the contamination problem, the proximity of receptors and the potential risk to those receptors, and other characteristics of the environmental setting (*e.g.*, hydrogeology, ground cover, climatic conditions) (emphasis in original).

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[30] As stated on p. 16 of the 1999 MNA guidance:

> (1) Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend18 of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a groundwater plume, decreasing concentrations should not be solely the result of plume migration. In the case of inorganic contaminants, the primary attenuating mechanism should also be understood.)
>
> (2) Hydrogeologic and geochemical data that can be used to demonstrate **indirectly** the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.
>
> (3) Data from field or microcosm studies (conducted in or with actual contaminated site media) which **directly** demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).

Furthermore, as discussed in the "Reasonable Timeframe for Remediation" section of the 1999 MNA guidance (p. 21):

> Thus, the EPA or other regulatory authorities should consider a number of factors when evaluating reasonable timeframes for MNA at a given site. These factors, on the whole, should allow the overseeing regulatory authority to determine whether a natural attenuation remedy (including institutional controls where applicable) will fully protect potential human and environmental receptors, and whether the site remediation objectives and the time needed to meet them are consistent with the regulatory expectation that contaminated groundwaters will be restored to beneficial uses within a reasonable timeframe. **When these conditions cannot be met using MNA, a remedial alternative that more likely would meet these expectations should be selected** (emphasis in original).

Consistent with the 1999 MNA guidance, MNA may normally be considered a feasible groundwater alternative if data and information obtained pursuant to Phases I through III suggest cleanup goals can be achieved within a reasonable time frame. Recommended objectives that generally should be addressed and the types of site-specific data that generally should be collected under each successive phase are described below (EPA 2007a).

The primary objectives of progressing through the tiered site analysis are to reduce uncertainty in the MNA remedy selection process and to compile data and information in the administrative record supporting the Agency's remedy selection decision. The recommended tiered analysis process can provide a means to organize the data collection effort in a cost-effective manner that allows sites to be evaluated at intermediate stages of the site characterization effort. A general synopsis of the recommended objectives along with possible analysis approaches and data types to collect under each phase is provided in Table 3.1. Data collected for assessment of MNA are often similar to data collected to evaluate engineered remedies such as pump and treat or in situ treatment methods. This recommended approach is designed to optimize site characterization and data collection, facilitate development of multiple lines of evidence, and ensure adequate administrative record support for remedy selection decisions.

Table 3.1. Synopsis of the recommended site characterization objectives to address throughout the tiered analysis process and potential supporting data types and analysis approaches associated with each phase.

PHASE	RECOMMENDED OBJECTIVE	POTENTIAL DATA TYPES AND ANALYSIS
I	Demonstrate plume stability	• Groundwater flow direction (calculation of hydraulic gradients); aquifer hydrostratigraphy • Contaminant concentrations in groundwater • General groundwater chemistry data for preliminary

PHASE	RECOMMENDED OBJECTIVE	POTENTIAL DATA TYPES AND ANALYSIS
		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 microbiology • Contaminant speciation (groundwater and aquifer solids) • Evaluate reaction mechanism (site data, laboratory testing, develop chemical reaction model)
III	Determine system capacity and stability	• Determine contaminant and dissolved reactant fluxes (concentration data and water flux determinations) • Determine mass of available solid phase reactants • Laboratory testing of immobilized contaminant stability (ambient groundwater; sequential extraction 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” re-evaluation of adequacy of monitoring program (frequency, locations, data types) • Select alternative remedy best suited for site-specific conditions

3.1 Phase I: Demonstration that the groundwater plume is not expanding

As stated in the 1999 MNA guidance (p. 18): “Therefore, sites where the contaminant plumes are no longer increasing in extent, or are shrinking, would be the most appropriate candidates for MNA remedies.”

The recommended objective under Phase I analysis is to obtain data and information that can be used to evaluate whether MNA should be eliminated from further consideration for sites where the groundwater plume is not stable or continuing to expand. Efforts generally should focus on delineating the areal and vertical extent of plume boundaries. Time-series data collected from monitoring wells normally can be used to evaluate whether concentrations are increasing or decreasing at monitoring locations downgradient from a source area. An increasing concentration trend generally indicates that sufficient attenuation is not occurring and the groundwater plume is expanding and, as a result, MNA is generally not appropriate. However, short-term increases in contaminant concentration may not automatically indicate an expanding groundwater plume and should be evaluated in the context of a longer-term monitoring trend analysis. This approach is recommended to account for variations in groundwater contaminant concentration because of natural subsurface variability and seasonal fluctuations.

3.2 Phase II: Determination that the mechanism and rate of the attenuation process are sufficient

As discussed in the 1999 MNA guidance (p. 20): "A decision on whether or not MNA is an appropriate remedy for a given site is usually based on estimates of the rates of natural attenuation processes. Site characterization (and monitoring) data are typically used for estimating attenuation rates."

Furthermore, the 1999 MNA guidance states (p. 21):

> As an example, analysis of natural attenuation rates from many sites indicates that a measured decrease in contaminant concentrations of at least one order of magnitude is necessary to determine the appropriate rate law to describe the rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at a 95% level of confidence (Wilson, 1998) (citation in original). Due to variability resulting from sampling and analysis, as well as plume variability over time, smaller apparent reductions are often insufficient to demonstrate (with 95% level of confidence) that attenuation has in fact occurred at all.

The recommended objectives under Phase II analysis are to obtain data and information that can be used to accomplish the following: (1) evaluate the mechanism and rate of the attenuation process or processes, and (2) evaluate whether MNA should be eliminated from further consideration. This second consideration normally is appropriate for sites where further analysis shows that attenuation rates are insufficient for attaining site cleanup objectives within a timeframe that is reasonable compared with other remedial alternatives (EPA 1999c). Data should be collected to define groundwater chemistry, aquifer solids composition and mineralogy, and the chemical speciation of the contaminant in groundwater and associated aquifer solids to evaluate the attenuation mechanism. Radioisotopes and associated daughter products should be identified for radionuclide-contaminated sites, as these may have different fate and transport properties. This site-specific data collection effort may be significant, but it is intended ultimately to provide the underpinning for further evaluation of MNA performance to be addressed in subsequent stages of site characterization. Data collection efforts may include water quality data collected in the field (for example, pH, dissolved oxygen, alkalinity, ferrous iron and dissolved sulfide); laboratory measurements of groundwater and aquifer solids chemical composition; microbial characteristics and mineralogy of the aquifer solids (as relevant to degradation or immobilization); and determination of contaminant speciation in groundwater and the aquifer solids (EPA 2007a). Contaminant speciation for this recommended analysis refers to both oxidation state characterizations (for example, As[III] vs. As[V]; U[IV] vs. U[VI]) as well as specific associations with chemical constituents in aquifer solids (for example, precipitation of lead carbonate vs. adsorption of lead to iron oxides). Evaluation of subsurface microbiology may be necessary in situations where biotic processes play a direct or indirect role in governing contaminant attenuation. Microbial influences may be predominant in plumes where readily degradable organic contaminants, such as hydrocarbons, also are present. Ultimately, knowledge of the attenuation process along with a detailed knowledge of the groundwater flow field can provide the basis for subsequent evaluations to assess the long-term capacity of the aquifer to sustain contaminant attenuation.

An estimate of attenuation rates for inorganic contaminants typically will involve calculations of apparent mass transfer from the aqueous to the solid phase, based on sampling of groundwater or aquifer solids.[31] These estimates should be based as much as possible on field measurements rather than on modeling predictions (EPA 2007a). Where radioactive decay is a primary attenuation process, both intermediate and terminal decay products should be identified, and the time to reach cleanup levels should be estimated as described in Section 2.1 of this document.

3.3 Phase III: Determination that the capacity of the aquifer is sufficient to attenuate the mass of contaminant within the plume and the stability of the immobilized contaminant is sufficient to resist re-mobilization

Sites that possess insufficient capacity to adequately attenuate the groundwater plume generally are not suitable candidates for MNA.

The recommended objective under Phase III is to obtain data and information that can be used to evaluate whether MNA should be eliminated from further consideration for sites where there is insufficient capacity in the aquifer to attenuate contaminant mass to groundwater cleanup levels. Likewise, the data may show that the stability of the immobilized contaminant is insufficient to prevent re-mobilization caused by future changes in groundwater chemistry (EPA 2007a). Possible factors that could result in an insufficient capacity for attenuation include the following: (1) changes in groundwater chemistry that result in slower rates of attenuation or re-mobilization of contaminants, and (2) insufficient mass of solid constituents in the aquifer solids that participate in the attenuation reaction. These factors may apply to situations where either degradation or immobilization is the primary attenuation process. For example, contaminant desorption could be caused by changes in groundwater pH, because the degree of adsorption typically is sensitive to this parameter.

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[31] With regard to consideration of modeling as a general matter, the following preamble language may be useful in the context of MNA specifically: “However, limited fate and transport modeling and site information may be used to establish cleanup levels for contaminated soils and waste materials remaining at the site. For example, the ground-water route of exposure would be protected by determining a level in the soils that would be consistent with the levels established for ground water. Typically, monitoring will be necessary after the completion of the remedial measure to verify that the levels established at the site are protective of ground water and other routes of exposure” (53 Fed. Reg. at p. 51446, December 21, 1988).

Assessment of attenuation capacity usually depends on knowledge of the mass flux of contaminants and associated reactants in groundwater, as well as the mass distribution of reactive aquifer solids along groundwater flow paths. Mass flux for this recommended analysis is defined as the contaminant mass per time passing by a plume transect perpendicular to groundwater flow (Farhat and others 2006). The general approach that can be taken is to estimate the attenuation capacity within the plume boundaries and compare this capacity with the estimated mass flux of aqueous-phase contaminants emanating from source areas, assuming source zone removal or containment has been completed to the extent practicable (EPA 2007a). It is recommended that a detailed characterization of the site's hydrology be performed to ensure that sufficient data are available to determine system capacity in the subsurface environment.

The stability of an immobilized contaminant can be evaluated through a combination of laboratory testing and chemical reaction modeling considering existing and anticipated site conditions. Both analysis approaches normally can be developed based on the information gathered during recommended Phase II efforts to characterize the specific attenuation process active within the groundwater plume (EPA 2007a).

The sensitivity to contaminant re-mobilization typically can be assessed with laboratory tests employing aquifer solids collected from within the plume boundaries. These solids can be exposed to solutions that mimic anticipated groundwater chemistries (for example, ambient groundwater samples or laboratory-created solutions in which the concentrations of specific dissolved constituents can be varied). A supplementary approach to test contaminant stability could include use of chemical reaction models to efficiently explore contaminant solubility under a range of hypothetical groundwater conditions to identify the groundwater parameters to which the attenuation reaction may be most sensitive.

3.4 Phase IV: Design of a performance monitoring program based on an understanding of the mechanism of the attenuation process, and establishment of contingency remedies tailored to site-specific characteristics

As discussed in the 1999 MNA guidance (p. 20):

> It should be noted that the timeframe required for MNA remedies is often longer than that required for more active remedies. **As a consequence, the uncertainty associated with the above factors increases dramatically. Adequate performance monitoring and contingency remedies (both discussed in later sections of this Directive) should be utilized because of this higher level of uncertainty.** When determining reasonable timeframes, the uncertainty in estimated timeframes should be considered, as well as the ability to establish performance monitoring programs capable of verifying the performance expected from natural attenuation in a timely manner (*e.g.*, as would be required in a Superfund five-year remedy review) (emphasis in original).

The recommended objective under Phase IV analysis is to develop a monitoring program to assess long-term performance of MNA and to identify alternative remedies that could be implemented in case MNA fails. Site data collected during the previous phases should focus on identification of alternative remedies that best match site-specific conditions.

The 1999 MNA guidance includes recommendations in the section on Performance Monitoring and Evaluation (pp. 22-23). The monitoring program for inorganic contaminants should consist of establishing a network of wells that meet the following criteria: (1) can provide adequate areal and vertical coverage to verify that the groundwater plume remains static or shrinks, and (2) can provide the ability to monitor groundwater chemistry throughout the zones where contaminant attenuation is occurring. The monitoring program generally should include an assessment of groundwater flow patterns so the monitoring network can be adjusted to evaluate the influence of potential flow changes within the plume. Monitoring should include continued verification of contaminant removal from groundwater, but also should include tracking trends in other reactants that participate in the attenuation reaction (for example, pH, alkalinity, ferrous iron, oxidation-reduction potential and sulfate). Where radioactive decay is a contributing attenuation process, the monitoring program should also track concentrations of daughter products in groundwater. Periodic collection of aquifer solids may be warranted to verify consistency in reaction mechanisms for sites where contaminant immobilization is the primary attenuation process. Groundwater parameters should be selected to monitor constituents that provide information on continued stability of the solid phase that is associated with an immobilized contaminant. Examples include ferrous iron or sulfate to track dissolution of iron oxides or sulfide precipitates. Non-contaminant performance parameters such as these are likely to serve as “triggers” to alert site managers to potential remedy failure or performance losses, since the attenuation reaction should respond to these changed conditions. Monitoring these indicator parameters may improve the ability of site managers to evaluate and address the potential for groundwater plume expansion because increases in mobile contaminant concentrations may be delayed relative to changes in site conditions.

With regard to developing contingency remedies as part of the Phase IV analysis, please refer to the Contingency Remedies section of the 1999 MNA guidance (pp. 24-25).

4.0 SITE CHARACTERIZATION

As discussed in the 1999 MNA guidance (pp. 13-14):

> Site characterization should include collecting data to define (in three spatial dimensions over time) the nature and distribution of contaminants of concern and contaminant sources as well as potential impacts on receptors (see "Background" section for further discussion pertaining to "Contaminants of Concern"). However, where MNA will be considered as a remedial approach, certain aspects of site characterization may require more detail or additional elements. For example, to assess the contributions of sorption, dilution, and dispersion to natural attenuation of contaminated groundwater, a very detailed understanding of aquifer hydraulics, recharge and discharge areas and volumes, and chemical properties is necessary. Where biodegradation will be assessed, characterization also should include evaluation of the nutrients and electron donors and acceptors present in the groundwater, the concentrations of co-metabolites and metabolic byproducts, and perhaps specific analyses to identify the microbial populations present. The findings of these, and any other analyses pertinent to characterizing natural attenuation processes, should be incorporated into the conceptual model of contaminant fate and transport developed for the site.

The primary objective of site characterization at sites with inorganic contaminants in the groundwater generally is to obtain data and information that can be used to identify attenuation mechanisms at a given site. This characterization effort should emphasize direct measurements of groundwater conditions and the associated solid phase characteristics of the aquifer. Measurements or tests conducted with subsurface samples retrieved within the zones where attenuation occurs should provide the most direct means to evaluate ongoing reaction processes. This knowledge may guide approaches to assess the capacity of the aquifer to sustain contaminant attenuation within the plume and to evaluate the long-term stability of immobilized contaminants. Evaluations conducted on subsurface samples also have the potential advantage of incorporating actual characteristics and factors of groundwater and aquifer solids that may be difficult to adequately parameterize within geochemical models.

Delineation of the inorganic plume in three dimensions and subsequent monitoring of the groundwater plume with time generally should be a central component of the recommended tiered analysis. The following sections describe some of the key site characterization objectives relevant to evaluating the potential use of MNA for inorganic contaminants.

4.1 Hydrogeologic and Contaminant Distribution Characterization

The recommended first step (Phase I) in any natural attenuation evaluation is obtaining a thorough working knowledge of site hydrogeology, including direction and rate of groundwater flow, potential impact of interactions between groundwater and surface water or sediment, and potential impact of active pumping, if applicable (EPA 2007a). Information on the nature and extent of contamination and potential contaminant loading to groundwater also is needed, including the existence and distribution of both organic and inorganic plumes in soil and groundwater. These data then may be used to create or update a three-dimensional CSM describing site conditions.

4.2 Determination of Attenuation Rates

The plume should be demonstrated to be stable or shrinking for MNA to be viable for inorganic contaminants in groundwater. The hydrogeologic and contaminant distribution data recommended above (collected during the recommended Phase I evaluations) normally can be used to estimate attenuation rates during Phase II evaluations. *Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies* discusses the following two methods to determine rate estimates: (1) plume concentration vs. distance from a source, and (2) plume concentration measured over time at a point (EPA 2002c). Estimates of mass flux may be used as additional supporting information in determining the rate of contaminant attenuation because these estimates may be affected by changing directions and rates of groundwater flow. It is important to note that determination of mass flux normally is constrained by the same limitations that exist for determining attenuation rate estimates, namely that groundwater flow rates can change in both space and time. An additional factor is that mass flux generally is estimated only for horizontal flow. If vertical gradients are present, the typical estimates of mass flux will likely be incorrect. Multiple lines of evidence should be used to identify whether attenuation is occurring. **Therefore, neither the attenuation rate nor the mass flux estimates should be used as the primary supporting evidence that attenuation is occurring. Demonstration of decreasing concentrations is the primary supporting evidence that attenuation is occurring.**

Both direct measurements and indirect evidence may be used to identify the mechanism and rate of attenuation in groundwater. For example, decreased nickel concentrations collocated with decreased ferrous iron or sulfide concentrations in groundwater would suggest potential co-precipitation of nickel with iron sulfide. Various types of data can provide multiple lines of evidence to assess the likelihood of inorganic attenuation and the viability of MNA. An analysis of groundwater concentration data alone generally will not be adequate to confirm any precipitation or co-precipitation mechanism of attenuation (EPA 2007a).

4.3 Geochemical Considerations

Generally, hydrogeology and groundwater and aquifer geochemistry together form the framework for understanding contaminant fate and transport at a site. Evaluation of aquifer mineralogy and solid-phase contaminant speciation is typically an important part of identification of the contaminant immobilization process (EPA 2007a) for inorganic contaminants. Both groundwater and aquifer solids samples collected using methods that preserve the in situ integrity of the samples help to support this evaluation. Appendices 1 and 2 summarize the recommended physical and chemical analyses and data uses for development of a CSM to support an MNA evaluation for inorganic contaminants. Appendices 3 and 4 provide recommended analytical methods and data quality objectives and goals for the analyses suggested in Appendices 1 and 2. Determining aquifer capacity and the stability of reactions likely will include use of laboratory-based tests using site groundwater and aquifer solids.

4.4 Groundwater Geochemistry Characterization

Data collected during the recommended Phase II evaluation for geochemical characterization of groundwater generally should include pH, oxidation-reduction potential and dissolved oxygen, dissolved organic and inorganic carbon, major cations and anions, and chemical speciation of the contaminants and key reactants in groundwater. Sufficient data should be collected to understand both the temporal and spatial variability of these parameters (EPA 2007a).

4.5 Solid Phase Characterization

Solid phase characterization often is an important aspect of evaluating natural attenuation of inorganic contaminants during the recommended Phase II and Phase III analysis. Procedures for characterizing aquifer materials include the following: X-ray diffraction or X-ray fluorescence for characterizing mineralogy; sequential extraction procedures (SEP) for characterizing the solid-phase components the contaminants are associated with; geochemical speciation analysis for determining the redox conditions of the aquifer; and laboratory batch and flow-through column tests for determining the sorptive capacity of the aquifer materials.

In SEP, contaminated soils are subjected to successively harsher solutions in an attempt to sequentially leach soil contaminants. While environmental risk may be assessed using the results of the water soluble or exchangeable soil fractions (step 1 of the multiple-step SEP process), such an approach will generally be inadequate for developing the necessary understanding of attenuation mechanisms and long-term contaminant behavior to support selection of MNA (EPA 2007a). As a result, partial SEP analyses are not the sole line of evidence that can be used to demonstrate inorganic attenuation. Therefore, the results should not be accepted without question because of the wide variety of methods used to implement the SEP.[32]

If redox processes are believed to be an important component of attenuation mechanisms, special attention should be given to preserving the redox status of materials after they are retrieved from the subsurface. For example, if anoxic materials are collected, they should be frozen after collection or stored in evacuated containers that have been purged with inert gas to preserve primary mineralogy (EPA 2002a and 2006b). Methods for characterizing the oxidation capacity and reducing capacity of aquifer solids are summarized in *Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration* (EPA 2002a).

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[32] Refer to Section IIIB.2.4.2 in *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume I* (EPA 2007a) for a discussion of sequential extraction considerations.

Aquifer capacity for contaminant attenuation is often estimated during the Phase III evaluation. As thoroughly described in *Understanding Variation in Partitioning Coefficient, K_d Values, Volumes I-III* (EPA 1999a, 1999b and 2004c), there are multiple approaches to measure or estimate distribution/partition coefficient (K_d) values, such as laboratory batch tests, in situ batch tests or flow-through column tests. Each has its inherent advantages and limitations, and each involves a unique set of assumptions. The K_d, for this guidance, is considered the ratio of contaminant mass per unit mass of solid to the mass of contaminant remaining in solution at equilibrium (EPA 1999b).

Contaminant sorption behavior can be simulated by geochemical models. The use of the Langmuir and Freundlich isotherms (also known as empirical models) and surface complexation models (SCM, known as mechanistic models) can be used to develop the K_d value (EPA 1999a and 2007a). The predictive capability of empirical models (using empirically derived values of K_d) are limited to the range of experimental data when K_d is determined. However, mechanistic models like SCMs have the advantage of being able to modify input parameters and account for changes in groundwater chemistry, such as solution pH and the impact of major ions in solution on available sorption sites. Thus, SCMs are potentially more robust in their predictive capabilities to evaluate the impact of changing chemical conditions in the system. Further discussion of the use of models in the assessment of natural attenuation of inorganic contaminants may be found in Section 6 of this document.

It is normally important that solid samples be representative of aquifer materials and contaminant concentrations. Contaminant attenuation is not linear in that the attenuation rate does not increase in direct proportion to the concentration. Therefore, solid samples used to define solid-phase attenuation should contain a range of contaminant concentrations. In addition, they should represent a range of soil textures and other factors that affect attenuation. Measured contaminant concentrations represent a mean concentration of the soil volume sampled and can be determined for each of the contaminants of interest. SEP may be used to differentiate contaminant concentrations associated with different phases of soil (for example labile vs. sorbed vs. structural) in the designated representative sampling area based on the CSM. This same designated representative sampling area can be re-sampled during subsequent sampling events—again at random locations and depths below the water table and within the same lithology—and SEP results compared to determine if a significant change in concentrations has occurred over time. Ideally, this approach provides a representative and repeatable simulation of aquifer materials and minimizes the negative impact of soil heterogeneity on the evaluation of attenuation processes.

4.6 Special Considerations for Radionuclides

The amount of radioactive material in soil or water is typically measured in units of decay rate or activity and reported as picocuries (pCi) per mass of soil or volume of water — for example, picocuries per liter (pCi/L) (1 picocurie equals 0.037 becquerels [Bq]). Activity units are used to evaluate exposure risk that forms the basis for remediation, whereas mass-based concentration levels (for example, µg/L) are used in selecting and designing a remediation technology. The activity corresponding to a given mass of radioactive material varies depending on the radionuclide. For example, 1 gram of uranium-238 has an activity of 0.33 pCi, whereas 1 gram of uranium-234 has an activity of 6,200 pCi.

Decay rate-based activities are different than mass-based concentrations, and neither should be used alone to identify potential remedial components For example, transport models that are employed to understand the solid-liquid partitioning and fate and transport of a radionuclide are developed using mass concentration units and mass-action reaction expressions. Isotopic composition and activity of radioactive material generally are important for risk assessment and plume decay predictions (EPA 2010a).

5.0 ATTENUATION PROCESSES FOR INORGANIC CONTAMINANTS

The following sections briefly describe microbial, chemical and physical attenuation processes for metals and other inorganic contaminants, as well as radioactive decay as an attenuation process for radionuclides. These attenuation processes may act in isolation or together to retard or arrest migration of inorganic contaminants in an aquifer. Factors that can help evaluate which process is likely to dominate contaminant attenuation include chemical properties of the contaminant, chemical characteristics of the groundwater, and properties of the aquifer solids. Microbial activity may exert a significant but primarily indirect influence on contaminant attenuation for many of the inorganic contaminants discussed in this document; however, in the case of both nitrate and perchlorate, direct microbial degradation should be the controlling attenuation process (EPA 2007b). Redox conditions in an aquifer normally are a key controlling factor of contaminant fate and transport of inorganic contaminants in groundwater and will be mentioned repeatedly in the discussions that follow.

5.1 Microbial Degradation

Subsurface microbes typically play an important and dynamic role in controlling aquifer geochemistry and fate of inorganic contaminants in situ; they tend to alter most attenuation processes in groundwater. Subsurface microorganisms exhibit a remarkable array of metabolic capabilities. For example, microbes derive energy through oxidation of organic or inorganic compounds as electron donors. The electrons are transferred to an electron acceptor which, in the case of aerobic respiration, is oxygen. Anaerobic respiration is also possible, whereby chemically reducible inorganic compounds (such as nitrate, sulfate, ferric iron or iron/manganese oxyhydroxides) are used as electron acceptors (EPA 2007a). The coupled reactions of electron acceptors and donors are termed oxidation-reduction or “redox” reactions. These redox reactions are often mediated by microbes in situ. In general, microbes preferentially consume oxygen and nitrate as the most favorable electron acceptors, followed by manganese and iron oxyhydroxides, sulfate, and finally, carbon dioxide. An aquifer progresses from oxidizing (aerobic) to reducing (anaerobic) redox conditions as microbes consume this series of electron acceptors.

In some situations, intense local microbial activity may be entirely responsible for the redox status of the aquifer. The nature of the active microbial population (for example, iron-reducing, sulfate-reducing, or sulfur-oxidizing bacteria) can often be inferred from geochemical data. Thus, trends in the concentration of organic substrates (dissolved organic carbon) and their metabolites (for example, H_2, H_2S, CH_4, CO_2, NO_2^-, HS^- or Fe^{2+}) can indicate whether and which microorganisms are active in a particular subsurface region.

Conversion of dissolved organic carbon by microbial activity can create and replenish the reductive capacity of a site. In some instances, direct and specific determination of microbial population by culturing or genetic analysis (for example, messenger ribonucleic acid profiles) of aquifer solids extracts may be warranted.

Although metals and radionuclides may change valence state or form different anion complexes in response to microbial activity or redox conditions, they generally are not degraded. Microbial degradation involves breaking chemical bonds in a contaminant compound, the subsequent formation of new bonds and, ultimately, creation of another compound that may be more or less toxic.

Both nitrate and perchlorate are highly soluble and thus mobile contaminants in groundwater that may directly serve as electron acceptors for subsurface microorganisms in situ. However, subsurface microbes may be limited in situ by organic carbon, energy substrate, or trace nutrients. Given the high solubility and mobility of nitrate and perchlorate in groundwater under organic carbon-limited conditions, MNA by itself may not be appropriate for these contaminants. It may be appropriate to consider MNA in combination with active remedies such as in situ bioremediation through organic carbon substrate injections or other treatments, however.

Soil microbes may be responsible for the methylation of iodine-129 to form methyl-iodide in wetland environments under low redox conditions and in the presence of high concentrations of organic matter (EPA 2010a). Methyl-iodide is subject to volatilization. While the microbial activity is not directly responsible for destruction of the iodine, it is an example of the indirect impact of microbial activity on chemical fate. Failure to account for microbially induced methylation can result in misinterpretation of the volatilized iodine-129 as sorbed iodine-129, which in turn can result in an overestimation of contaminant mass sorbed to aquifer solids.

5.2 Chemical Transformation/Redox

An understanding of redox conditions in the aquifer often is important, as redox processes have a significant impact on the aqueous and solid phase speciation of inorganic contaminants. Although most metals generally are not degraded through microbial action, some can change oxidation state, which in turn significantly influences their solubility and transport in groundwater. Changes in oxidation state of a metal occur through abiotic or microbially mediated redox reactions where the metal serves as an electron acceptor or donor. This section is focused on redox transformations of inorganic contaminants (metals, metalloids and radionuclides).

Ferrous sulfide rich formations may promote abiotic reduction of soluble metal species to their less mobile lower oxidation states. Alternatively, microbes may deplete oxygen and other highly energetic electron acceptors from groundwater under organic carbon rich conditions. In this way, they promote anaerobic or reducing conditions that favor reduction and immobilization of some metals. Under iron- and sulfate-reducing conditions, metals such as chromium(VI), selenium(VI or IV), and copper(II) may be reduced to lower valence states, which may form sparingly soluble metal-oxide minerals or may co-precipitate with sulfides. Likewise, radionuclides such as uranium(VI) and technetium(VII) become favorable electron acceptors under iron- or sulfate-reducing conditions and may precipitate as radionuclide-oxide minerals or may co-precipitate with sulfides. These redox sensitive metals and radionuclides are generally less soluble and less mobile in their reduced oxidation states; however, there are exceptions to this generalization.

Studies have shown that addition of organic carbon to stimulate iron reduction results in transformation of some contaminants, such as U(VI), to less mobile forms and as a consequence result in decreased groundwater concentrations in metal or radionuclide contaminated plumes where organic carbon is limited (Anderson and others 2003; Istok and others 2004; Michalsen and others 2006). However, these same reduced metal- or radionuclide-oxide precipitates may be vulnerable to oxidation by nitrate and other oxidants, which could reverse the process, causing a related increase in contaminant concentrations in groundwater (Anderson and others 2003; Senko and others 2002). Shifts in groundwater pH or bulk geochemistry may affect the metal solubility and could reverse the attenuation process. Thus, the stability of the attenuated contaminant will ultimately be governed by the type of contaminant-solid phase association and by the stability of groundwater geochemistry.

It is important to recognize that reversals in oxidation state of inorganic contaminants may result from attempts to remediate other contaminants present at a site. For example, the use of in situ chemical oxidation methods to remediate high concentrations of hydrocarbon-based compounds may result in a related increase in soluble U(VI). Similarly, the injection of organic electron donors intended to create reducing conditions in an aquifer may result in the reductive dissolution of arsenic species, with a corresponding increase in groundwater concentrations. SEP analysis may also be used to assess changes in concentrations associated with different soil phases (for example, sorbed vs. precipitated).

5.3 Sorption and Precipitation

Physical partitioning of a contaminant from a soluble and mobile form in groundwater to a less mobile form on aquifer solids is a primary natural attenuation process for many metals and radionuclides. This partitioning process generally involves the following three primary mechanisms: (1) adsorption, which is the accumulation of a contaminant ion at the aqueous and solid phase adsorbent interface; (2) precipitation, which is the growth of solid phase containing repeated molecular units in three dimensions; and (3) absorption, which is diffusion of the aqueous or adsorbed contaminant ion into the solid phase (Sposito 1986). “Sorption” will be used in this guidance to describe, in a generic sense (that is, adsorption and absorption mechanisms), the partitioning of aqueous phase constituents to a solid phase. One or more sorption mechanisms are likely important if the inorganic contaminant of concern at a site is a metal or a radionuclide.

In general, adsorption or desorption of metal or radionuclide cations onto and off of aquifer materials is pH dependent and increases with increasing pH, typically reaching a maximum under circumneutral pH conditions, depending on groundwater chemistry and properties of the adsorbent surface (Sparks 2003). Important adsorbent phases commonly found in the environment include phyllosilicate minerals (“clays”), metal oxyhydroxide phases, and natural organic matter (Dixon and Schulze 2002; EPA 2007a, Section IIB.1.1). However, most clay minerals possess a permanent negative charge as a result of the substitution of lower valence cations within mineral layers of the clay. This permanent negative charge is unaffected by changes in groundwater pH and is typically balanced through ion exchange reactions involving major cations in groundwater (for example, Na^+, K^+, Ca^{2+} or Mg^{2+}) but potentially also contaminant metal or radionuclide ions.

Precipitation is another important attenuation mechanism for removal of metals and radionuclide contaminants from groundwater. Contaminant ions may precipitate as a pure phase (for example, $CdCO_3[s]$) or may co-precipitate by incorporation of the contaminant ion within the structure of another mineral phase. Examples of co-precipitation include Cr(III) in hydrous ferric oxide and Cd(II) in calcium carbonate. Strontium may co-precipitate during formation of calcium or ferrous iron carbonates (for example, in the presence of elevated alkalinity or ferrous iron formed during microbial degradation of organic compounds) (Fujita and others 2004; Roden and others 2002; EPA 2010a, Strontium Chapter). Precipitation is also an important attenuation pathway for radium, which may also co-precipitate as a sulfate mineral (for example, as $RaSO_4$ or $BaRa[SO_4]_2$, in the presence of moderate sulfate concentrations) (Langmuir and Reise 1985); however, under sulfate reducing conditions, these minerals may dissolve and result in radium release to groundwater (Huck and Anderson 1990; Pardue and Guo 1998; EPA 2010a, Radium Chapter).

Most precipitation reactions have a strong dependence on solution chemistry and pH. The tendency for a system to support a specific precipitation or dissolution reaction can be evaluated through comparison of the equilibrium solubility constant for a given solid phase mineral to the ion activity product calculated using the site groundwater geochemical data. The ion activity product is useful for evaluating the potential for contaminant precipitation; however, it is not unequivocal evidence that a given phase is at equilibrium or even present in the system (Sposito 1984; EPA 2007a, Section IIB.2.1).

Physical partitioning is a particularly important attenuation process for cadmium, lead, nickel, and copper because these metals are stable in their +2 valence state and are not subject to direct chemical transformation or changes in valence state, which can significantly alter the solubility of metals. However, these metals may form stable precipitates with redox-sensitive elements such as sulfur and iron; thus, the solubility and mobility of these metals are indirectly tied to redox conditions. For example, if sorption to iron oxides is a primary attenuation pathway and the redox conditions change such that reductive iron dissolution occurs, this process could mobilize or remobilize the metal of concern in groundwater. Likewise, if the primary attenuating phase of the metal of concern is a metal-sulfide precipitate and the groundwater redox conditions shift such that oxidative dissolution of sulfides occurs, this shift could also mobilize or remobilize the metal of concern in groundwater. Furthermore, shifts in groundwater pH or bulk geochemistry may alter the metal partitioning and could reverse the attenuation process. For example, sorption to carbonate minerals may be an important attenuation process for thorium (EPA 1999a) and americium (Shanbhag and Morse 1982; EPA 2010a, Americium-Strontium Chapter). However, decreases in pH can destabilize carbonate minerals and result in increased radionuclide concentrations in groundwater. Thus, the stability of the immobilized contaminant (precipitated or sorbed) will ultimately be governed by the type of contaminant-solid phase association and by groundwater geochemistry.

In general, the absorption of metal or radionuclide cations is limited to Group 1 (Alkali metals), mainly potassium, cesium and rubidium. These elements exhibit low hydration energy and unique hydrated radii that allow them to diffuse into the structure of vermiculite minerals. This process promotes the “fixation” of the cations by the subsequent collapse of the vermiculite into a mica-type structure.

5.4 Radioactive Decay

Radioactive contaminants share many fate and transport properties in common with metals, as illustrated in previous sections. However, radioactive decay is a unique attenuation process specific to this group of contaminants that warrants special discussion. Radioactive decay typically functions in conjunction with other attenuating processes as part of MNA, but it is the primary attenuating process for radon and tritium, as they are generally considered unreactive in groundwater and have relatively short half-lives (EPA 2010a).

Radioactive decay ultimately decreases the concentration of parent atoms or compounds in groundwater but can result in increased concentrations of *daughter products*, which are the products of parent isotope decay. Eventually, a stable daughter product is created and no further radioactive decay follows.

If the decay rate of the daughter product is less than the decay rate for the parent isotope or is infinite because the daughter is stable, then the daughter product may accumulate and affect the activity of the plume in a process called ingrowth. Ingrowth is a particularly important concept when use of MNA is evaluated for radionuclides because daughter products may exhibit increased toxicity and solubility, which may affect plume fate and transport (EPA 1999c). Radioactive decay can be simple (for example, decay of I-129 to stable Xe-129); however, radionuclides with complex, multi-step decay series (for example, decay of Ra-226 to Pb-210) are most commonly encountered at National Priorities List (NPL) sites (EPA 1993). Table 5.1 below provides a summary of radiochemical information for select radionuclides, including half-lives and energy levels of emitted radiation, as well as associated decay chains and terminal products. It is important to identify specific isotopes present in groundwater so that associated decay chains, intermediate daughter, and terminal daughter products can be identified and accounted for during remedy selection and monitoring program development.

Table 5.1. Radiochemical information for select radionuclide isotopes (EPA 1993 and 2000).

Select Radionuclides		**Radiation Type (MeV)**			**Associated Decay Chain[33]**	**Terminal Nuclide or Radionuclide[34]**	
Nuclide[35]	**Half-life (yr)**	**α**	**β(avg)**	**γ**		**Nuclide**	**Half-life (yr)**
Am-241	432	5.486		0.0595	-	Np-237	2.1E+6
Am-243+D	7,400	5.3	0.022	0.055	Np-239 (2d)	Pu-239	2.4E+4
Cs-134	2		0.1520	0.605	-	Ba-134 (~100%)	stable
Cs-135	3E+6		0.0570	0.787	-	Ba-135	stable
Cs-137+D	30		0.1950	0.662	Ba-137m (95%, 3min)	Ba-137	stable
H-3	12		0.0050		-	He-3	stable
I-129	1.6E+7		0.0400		-	Xe-129	stable
Pu-238	88	5.499			-	U-234	2.4E+5
Pu-239	2.4E+4	5.156		0.0516	-	U-235	7E+8
Pu-240	6,500	5.168			-	U-236	2.3E+6
Pu-244+D	9.3E+7	4.6	0.0071	0.0012	U-240 ~100% Np-240	Pu-240	6,500
Ra-226+D	1,600	4.784		0.1861	Rn-222 (4 d) Po-218 (3 min) Pb-214 (~100%, 27 min) Bi-214 (20 min) Po-214 (~100%, 1 min)	Pb-210	22
Ra-228+D	8		0.0140		Ac-228 (6 h)	Th-228	2
Rn-222	1.0E-2	5.490		0.5100	Po-218 (3 min) Po-214 (0.2 ms) Po-210 (138 d)	Pb-206	stable
Sr-90+D	29		0.2000		Y-90 (64 h)	Zr-90	stable
Tc-99	2.1E+5		0.0850		-	Ru-99	stable
Th-228+D	2	5.423			Ra-224 (4 d) Rn-220 (56 s) Po-216 (0.2 s) Pb-212 (11 h) Bi-212 (61 min) [Po-212 (64%, 0.3 μs) Tl-208 (36%, 3 min)]	Pb-208	stable
Th-229+D	7,300	4.9	0.12	0.096	Ra-225 (15d) Ac-225 (10 d)	Bi-209	stable

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[33] The chain of decay products of a principal radionuclide extending to (but not including) the next principal radionuclide or a stable nuclide. Half-lives are given in parentheses. Radioactive ingrowth branches are indicated by square brackets with branching ratios in parentheses.

[34] The principal radionuclide or stable nuclide that terminates an associated decay chain.

[35] "+D" designates radionuclides with associated decay chain.

Select Radionuclides		**Radiation Type (MeV)**			**Associated Decay Chain[33]**	**Terminal Nuclide or Radionuclide[34]**	
Nuclide[35]	**Half-life (yr)**	**α**	**β(avg)**	**γ**		**Nuclide**	**Half-life (yr)**
					Fr-22 (5 min) At-217 (32 ms) Bi-213 (46 min) [Po-213 (98%, 4 µs) Tl-209 (2%, 2 min)] Pd-209 (3 h)		
Th-230	7.7E+4	4.688		0.0677	-	Ra-226	1,600
Th-232	1.4E+10	4.013			-	Ra-228	6
U-234	2.4E+5	4.776		0.0532	-	Th-230	8E+4
U-235+D	7.0E+8	4.400		0.1857	Th-231 (26 h)	Pa-231	3.4E+4
U-238+D	4.5E+9	4.197			Th-234 (24 d) Pa-234m (99.8%, 1 min) Pa-234 (0.2%, 7 h)	U-234	2.4E+5

α	Alpha	h	hour	µs	microsecond
β	Beta	s	second	ms	millisecond
γ	Gamma	MeV	Megaelectronvolt		
d	day	min	minute		

Unstable parent radionuclides decay to form either unstable or stable radionuclide daughter products. The decay of an unstable radionuclide parent to a stable radionuclide daughter results in ingrowth. An unstable radionuclide daughter results in one of three equilibrium conditions, all exhibiting a period of ingrowth. The three parent/daughter equilibrium relationships are identified as "secular," "transient," and "no equilibrium." The "ingrowth only" example in Figure 5.1A demonstrates the decay of the unstable parent leading to the ingrowth in the stable daughter (for example, Cs-137 decay to stable Ba-137). The first of the equilibrium cases is the limiting "secular equilibrium," where the half-life of the parent is much larger (approximately 10^{-4}) than the daughter (for example, Ra-226 decay to Rn-222). The period of the daughter product's ingrowth occurs until its activity reaches that of the initial parent activity (Figure 5.1B).

Thereafter, the daughter decays at the same rate that it is formed. The second equilibrium case is "transient equilibrium," where the half-life of the parent is somewhat larger (approximately 10 times) than the daughter (for example, Th-227 decay to Ra-223). The period of the daughter product ingrowth initially reaches a maximum followed by a decrease until both parent and daughter decay become constant (Figure 5.1C). The last equilibrium case is "no equilibrium," where the half-life of the parent is smaller than the daughter (example, Am-241 decay to Np-.237). The period of daughter ingrowth peaks later than for "transient equilibrium" and eventually decays according to the daughter half-life characteristics (Figure 5.1D).

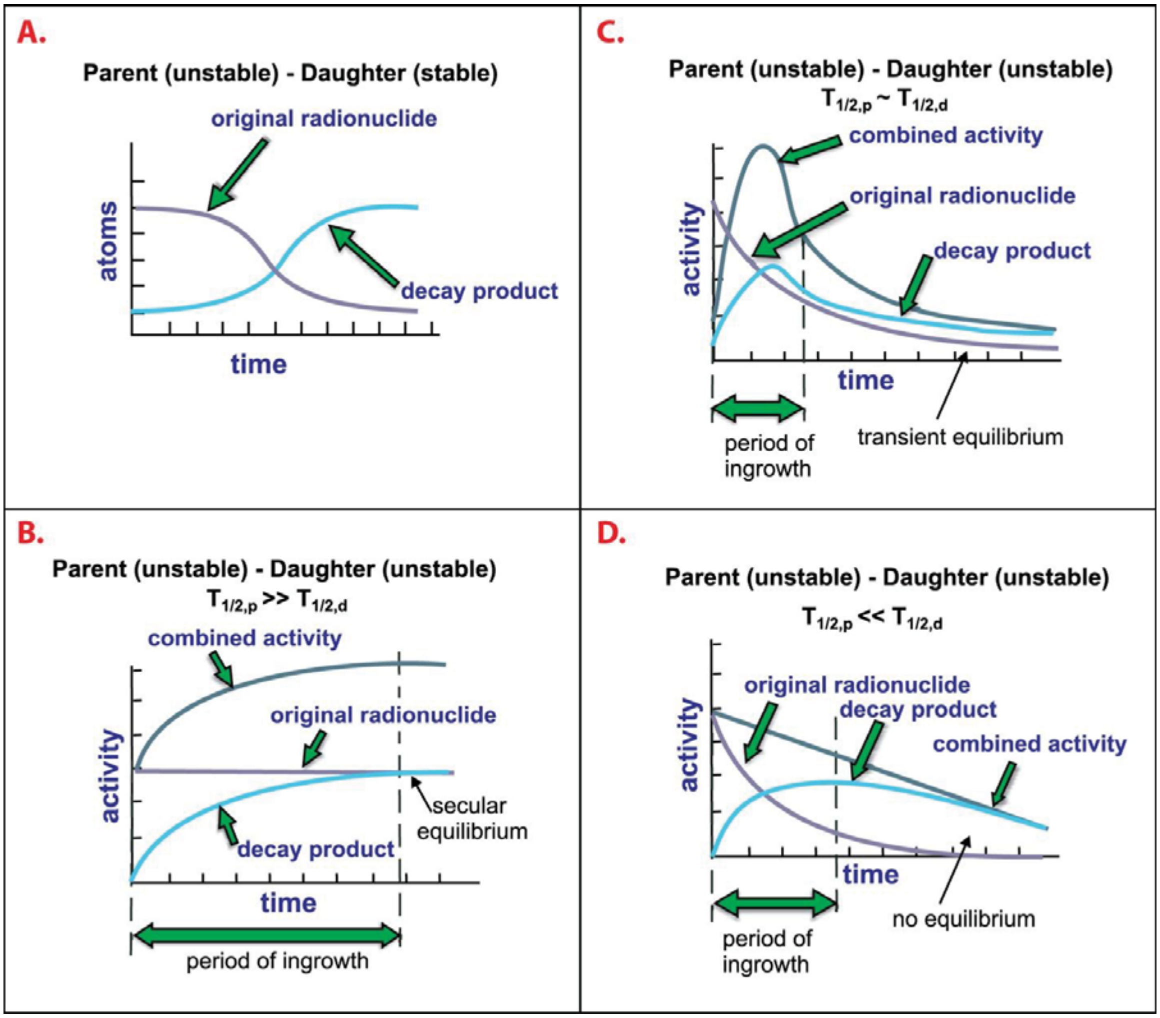

Figure 5.1. Illustration of four decay ingrowth scenarios in groundwater plumes contaminated with radionuclides. $T_{1/2,p}$=decay half-life of parent radionuclide, $T_{1/2,d}$=decay half-life of daughter radionuclide. Illustrations derived from the EPA website www.epa.gov/radiation/understand/equilibrium.html

It can be seen that the production of daughter products can influence plume composition, potential radiological risks, and the dimensions of the plume if, as is typical, the daughter product displays radiological or chemical risk and transport characteristics different from that of the parent radionuclide. It is important to note that, as with organics, daughter products of radionuclides may pose greater risk, be more mobile, and have longer half-lives than the parent in the decay series. Radionuclide ingrowth corrections may be important for accurate descriptions of plume characteristics over time because of the relatively low regulatory benchmarks for activity- (picocuries per liter, pCi/L) and mass-based concentrations (micrograms per liter, µg/L) in groundwater. Such radioactive decay relationships may be used to predict increases in decay products and activity or ingrowth, with or without consideration of groundwater transport.

Alpha recoil is a decay-related physical fractionation process that may impede achievement of groundwater cleanup levels for some radionuclides. Briefly, alpha recoil occurs when ejection of an alpha particle propels the daughter product away from the decay site (Kigoshi 1971; EPA 2010a, Front Matter, ID.1.3) — for example, from a mineral surface into groundwater. Ejection of an alpha particle can destabilize the host solid (Fleischer 1980; EPA 2010a, Front Matter, ID.1.3) and increase its susceptibility to dissolution (Eyal and Fleischer 1985). Potential influence of alpha recoil on contaminant fate is exemplified by the behavior of U-238 and U-234 solid-solution partitioning in groundwater systems, which results in U-234 enriched groundwater (Ivanovich 1994; EPA 2010a, Front Matter, ID.1.3). U-238 decay produces Th-234 plus an alpha particle of sufficient energy to cause ejection of Th-234 into groundwater. Subsequent serial decay of Th-234 (24.1 day half-life) to Pa-234 (6.7 hour half-life) and ultimately U-234 results in an elevated activity/concentration of U-234 relative to what would be anticipated based strictly on the solid-liquid partitioning for uranium or thorium. Additional examples of decay chains that may produce recoil effects include Th-228, Th-229, and Ra-226 (Sun and Semkow 1998; EPA 2010a, Front Matter, ID.1.3). In general, the impact of this process is difficult to predict in an aquifer and may play a minor role in contaminant plumes with concentrations that greatly exceed natural levels; however, alpha recoil may impart a large contribution to radioactive-enriched groundwater when concentrations of alpha emitters are large.

6.0 USE OF MODELS

Models that rely solely on estimated or computer-derived parameters, rather than on site-specific measured parameters, are generally inappropriate as the dominant justification for MNA. Modeling can be used to support or corroborate observed field conditions or can be used as another line of evidence in support of MNA. However, modeling simulations generally should not be the sole line of evidence used to support MNA. There should be site-specific monitoring data that provide evidence of contaminant attenuation, such as stable or declining groundwater concentrations or evidence of increasing contaminant concentrations in the solid phase (either via precipitation or sorption to aquifer solids). Site-specific information supporting continued attenuation of site contaminants should be obtained. Modeling should be supported with actual site data, and multiple lines of evidence should be used to indicate MNA is appropriate.

As noted previously, a CSM is not the same as a computer model, but a valid and sound CSM generally should be used to obtain meaningful computer modeling results. In the discussion that follows, the term “model” or “modeling” refers to a computer model or other mathematical representation of reality, whereas references to the CSM will be explicit. If a correct and robust CSM is not derived, any computer modeling results, no matter how detailed or extensive, may contribute little to understanding the site. EPA guidance generally recommends not relying on modeling as the sole criterion for determining whether MNA is an appropriate response action. Any model predictions should be substantiated by performance monitoring.

The modeling effort should begin with the careful identification of processes that can play significant roles in contaminant migration and attenuation at the site. Fundamental data regarding the rate and direction of groundwater flow, degree of aquifer heterogeneity, and current distribution of contamination typically should be included in the CSM. Identification of specific reaction mechanisms that may be active in the plume (for example, precipitation or sorption to solid surfaces, complexation with other chemical constituents, or microbially induced changes in groundwater chemistry) can provide the basis for developing models that allow projection of contaminant transport into the future.

Planning for computer modeling should occur early in the site assessment process so that the modeling can be integrated with the evaluation of the site and the appropriate data can be collected. In all the models, it is always important to characterize the assumptions, boundary conditions, and uncertainty. The EPA often uses a tiered modeling approach. Generally, more complex models require more site-specific data. When radionuclides are modeled, a model that can account for parent-daughter decay chains and the accompanying change in fate and transport parameters as the radionuclides change needs to be selected.

For further information on modeling at radioactively contaminated sites, see *Documenting Ground Water Modeling at Sites Contaminated with Radioactive Substances* [EPA 540-R-96-003] January, 1996. (www.epa.gov/rpdweb00/docs/cleanup/540-r-96-003.pdf) and the associated fact sheet (www.epa.gov/rpdweb00/docs/cleanup/540-f-96-002.pdf).

6.1 Types of Models

Several types of models may prove useful for characterizing attenuation processes at a site. Initiating the modeling effort with the simplest possible models is recommended. Highly complex models usually are difficult to work with, expensive to produce and difficult to interpret. A more efficient strategy normally is to begin with simple models of various aspects of the system, combining these as necessary into progressively more complex models, until a satisfactory final result has been reached, one that reproduces the salient aspects of the system's behavior without introducing unnecessary complexity.

Simple Calculations. Simple calculations performed by hand or via computer applications may serve as an important component of the overall modeling strategy. These calculations may be useful in any of the four phases in the tiered analysis approach. An example of a simplified approach would be calculation of the mass of contaminant and the mass of reactant within a predefined volume of the aquifer to assess whether sufficient reactant mass is available for an identified attenuation process. This calculation provides a general sense of the relative degree to which the aquifer could support attenuation and may provide some perspective as to the relative importance of investing resources to fully characterize reactant mass or flux. This calculation does not, however, likely provide any insight into the efficiency of the attenuation process.

Another example of simplified calculations that may be used is input parameters for more complex transport or reaction models using specific mathematical formulas. Several examples of these types of calculations are provided at the following the EPA website: www.epa.gov/athens/learn2model/part-two/onsite/index.html. These calculations may support analysis of the adequacy of monitoring network design in addition to estimating model input parameters and hence play an important role in the site characterization effort.

Mass Transport Models. Mass transport models seek to describe the flow of groundwater at a site and the transport of chemical species by the groundwater. Because mass transport models typically consider migration of non-reacting species, they seldom can be relied on to accurately describe natural attenuation. However, they can still be useful for estimating the transit time of contaminants within the site, absent attenuating processes. This "worst case" transport scenario has value in evaluating a site's potential for MNA. Mass transport models are best suited for application in Phase I or Phase II of the tiered analysis approach.

Speciation and Reaction Models. Speciation models seek to describe the distribution of chemical mass between solution, minerals, mineral surfaces, gases, and biomass. Models of this class are useful because they can predict the conditions that might attenuate contaminants by sequestration, and those in which they are likely to be mobile in the groundwater flow. For example, a speciation model might demonstrate that a contaminant is likely to adsorb to the surface of a component of the aquifer solids over the pH range of interest. Alternatively, the model might show that the contaminant will tend to complex strongly with dissolved chemical species, leaving it mobile and resistant to attenuation. Speciation models assume the modeled system is in partial or complete chemical equilibrium. One example of a speciation model is MINTEQA2, which can be found at www2.epa.gov/exposure-assessment-models/minteqa2.

Reaction models are similar to speciation models in that they consider the distribution of chemical mass, but have the additional ability of modeling the chemical evolution of the system with changing site conditions. Examples of uses for reaction models include estimating sequestration of contaminants onto a mineral surface as the mineral forms, or estimating precipitation of contaminant-bearing minerals as water chemistry changes.

Speciation models and reaction models would typically be used in Phase II or Phase III of the tiered analysis approach. However, they can also be helpful in Phase IV (monitoring) to identify critical chemical parameters to which the attenuation process is sensitive.

Reactive Transport Models. Reactive transport models, as the name suggests, couple reaction models to transport models. Unlike a reaction model, a reactive transport model predicts not only the reactions that occur as the groundwater flows, but how those reactions vary in space and change through time. A reactive transport model may have several advantages over a simple reaction model, including the ability to account for heterogeneity at the site, such as an uneven distribution of a sorbing mineral or variation in pH conditions.

Reactive transport modeling is a relatively complex and time-consuming undertaking, since it combines the data needs and uncertainties inherent in modeling reaction as well as transport of contaminants. As such, reactive transport models are typically reserved for use in Phase III analysis. It may be the capstone of the modeling effort but is seldom the best tool for initial scoping of the attenuation capabilities at a site. This modeling, on the other hand, may play an important role in the site characterization effort because it represents the integration of all of the components of the conceptual site model.

6.2 Model Calibration

Because of the uncertainties discussed above, it generally is important to calibrate a model to observations and to verify that the model behaves in a manner that adequately describes the natural system. Calibration is typically designed to bring the model into alignment with observed data. To have optimal confidence in results, models are recommended that (1) utilize to the greatest extent possible parameter values specific to the site, and (2) are calibrated to the observed evolution and distribution of the contaminant plume. It is further recommended that steps taken to calibrate the model application be documented and provided for review to build confidence in the use of the model as an assessment tool.

More direct lines of evidence should be included in the recommended tiered analysis process because of the complexity of modeling efforts and the potential level of uncertainty associated with model predictions. The acquisition of these data often depends on establishing a network of monitoring locations throughout the aquifer. The site-specific data collected from these monitoring locations should provide a reliable way to identify the attenuation process and assess the performance characteristics of MNA. As with any technology used as part of a cleanup, continued assessment of performance is normally important for ensuring cleanup goals will be attained.

6.3 Interpreting Model Results

It is generally not possible to account for all variability in a modeling study because of the heterogeneity of most geologic systems. Modeling results should therefore be interpreted in realistic rather than absolute terms. Modeling is often most helpful for identifying relative changes in contaminant speciation and distribution in response to geochemical changes in the system. Models can provide an indication of whether a particular reaction or system response is expected under specific conditions. When the potential for MNA of inorganic contaminants is evaluated, modeling should be validated with observational study to confirm whether the expected reactions occur. Discrepancies between modeled and actual conditions can lead to new insights into the geochemical system and may result in changes to the CSM.

Discrepancies between modeled and actual conditions can result from uncertainty introduced at several points in the modeling process. Geochemical modeling applications generally require complete chemical analyses, including not only the contaminants of interest, but the major ion chemistry, pH, and distribution of metals among their mobile redox states. Errors in chemical analysis may therefore alter model results. Similarly, errors in measuring hydrologic parameters may result in differences between measured and modeled distributions of chemical species.

Errors or omissions in sampling also affect model results. Sample choice and dataset size can introduce error through sampling bias. Fluid samples may be collected from monitoring wells completed in highly conductive layers, where they can be extracted rapidly, leaving unaccounted significant quantities of residual contamination in slightly less conductive layers. In addition, samples may not be collected from upgradient or downgradient stations located outside the immediate plume, which precludes an accurate evaluation of the groundwater chemistry of unaffected portions of the aquifer. Uncontaminated groundwater migrating onto a site can induce changes in groundwater chemistry that may affect the stability of attenuated compounds. Similarly, as contaminated groundwater mixes with uncontaminated groundwater downgradient of a site, changes in groundwater chemistry may occur, with impacts to the stability of the attenuated compound. Collecting samples upgradient and downgradient of the site is recommended to accurately evaluate site-induced chemistry changes.

Geochemical models rely on thermodynamic databases that contain data on aqueous species and potential reactions between them. These databases, and the thermodynamic data contained within them, vary widely in breadth and accuracy. Modeling results will vary depending on the thermodynamic database used in the model.

For best results, data used as input in a model must be accurate and representative of site conditions. Inaccurate information will lead to skewed results. Where differences in modeled and measured site conditions are observed, changes in the CSM for a site may be needed or new information obtained.

6.4 Site-Specific Data

Site-specific data should be collected to define the physical, chemical, and biological characteristics of the aquifer to derive meaningful modeling results and test the validity of model predictions. It is important to calibrate models to observations and to verify that the model adequately describes the natural system. Steps taken to calibrate any models used to support selection of MNA should be documented and available for review to increase confidence in the use of the model.

7.0 SUMMARY

The EPA remains fully committed to its goals of protecting human health and the environment by remediating contaminated soils, restoring contaminated groundwaters to their beneficial uses, preventing migration of contaminant plumes, and protecting groundwater and other environmental resources. The EPA does not view MNA as a "no action" remedy, but rather considers it a potential means of addressing contamination under a limited set of site circumstances where its use is consistent with CERCLA and the NCP. In general, MNA should not be considered as a "presumptive" or "default" remediation alternative, but rather should be evaluated and compared with other viable remediation methods (including innovative technologies) during the assessment phases leading to the selection of a remedy. The evaluation of MNA should include a comprehensive site characterization, risk assessment where appropriate and measures to control sources. In addition, the progress of MNA toward a site's cleanup levels should be carefully monitored and compared with expectations to ensure that it will meet RAOs within a timeframe that is reasonable compared with timeframes associated with other methods. Where MNA's ability to meet these expectations is uncertain and based primarily on lines of evidence other than documented trends of decreasing contaminant concentrations, decision-makers should incorporate contingency measures into the remedy.

In summary, there are several key issues and ideas to note regarding MNA for inorganic contaminants:

- Because MNA does not use any active remedial measures, MNA does not constitute a treatment process for inorganic contaminants.
- Dilution and dispersion generally are not appropriate as primary MNA mechanisms because they accomplish concentration reduction through dispersal of contaminant mass rather than mass destruction or immobilization.
- MNA is generally not appropriate for plumes that are considered stable, yet there is confirmed discharge to surface water bodies or potential human or ecological receptor exposure.
- MNA should be supported by actual site data and information in the administrative record demonstrating a decreasing trend of the contaminant concentration.
- Attenuation rates and mass flux estimates can be used as supporting lines of evidence but should not be used as the primary supporting evidence that attenuation is occurring.
- Reliance on models without monitoring data to demonstrate continued attenuation would generally be inconsistent with this guidance.

The EPA is confident that MNA can be, at many sites, a reasonable and protective component of a broader remediation strategy. However, the EPA also believes that there may be many other sites where either the uncertainties are too great or there is a need for a more rapid remediation that precludes the use of MNA as a stand-alone remedy because it would not ensure protectiveness of human health and the environment. This guidance is intended to help promote consistency in how MNA remedies for inorganic contaminants are, evaluated, and if appropriate, proposed and selected as remedial actions.

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APPENDIX A

RECOMMENDED GROUNDWATER ANALYSES

Appendix A. Recommended Groundwater Analyses (EPA 2007a and 2007b)

Analysis	Associated Phase	Data Use	Recommended Frequency of Analysis[1]	Comments
Water level data	I, II, III, IV	Can be used to determine groundwater flow directions and rate of flow.	Each sampling round	Water levels from a sufficient number of wells on a project should be collected to determine groundwater flow direction. Measurements should be taken over a time period to minimize impacts from changing hydrogeologic conditions (for example, tidal influences, pumping drawdown).
Total Metals	I, II, III, IV	Can be used in defining plume boundary, confirming static or shrinking plume conditions, modeling geochemical speciation/ environmental fate and transport, and determining overall appropriateness of MNA for meeting remediation objectives within the specified regulatory time frame. Data is ultimately useful to MNA performance/ compliance monitoring program.	Each sampling round	Exposure of samples to air should be prevented and samples should be preserved to prevent sample oxidation and potential metal co-precipitation with iron oxides. For further discussion of total and dissolved metal sampling, refer to *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume I* (EPA 2007a).

Notes:

1. Recommended frequency of analysis may need to be adjusted to meet site-specific data needs.

Analysis	Associated Phase	Data Use	Recommended Frequency of Analysis[1]	Comments
Radionuclides	I, II, III, IV	Same as total metals in water. In addition, some analytical methods for radionuclides measure total mass while others measure specific isotopes or activity, which may be important for evaluating ingrowth contributions to plume activity and mobility.	Each sampling round	Same as total metals in water. Keep anaerobic samples anaerobic to prevent potential co-precipitation of target radionuclides with iron or other oxides. Measurement of activity is more appropriate for short half-life radionuclides where decay processes dominate, while measurement of total mass is more appropriate for long half-life radionuclides where attenuation is dominated by physicochemical processes such as sorption or precipitation.
pH	I, II, III, IV	Can be used in modeling geochemical speciation/ environmental fate and transport. Important in evaluating sorption capacity of soil.	Each sampling round	Improperly calibrated electrodes could impair results; should measure immediately or in a flow-through cell to prevent equilibration of groundwater with atmosphere.
Major Anions	II, III, IV	Includes Br, Cl, F, NO_3 / NO_2, o-PO_4 and SO_4. Used in modeling geochemical speciation and environmental fate and transport. Trends in nitrate/nitrite and sulfate/ sulfide concentrations also indicate redox conditions.	Each sampling round	Relative amounts of NO_3^- / NO_2^- and SO_4^{2-} / S^{2-} provide additional lines of evidence of oxidizing/ reducing conditions in the aquifer and provide data on changing aquifer conditions. Note: Br, F and o-PO_4 are typically present at trace concentrations and are not considered “major anions.”

Notes:

1. Recommended frequency of analysis may need to be adjusted to meet site-specific data needs.

Analysis	Associated Phase	Data Use	Recommended Frequency of Analysis[1]	Comments
Major Cations	II, III, IV	Includes Na, K, Ca, Mg and Fe. Used in modeling geochemical speciation/ environmental fate and transport. Ca and Mg in solution may compete with other metals for sorption sites and thereby reduce sorptive capacity of soils.	Each sampling round	Relative amounts of Fe(II)/Fe(III) provide additional lines of evidence of oxidizing/reducing conditions in the aquifer and provide data on changing aquifer conditions.
Ferrous iron and Sulfide	II, III, IV	Can be used to determine whether a system is reducing. Also used to determine the potential for contaminant precipitation or co-precipitation and for geochemical modeling.	Initial sampling round, then semi-annually	Field measurement. Can determine if ferric iron is present by subtracting ferrous iron concentration from total iron concentration.
Temperature	I, II, III, IV	Standard parameter; may be used to evaluate reaction kinetics.	Each sampling round	
Oxidation-Reduction Potential (ORP)	I, II, III, IV	Indicates whether oxidizing or reducing conditions prevail in site groundwater. Some redox-sensitive metals and radionuclides may form sparingly soluble complexes or precipitates under reducing conditions	Each sampling round	Groundwater system redox affects mineral solubility and relative concentrations of redox-sensitive elements in groundwater.
Dissolved Oxygen (DO)	I, II, III, IV	Use with ORP to determine if system is oxic or anoxic.	Each sampling round	Measure in a flow-through cell to prevent equilibration of groundwater with atmosphere.

Notes:

1. Recommended frequency of analysis may need to be adjusted to meet site-specific data needs.

Analysis	Associated Phase	Data Use	Recommended Frequency of Analysis[1]	Comments
Dissolved Organic Carbon (DOC)	II, III, IV	Elevated DOC may promote metal complexation with humic acids and affect sorption to soil; DOC may also promote reducing aquifer conditions that could impact speciation of redox-sensitive metals.	Initial sampling round, then annually	Can be used initially to help understand the attenuation process at work and aquifer capacity for contaminant reduction. Used during long-term monitoring to signify changes in water chemistry that may impact attenuation sustainability.
Total Inorganic Carbon (TIC)	II, IV	Can be used with pH data to determine carbonate speciation and buffering capacity of groundwater. Some metals may form sparingly soluble complexes with carbonates (for example, lead) while others become more mobile when complexed with carbonate (for example, uranium).	Initial sampling round, then semi-annually	Total inorganic carbon is similar to alkalinity, but includes additional species (for example, CO_2 or H_2CO_3) not typically accounted for in alkalinity measurement. Alkalinity may be an acceptable substitute for TIC. Used during long-term monitoring to signify changes in water chemistry that may impact attenuation.
Conductivity	I, II, III, IV	Conductivity can provide indications of ionic strength and total dissolved solids.	Each sampling round	

Notes:

1. Recommended frequency of analysis may need to be adjusted to meet site-specific data needs.

APPENDIX B

RECOMMENDED SOIL ANALYSES

Appendix B. Recommended Soil Analyses (EPA [2007a, 2007b])

Analysis	Associated Phase	Data Use	Recommended Frequency of Analysis[1]	Comments
Hydraulic conductivity	I	Can be used with groundwater level data to determine groundwater flow velocity.	Initial sampling round	Component in the development of the conceptual site model and sampling frequency.
Total Metals	II, III, IV	Can be used in determining the extent of soil contamination, contaminant mass present, and potential for source attenuation.	Initial site characterization and MNA evaluation	Frequency of soil sampling and analysis during MNA program should be established as part of the performance and compliance monitoring program.
Radionuclides	II, III, IV	Same as total metals in soils. In addition, some analytical methods for radionuclides measure total mass while others measure specific isotopes and/or activity. Mass measurements are collected for determining soil uptake capacity.	Initial site characterization and MNA evaluation	Analytical data should be adjusted to account for decay losses during the interval between sample collection and analysis for radionuclides with short half-lives. Measurement of activity for short half-life radionuclides or total mass for long half-life radionuclides is same as for groundwater.
Mineralogy	II, III	Can be used to evaluate attenuation capacity of aquifer; identification of site-specific metal and mineral associations may be used to evaluate long-term metal retention capacity of soil.	Initial site characterization and MNA evaluation	Both mineralogical composition and contaminant distribution in soil may be highly heterogeneous at the field scale. Data can also be used to support geochemical modeling of the site.

Notes:

1. Recommended frequency of analysis may need to be adjusted to meet site-specific data needs.

Analysis	Associated Phase	Data Use	Recommended Frequency of Analysis[1]	Comments
Cation Exchange Capacity (CEC)	II, III, IV	Provides relative indication of sorptive capacity of soil under specific solution conditions.	Initial site characterization and MNA evaluation	Dependent on pH and soil organic matter.
Total Organic Carbon (TOC)	II	Can be used along with cation exchange capacity to obtain relative indication of soil sorptive capacity.	Initial site characterization and MNA evaluation	Can be used with the organic carbon soil-water partition coefficient, K_{oc}, to determine contaminant partitioning coefficient.
Acid Volatile Sulfides (AVS)/ Simultaneously Extracted Metals (SEM)	II, III, IV	Can be used to assess metal and metalloid partitioning to the sulfide fraction of soils and sediments, and to estimate potential metal toxicity in aquatic sediments.	Initial site characterization and MNA evaluation	Outside the source area samples are generally taken from the saturated zone to determine potential reaction between dissolved contaminants and mineral solids.
Sequential Extraction Procedures (SEP)	II, III, IV	Can be used to obtain a relative assessment of contaminant environmental availability. Site samples are subjected to successively harsher extracting solutions; contaminants released earlier are presumed to be relatively more available.	Initial MNA evaluation; thereafter at intervals based on groundwater flow velocity	Can provide quantitative information on the capacity of a material to attenuate inorganic contaminants. Measurements done over time can provide data on changes in available contaminant mass sorbed to or precipitated in the soil matrix. Assumes components released in earlier extractions are more environmentally mobile.

Notes:

1. Recommended frequency of analysis may need to be adjusted to meet site-specific data needs.

APPENDIX C

RECOMMENDED ANALYTICAL METHODS AND DATA QUALITY REQUIREMENTS FOR GROUNDWATER ANALYSES

Appendix C. Recommended Analytical Methods and Data Quality Requirements for Groundwater Analyses (EPA [2007a, 2007b])

Analysis	Method Reference and/or Description (most recent revision or date)	Sample Volume, Sample Container, Sample Preservation	Minimum Required Limit of Quantitation or Resolution	Comments
Total Metals/ Inorganic	SW 6010C (Revision 3, February 2007)/6020A (Revision 1, February 2007): *As, Cr, Cu, Pb, Ni, Se* EPA 200.8 (Revision 5.4)/SW 6020A (Revision 1, February 2007): *Cd* SW 6850 (Revision 0, January 2007/6860 (Revision 0, January 2007): ClO_4 EPA 2007a	250 mL, polycarbonate bottle, nitric acid (pH<2), cool to 4° C	1 µg/L	If aquifer is anaerobic, exposure of samples to air should be prevented or samples should be preserved to prevent sample oxidation and potential co-precipitation with iron oxides.
Radionuclides	*Standard Analytical Methods for Environmental Restoration Following Homeland Security Events v. 5.0* (EPA 2009); *Inventory of Radiological Methodologies* (EPA 2006c); *Multi-Agency Radiological Laboratory Analytical Protocols Vol. II* (EPA 2004a)	250 mL, polycarbonate bottle, cool to 4°C; also see method-specific recommendations		Analytical data should be adjusted to account for decay losses during the interval between sample collection and analysis for radionuclides with short half-lives. Use of either activity- or mass-based analytical methods may be appropriate depending on data needs.

Notes:

1. Most recent version of listed method is assumed.
2. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, EPA, most recent edition.
3. "SM" refers to *Standard Methods for the Examination of Water and Wastewater*, most recent edition.
4. "EPA" refers to *Methods for Chemical Analysis of Water and Wastes*, EPA, most recent edition.

Analysis	**Method Reference and/or Description (most recent revision or date)**	**Sample Volume, Sample Container, Sample Preservation**	**Minimum Required Limit of Quantitation or Resolution**	**Comments**
pH	EPA 150.2 (Revision 0, December 1982) or field probe with direct reading meter	Measure in field following procedures in the EPA 150.2 or per manufacturer instructions	0.2 units	Improperly calibrated electrodes could impair results; should measure immediately to prevent equilibration of groundwater with atmosphere.
Major Anions	EPA 300.1/SW 9056 A (Revision 1, February 2007)	250 mL, Polycarbonate bottle, cool to 4°C	100 µg/L	
Major Cations	SW 6010C C (Revision 3, February 2007)/7000B (Revision 2, February 2007)	250 mL, polycarbonate bottle, Nitric acid (pH<2), cool to 4°C	100 µg/L	
Ferrous Iron, Sulfide	EPA 2002a	25 mL, glass bottle, unpreserved	1 mg/L	Measured in field using colorimetric method. Analysis should be done quickly as the analytes are sensitive to exposure to atmospheric oxygen.
Temperature	Field temperature probe with direct reading meter	Measure in the field using a flow-through cell or an overflow cell filled from the bottom	0.5°C	
Oxidation-Reduction Potential (ORP)	SM 2580B (1997) EPA 2002a	Measure in the field using a flow-through cell or an overflow cell filled from the bottom	+/- 100 mV	Field measurement should be in situ or in flow-through cell to prevent introduction of atmospheric oxygen. Improperly calibrated electrodes or introduction of atmospheric oxygen during sampling could impair results.

Notes:

1. Most recent version of listed method is assumed.
2. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, EPA, most recent edition.
3. "SM" refers to *Standard Methods for the Examination of Water and Wastewater*, most recent edition.
4. "EPA" refers to *Methods for Chemical Analysis of Water and Wastes*, EPA, most recent edition.

Analysis	**Method Reference and/or Description (most recent revision or date)**	**Sample Volume, Sample Container, Sample Preservation**	**Minimum Required Limit of Quantitation or Resolution**	**Comments**
Dissolved Oxygen (DO)	Dissolved oxygen meter calibrated between each well according to the supplier's specifications	Measure in the field using a flow-through cell or an overflow cell filled from the bottom	0.2 mg/L	Field measurement should be in situ or in flow-through cell to prevent introduction of atmospheric oxygen.
Dissolved Organic Carbon (DOC)	EPA 415.3 (Revision 1.0, June 2003)	250 mL, polycarbonate bottle, 0.45 µm field filtered and H_2SO_4 ($pH<2$), cool to 4°C		
Total Inorganic Carbon (TIC)	SM 2320 (1997)	250 mL, zero headspace glass bottle, cool to 4° C		Quickly collect sample to prevent equilibration of groundwater with atmosphere; Hach alkalinity test kit model AL AP MG-L could be considered as an alternative method.
Conductivity	EPA 120.1 (1982), SW 9050A (Revision 1, December 1996), or direct reading meter	250 mL plastic or glass bottle, cool to 4°C; or measure in the field	50 $\mu S/cm^2$	

Notes:

1. Most recent version of listed method is assumed.
2. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, EPA, most recent edition.
3. "SM" refers to *Standard Methods for the Examination of Water and Wastewater*, most recent edition.
4. "EPA" refers to *Methods for Chemical Analysis of Water and Wastes*, EPA, most recent edition.

APPENDIX D

RECOMMENDED ANALYTICAL METHODS AND DATA QUALITY REQUIREMENTS FOR SOIL ANALYSES

Appendix D. Recommended Analytical Methods and Data Quality Requirements for Soil Analyses (EPA [2007a, 2007b])

Analysis	Method Reference and/or Description (most recent revision or date)	Sample Volume, Sample Container, Sample Preservation	Minimum Required Limit of Quantitation or Resolution	Comments
Total Metals	SW 6010C (Revision 3, February 2007)/7000B (Revision 2, February 2007) *To be updated as necessary*	8 oz. wide-mouth glass jar, cool to 4 C	0.01 mg/kg	Sample prep methods to be chosen from SW 3050, 3051, or 3052; or from U.S. Geological Survey (USGS) Open File Report 02-223-I. Heterogeneity of metals concentrations in soils can be significant at the field scale. Should include reporting of Fe, Mn, Na, K, Ca, Mg and Al at a minimum.
Radionuclides	*Standard Analytical Methods for Environmental Restoration Following Homeland Security Events v. 5.0* (EPA 2009); *Inventory of Radiological Methodologies* (EPA 2006c); *Multi-Agency Radiological Laboratory Analytical Protocols Vol. II* (EPA 2004a)	8 oz. wide-mouth glass jar, cool to 4°C; also see method-specific recommendations		It is critical that analytical data be adjusted to account for decay losses during the interval between sample collection and analysis for radionuclides with short half-lives. Use of either activity- or mass-based analytical methods may be appropriate depending on data needs.
Mineralogy	X-ray fluorescence and X-ray diffraction	8 oz. wide-mouth glass jar, cool to 4 C	N/A	Petrographic analysis may also be appropriate.
Cation Exchange Capacity (CEC)	SW 9081 (Revision 0, September 1986)	8 oz. wide-mouth glass jar, cool to 4 C		Perform under various pH conditions to determine pH dependence of exchange capacity.

Notes:

1. Most recent version of listed method is assumed.
2. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, EPA, most recent edition.

Analysis	**Method Reference and/or Description (most recent revision or date)**	**Sample Volume, Sample Container, Sample Preservation**	**Minimum Required Limit of Quantitation or Resolution**	**Comments**
Total Organic Carbon (TOC)	Modified SW 9060A (Revision 1, November 2004)	8 oz. wide-mouth glass jar, cool to 4 C		Method not standard between labs. Can also consider organic matter loss on ignition with subsequent calculation of TOC.
Acid Volatile Sulfide (AVS)/ Simultaneously Extracted Metals (SEM)	EPA 821-R-91-100	8 oz. wide-mouth glass jar, cool to 4 C		
Sequential Extraction Procedures (SEP)	Tessier *and others*. (1979)	8 oz. wide-mouth glass jar, cool to 4 C		

Notes:

1. Most recent version of listed method is assumed.
2. “SW” refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, EPA, most recent edition.