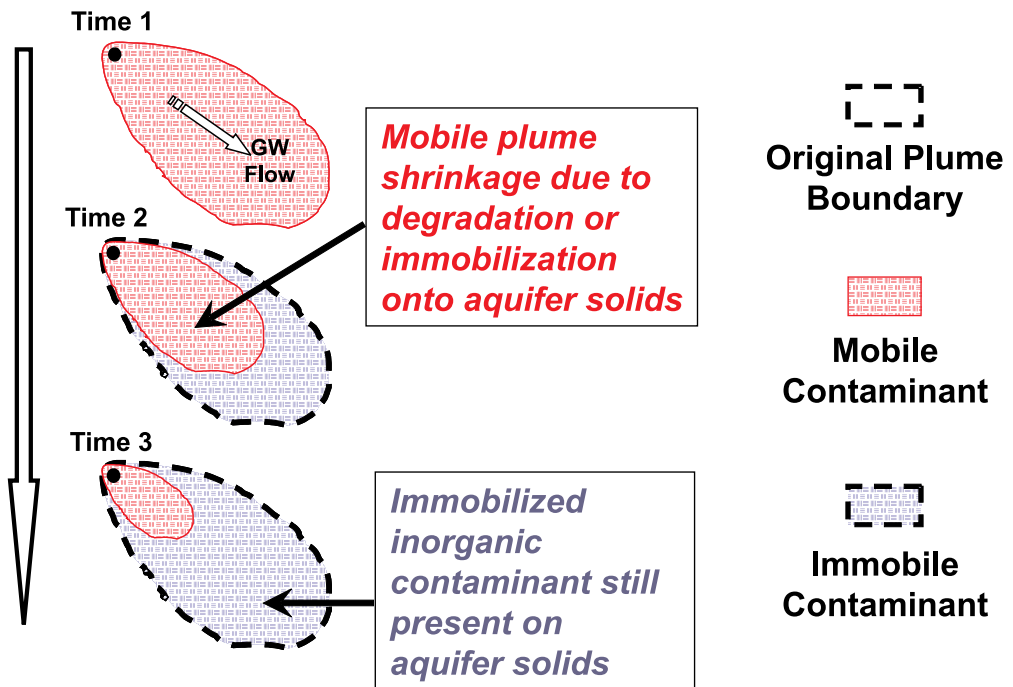# Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1
Technical Basis for Assessment

Evolution of Inorganic Contaminant Plume

Time 1

GW Flow

Time 2

Time 3

Mobile plume shrinkage due to degradation or immobilization onto aquifer solids

Immobilized inorganic contaminant still present on aquifer solids

Original Plume Boundary

Mobile Contaminant

Immobile Contaminant

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1 - Technical Basis for Assessment

Edited by
Robert G. Ford
Richard T. Wilkin
Robert W. Puls
U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Ada, Oklahoma 74820

Project Officer
Robert G. Ford
Ground Water and Ecosystems Restoration Division
National Risk Management Research Laboratory
Ada, Oklahoma 74820

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Notice

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All research projects making conclusions or recommendations based on environmental data and funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve the collection or use of environmental data and, as such, did not require a Quality Assurance Plan.
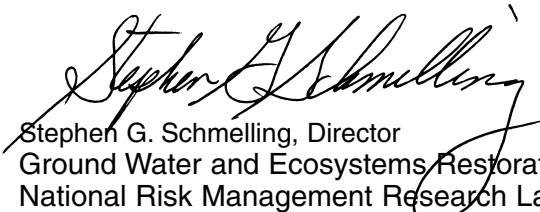
Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients. Understanding site characterization to support the use of monitored natural attenuation (MNA) for remediating inorganic contaminants in ground water is a major priority of research and technology transfer for the U.S. Environmental Protection Agency's Office of Research and Development and the National Risk Management Research Laboratory. This document provides technical recommendations regarding the development of conceptual site models and site characterization approaches useful for evaluating the effectiveness of the natural attenuation component of ground-water remedial actions.

Stephen G. Schmelling, Director
Ground Water and Ecosystems Restoration Division
National Risk Management Research Laboratory

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Acknowledgments

Executive Summary

The term "monitored natural attenuation," as used in this document and in the Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17P, refers to "the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods." When properly employed, monitored natural attenuation (MNA) may provide an effective knowledge-based remedy where a thorough engineering analysis informs the understanding, monitoring, predicting, and documenting of the natural processes. In order to properly employ this remedy, the Environmental Protection Agency needs a strong scientific basis supported by appropriate research and site-specific monitoring implemented in accordance with the Agency's Quality System. The purpose of this series of documents, collectively titled "Monitored Natural Attenuation of Inorganic Contaminants in Ground Water," is to provide a technical resource for remedial site managers to define and assess the potential for use of site-specific natural processes to play a role in the design of an overall remedial approach to achieve cleanup objectives.

The current document represents the first volume of a set of three volumes that address the technical basis and requirements for assessing the potential applicability of MNA as part of a ground-water remedy for plumes with non-radionuclide and/or radionuclide inorganic contaminants. Volume 1, titled "Technical Basis for Assessment," consists of three sections that describe 1) the conceptual background for natural attenuation for inorganic contaminants, 2) the technical basis for attenuation of inorganic contaminants in ground water, and 3) approaches to site characterization to support evaluation of MNA. Emphasis is placed on characterization of immobilization and/or degradation processes that may control contaminant attenuation, as well as technical approaches to assess performance characteristics of the MNA remedy. A tiered analysis approach is presented to assist in organizing site characterization tasks in a manner designed to reduce uncertainty in remedy selection while distributing costs to address four primary issues:

1. Demonstration of active contaminant removal from ground water & dissolved plume stability;
2. Determination of the mechanism and rate of attenuation;
3. Determination of the long-term capacity for attenuation and stability of immobilized contaminants; and
4. Design of performance monitoring program, including defining triggers for assessing MNA failure, and establishing a contingency plan.

Detailed discussion is provided on the importance of acquiring site-specific data that define ground-water hydrogeology and chemistry, the chemical and mineralogical characteristics of aquifer solids, and the aqueous and solid phase chemical speciation of contaminants within the ground-water plume boundary. Technical distinctions are drawn between characterization efforts to evaluate the applicability of MNA as part of a cleanup remedy for organic versus inorganic contaminants. Emphasis is placed on the need to collect site-specific data supporting evaluation of the long-term stability of immobilized inorganic contaminants. Also included is discussion on the role of analytical models as one of the tools that may be employed during the site characterization process. This discussion is intended to provide context to contaminant-specific site characterization approaches recommended in the remaining two volumes of this document.

This document is limited to evaluations performed in porous-media settings. Detailed discussion of performance monitoring system design in fractured rock, karst, and other such highly heterogeneous settings is beyond the scope of this document. Ground water and contaminants often move preferentially through discrete pathways (e.g., solution channels, fractures, and joints) in these settings. Existing techniques

may be incapable of fully delineating the pathways along which contaminated ground water migrates. This greatly increases the uncertainty and costs of assessments of contaminant migration and fate and is another area of continuing research. As noted in OSWER Directive 9200.4-17P, "MNA will not generally be appropriate where site complexities preclude adequate monitoring." The directive provides additional discussion regarding the types of sites where the use of MNA may be appropriate.

This document focuses on monitoring the saturated zone, but site characterization and monitoring for MNA or any other remedy typically would include monitoring of all significant pathways by which contaminants may move from source areas and contaminant plumes to impact receptors (e.g., surface water and indoor air).

Nothing in this document changes Agency policy regarding remedial selection criteria, remedial expectations, or the selection and implementation of MNA. This document does not supersede any guidance. It is intended for use as a technical reference in conjunction with other documents, including OSWER Directive 9200.4-17P, "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites" (http://www.epa.gov/swerust1/directiv/d9200417.pdf).

Section I

Conceptual Background for Monitored Natural Attenuation

Kenneth Lovelace, Stuart Walker, Ronald Wilhelm, Robert Puls, Robert G. Ford, Richard T. Wilkin, Steven Acree, Steve Mangion, Patrick V. Brady, Craig Bethke

IA. Background and Purpose

IA.1 Document Organization

The purpose of this document is to provide a framework for assessing the potential application of monitored natural attenuation as part of the remedy for inorganic contaminant plumes in ground water. It is organized into three volumes that provide: Volume 1 - a general overview of the framework and technical requirements for application of Monitored Natural Attenuation (MNA); Volume 2 - contaminant-specific discussions addressing potential attenuation processes and site characterization requirements for non-radionuclides, and Volume 3 - contaminant-specific discussions addressing potential attenuation processes and site characterization requirements for radionuclides. Volume 1 is divided into three sections that address the regulatory and conceptual background for natural attenuation, the technical basis for natural attenuation of inorganic contaminants, and site characterization approaches to support assessment and application of MNA. The contaminant-specific chapters in Volumes 2 and 3 provide an overview of contaminant geochemistry, applicable natural attenuation processes, and specific site characterization requirements. Criteria for selecting specific contaminants for these detailed overviews are described below.

The non-radionuclide contaminants selected for this document include: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), nitrate, perchlorate, and selenium (Se). The selection of these contaminants by USEPA was based on several criteria. First, a 1994 booklet containing information regarding common chemicals found at Superfund sites throughout the nation was consulted (USEPA, 1994). The most commonly found inorganic contaminants were included for consideration in this document. Another document specific to metal-contaminated Superfund sites (USEPA, 1995) identified arsenic (As), cadmium (Cd), chromium (Cr), and lead (Pb) as primary contaminants of concern based on toxicity, industrial use, and frequency of occurrence at Superfund sites. Second, selection was based on chemical behavior considering chemical traits such as: toxicity, ion charge (cation vs. anion), transport behavior (conservative vs. non-conservative), and redox chemistry to cover a broad range of geochemical behavior (USEPA,1999a; USEPA, 1999b; USEPA, 2004). Finally, USEPA regional staff were asked to nominate inorganic contaminants that occurred frequently or that were problematic in their Regions. The above list of nine inorganic contaminants was selected from this process.

The radionuclide contaminants selected for this document include: americium (Am), cesium (Cs), iodine (I), neptunium (Np), plutonium (Pu), radium (Ra), radon (Rn), technetium Tc), thorium (Th), tritium, strontium (Sr), and uranium (U). The selection of these contaminants by EPA was based on two criteria. First, a selected element had to be one of high priority to the site remediation or risk assessment activities of the USEPA (USEPA, 1993; USEPA, 2002). Second, selection was based on chemical behavior considering chemical traits such as: toxicity, cations, anions, conservatively transported, non-conservatively transported, and redox sensitive elements (USEPA, 1999b; USEPA, 2004). By using these characteristics of the contaminants, the general geochemical behavior of a wide range of radionuclide contaminants could be covered as well as the chemical classes that make up the Periodic Table. In addition, this selection accounts for many daughter and fission product contaminants that result from radioactive decay. This is important as the decay of radioisotopes can produce daughter products that may differ both physically and chemically from their parents. The selection of radionuclide contaminants for this document is representative of these characteristics.

IA.2 Purpose of Document

This document is intended to provide a technical resource for determining whether MNA is likely to be an effective remedial approach for inorganic contaminants[1] in ground water. This document is intended to be used during the remedial investigation and feasibility study phases of a Superfund cleanup, or during the equivalent phases of a RCRA Corrective Action (facility investigation and corrective measures study, respectively). The decision to select MNA as the remedy (or part of the remedy) will be made in a Superfund Record of Decision (ROD) or a RCRA Statement of Basis (or RCRA permit).

The USEPA expects that users of this document will include USEPA and State cleanup programs and their contractors, especially those individuals responsible for evaluating alternative cleanup methods for a given site or facility. The overall policy for use of MNA in OSWER cleanup programs is described in the April 21, 1999 OSWER Directive titled, "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites" (Directive No. 9200.4-17P).

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[1] The term "inorganic contaminants" is used in this document as a generic term for metals and metalloids (such as arsenic); and also refers to radiologic as well as non-radiologic isotopes.

Both radiological and non-radiological inorganic contaminants are discussed in this document. There are two reasons for this. First, except for radioactive decay, the potential attenuation processes affecting inorganic contaminants are the same for both contaminant types. Second, several OSWER directives clarify the USEPA's expectation that the decision-making approach and cleanup requirements used at CERCLA sites will be the same for sites with radiological and non-radiological inorganic contaminants, except where necessary to account for the technical differences between the two types of contaminants. Also, the 1999 OSWER Directive specified that the decision process for evaluating MNA as a potential remediation method should be the same for all OSWER cleanup programs.

This document is intended to provide an approach for evaluating MNA as a possible cleanup method for contaminated ground water. Although the focus of the document is on ground water, the unsaturated zone is discussed as a source of contaminants to ground water. Emphasis is placed on developing a more complete evaluation of the site through development of a conceptual site model[2] based on 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.

This document focuses on technical issues and is not intended to address policy considerations or specific regulatory or statutory requirements. The USEPA expects that this document will be used in conjunction with the 1999 OSWER Directive (USEPA, 1999c). Users of this document should realize that different Federal and State remedial programs may have somewhat different remedial objectives. For example, the CERCLA and RCRA Corrective Action programs generally require that remedial actions: 1) prevent exposure to contaminated ground water, above acceptable risk levels; 2) minimize further migration of the plume; 3) minimize further migration of contaminants from source materials; and 4) restore ground-water conditions to cleanup levels appropriate for current or future beneficial uses, to the extent practicable. Achieving such objectives could often require that MNA be used in conjunction with other "active" remedial methods. For other cleanup programs, remedial objectives may be focused on preventing exposures above acceptable levels. Therefore, it is imperative that users of this document be aware of and understand the Federal and State statutory and regulatory requirements, as well as policy considerations that apply to a specific site for which this document will be used to evaluate MNA as a remedial option. As a general practice, individuals responsible for evaluating remedial alternatives should check with the over-seeing regulatory agency to identify likely characterization and cleanup objectives for a particular site prior to investing significant resources.

Use of this document is generally inappropriate in complex fractured bedrock or karst aquifers. In these situations the direction of ground water flow can not 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. Understanding the contaminant flow field in the subsurface is essential for a technically justified evaluation of an MNA remedial option. MNA will not generally be appropriate where site complexities preclude adequate monitoring (USEPA, 1999c).

Because documentation of natural attenuation requires detailed site characterization, the data collected can be used to compare the relative effectiveness of other remedial options and natural attenuation. The technical information contained in this document can be used as a point of reference to evaluate whether MNA by itself, or in conjunction with other remedial technologies, is sufficient to achieve site-specific remedial objectives.

IA.3 Applicable Regulatory Criteria

All remedial actions at CERCLA sites must be protective of human health and the environment and comply with applicable or relevant and appropriate requirements (ARARs) unless a waiver is justified. Cleanup levels for response actions under CERCLA are developed based on site-specific risk assessments, ARARs, and/or to-be-considered material (TBCs). The determination of whether a requirement is applicable, or relevant and appropriate, must be made on a site-specific basis (see 40 CFR §300.400(g)).

"EPA expects to return usable ground waters to their beneficial uses whenever practicable" (see 40 CFR §30 0.430(a)(1)(iii)(F)). In general, drinking water standards provide relevant and appropriate cleanup levels for ground waters that are a current or potential source of drinking water. However, drinking water standards generally are not relevant and appropriate for ground waters that are not a current or potential source of drinking water (see 55 FR 8732, March 8, 1990). Drinking water standards include federal maximum contaminant levels (MCLs) and/or non-zero maximum contaminant level goals (MCLGs) established under the Safe Drinking Water Act (SDWA), or more stringent state drinking water standards. Other regulations may also be ARARs as provided in CERCLA §121(d)(2)(B).

IA.4 Policy Framework for Use of MNA

The term "monitored natural attenuation" is used in this document when referring to a particular approach to remediation. MNA is defined in the 1999 OSWER Directive as follows:

> "...the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-

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2 *A conceptual site model 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.*

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. (USEPA, 1999c, page 3.)

Even though several physical, chemical, and biological processes are included in the above definition, the 1999 OSWER Directive goes on to state a preference for those processes that permanently degrade or destroy contaminants, and for use of MNA for stable or shrinking plumes, as noted below:

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

"MNA should not be used where such an approach would result in either plume migration 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."** *(USEPA, 1999c, page 18.)*

Control of contaminant sources is also an important aspect of EPA's policy. The actual policy language is given below:

"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." (USEPA, 1999c, page 22.)*

The 1999 OSWER Directive also provides a few general guidelines for use of MNA as a remedial approach for inorganic contaminants. The key policy concerns are that the specific mechanisms responsible for attenuation of inorganic contaminants should be known at a particular site, and the stability of the process should be evaluated and shown to be protective under anticipated changes in site conditions. The actual policy language is given below:

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[3] 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 (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 radionulides (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

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3 *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.*

surface soil pathways be carefully evaluated and eliminated as potential sources of external direct radiation exposure.[4]

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.   (USEPA, 1999c, pages 8-9.)

The 1999 OSWER Directive provides the context for the Agency's expectations for evaluating the feasibility of employing MNA as part of a cleanup remedy for contaminated ground water. As indicated by the sections from the Directive that are transcribed above, it also points out specific issues concerning what constitutes natural attenuation for inorganic contaminants. In practice, most of the technical experience developed to date has primarily dealt with evaluations of MNA as applied to remediation of organic contaminant plumes. While this experience provides some perspective for the scope of site characterization that may be warranted to evaluate MNA for inorganic contaminants, there are some important distinctions that bear on the types of required data and the approaches available to obtain these data. The following section elaborates these distinctions in order to provide context for the technical aspects relevant to MNA for inorganic contaminants and the steps needed to implement a technically defensible site characterization effort.

IB.   Relevant Distinctions in Site Characterization for MNA of Inorganic Contaminants

As stated within the OSWER Directive on MNA (USEPA, 1999c), natural attenuation processes are those that 'reduce mass, toxicity, mobility, volume or concentration of contaminants'. Inorganic contaminants discussed within this document include both non-radioactive and radioactive constituents. For radioactive contaminants, radioactive decay processes result in the reduction of risk derived from radiation exposure. The rates of radioactive decay (characterized by the decay half-life) are known for the radioisotopes of concern, thus facilitating this aspect of site characterization. Guidelines for assessing the feasibility of MNA as a component of ground-water cleanup for radio-

nuclides are provided in Volume 3 of this document. For non-radioactive inorganic contaminants and radionuclides possessing long decay half-lives, *immobilization* within the aquifer via sorption to aquifer solids provides the primary means for attenuation of the ground-water plume. In general, an inorganic contaminant can be transferred between solid, liquid, or gaseous phases present within the aquifer, but the contaminant will always be present. Contaminant immobilization will prevent transport to sensitive receptors at points of compliance. There are limited examples where *degradation* of inorganic contaminants may be a viable attenuation process (e.g., biological degradation of nitrate or perchlorate), but degradation is not a viable process for most of the inorganic contaminants discussed in this document. For inorganic contaminants subject to degradation or reductive transformation processes, the supporting site characterization will likely be consistent with the approach employed to assess MNA for organic contaminant plumes (e.g., USEPA, 1998; USEPA, 2001; see also specific discussions for nitrate and perchlorate in Volume 2). The following discussion provides context for the potential significance of immobilization as a means for natural attenuation of inorganic contaminants in ground water.

There is an important distinction between site characterization as applied to assessment of MNA for organic and inorganic contaminants. For organic contaminants, site characterization typically is focused towards determining the mechanism of contaminant degradation and the capacity of site conditions to sustain degradation for treatment of the mass of contaminant within the plume. This analysis may include identification of ground-water characteristics and degradation byproducts that are characteristic for contaminant degradation. Thus, much of the emphasis on site characterization for MNA of organic contaminants has been directed towards the collection and analysis of ground-water samples. In some cases, this characterization effort may have been supplemented with the analysis of contaminant degradation behavior through the use of microcosm experiments employing aquifer solids collected within the plume boundary. For inorganic contaminants in which immobilization onto aquifer solids provides the primary means for attenuation of the ground-water plume, characterization of the solid substrate within the aquifer plays a more significant role during site assessment. In this case risk reduction in ground water is realized through the sorption of the inorganic contaminant onto aquifer solids in combination with the long-term stability of the immobilized contaminant to resist remobilization due to changes in ground-water chemistry. The importance of this distinction between natural attenuation for organic and inorganic contaminants is emphasized in Figure 1.1. In essence, for inorganic contaminants one can consider the existence of two distinct 'plumes' within the boundary of the ground-water plume: 1) the dissolved or "mobile" plume (including dissolved contaminant and contaminant associated with mobile colloids), and 2) the solid phase or "immobile" plume resulting from sorption of the contaminant to aquifer solids (Figure 1.1). Thus, for inorganic contaminants there are two overriding objectives to address through site characterization:

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[4] *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.*

1) Demonstration of removal of the inorganic contaminant from the dissolved phase leading to a stable or shrinking ground-water plume and,

2) Demonstration of stabilization of the inorganic contaminant immobilized onto aquifer solids such that future re-mobilization will not occur to a level that threatens health of environmental receptors.

Evaluating the overall success of natural attenuation for inorganic contaminant remediation will require demonstrating that the rate and capacity for inorganic contaminant attenuation meets regulatory objectives and, in addition, that inorganic contaminant immobilization is sustainable to the extent that future health risks are eliminated. The latter requirement necessitates identifying the chemical speciation of the inorganic contaminant partitioned to the solid phase. This information is critical towards identifying the process controlling attenuation and evaluating the long-term stability of the immobilized contaminant relative to observed or anticipated changes in ground-water chemistry.

Site characterization to support evaluation of MNA as a remedial alternative will involve assessment of contaminant transport in the aquifer. In general terms, this process will include assessment of ground-water hydrology and the biogeochemical processes that control contaminant migration within the plume. Defining the processes that control contaminant immobilization (or degradation) along the paths of ground-water flow will necessitate collection of a range of data that define the dynamics of system hydrology, the chemical characteristics of ground water, and the properties of the aquifer solids. In order to screen out sites that

are inappropriate for selection of MNA, it is recommended that collection of site-specific data be conducted in stages that serve to minimize expenditures while providing insight into the potential existence of natural processes that may attenuate contaminant migration. Description of a tiered analysis approach for organizing site characterization tasks is provided in the following section.

IC.   Tiered Analysis Approach to Site Characterization

Site characterization to support evaluation and selection of MNA as part of a cleanup action for inorganic contaminant plumes in ground water will involve a detailed analysis of site characteristics controlling and sustaining attenuation. The level of detailed data that may be required to adequately characterize the capacity and stability of natural processes to sustain plume attenuation will likely necessitate significant resource outlays. Thus, it is recommended that site characterization be approached in a step-wise manner to facilitate collection of data necessary to progressively evaluate the existing and long-term effectiveness of natural attenuation processes within the aquifer. Implementation of a *tiered analysis approach* provides an effective way to screen sites for MNA that is cost effective because it prioritizes and limits the data that is needed for decision making at each screening step. Conceptually a tiered analysis approach seeks to progressively reduce uncertainty as site-specific data are collected. The decision-making approach presented in this document includes three decision tiers that require progressively greater information on which to assess the likely effectiveness of MNA as a remedy for
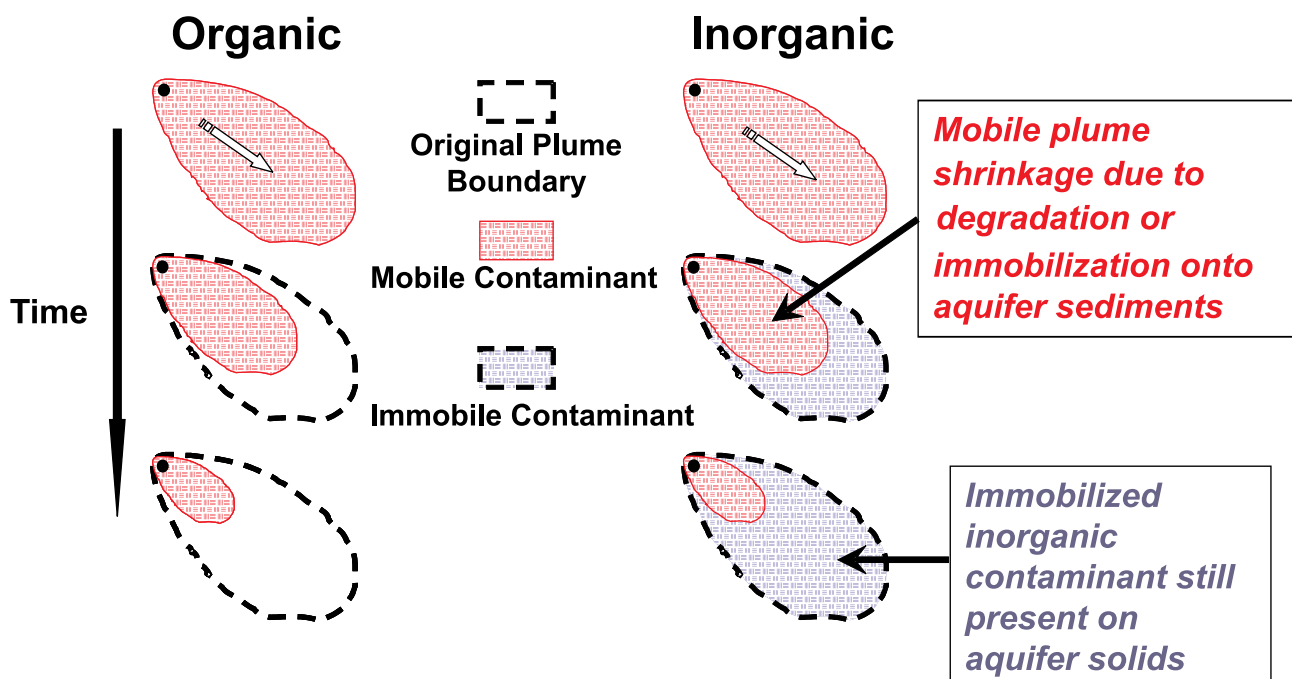
Figure 1.1 *Conceptual distinction between organic versus inorganic contaminant plume behavior where natural processes are active within the ground-water aquifer. Natural attenuation of inorganic contaminants is viable only if the immobilized contaminant remains stable and resistant to remobilization during changes in ground-water chemistry.*

inorganic contaminants in ground water. The fourth tier is included to emphasize the importance of determining appropriate parameters for long-term performance monitoring, once MNA has been selected as part of the remedy. Data collection and evaluation within the tiered analysis approach would be structured as follows:

I.   Demonstration that the ground-water plume is not expanding and that sorption of the contaminant onto aquifer solids is occurring where immobilization is the predominant attenuation process;

II. Determination of the *mechanism and rate* of the attenuation process;

III. Determination of the *capacity* of the aquifer to attenuate the mass of contaminant within the plume and the *stability* of the immobilized contaminant to resist re-mobilization, and;

IV. Design performance monitoring program based on the mechanistic understanding developed for the attenuation process, and establish a contingency plan tailored to site-specific characteristics.

Elaboration on the objectives to be addressed and the types of site-specific data to be collected under each successive tier is provided below.

IC.1   Tier I

The objective under Tier I analysis would be to eliminate sites where site characterization indicates that the ground-water plume is continuing to expand in aerial or vertical extent. For contaminants in which sorption onto aquifer solids is the most feasible attenuation process, an additional objective would be to demonstrate contaminant uptake onto aquifer solids. Analysis of ground-water plume behavior at this stage is predicated on adequate aerial and vertical delineation of the plume boundaries. Characterization of ground-water plume expansion could then be supported through analysis of current and historical data collected from monitoring wells installed along the path of ground-water flow. An increasing temporal trend in contaminant concentration in ground-water at monitoring locations down gradient from a source area is indicative that attenuation is not occurring sufficient to prevent ground-water plume expansion. Determination of contaminant sorption onto aquifer solids could be supported through the collection of aquifer cores coincident with the locations of ground-water data collection and analysis of contaminant concentrations on the retrieved aquifer solids. Illustration of the type of data trend anticipated for a site where sorption actively attenuates contaminant transport is provided in Figure 1.2. The spatial distribution in aqueous and solid contaminant
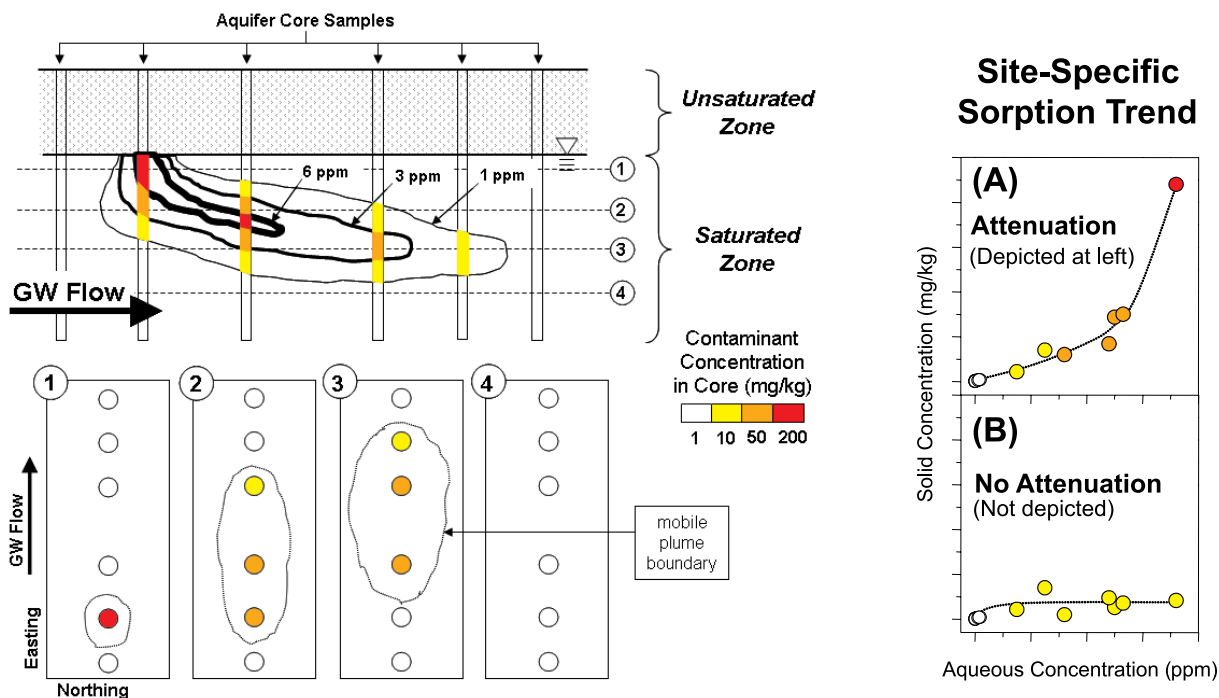
Figure 1.2 *Conceptual depiction of the data collection effort to demonstrate whether sorption to aquifer solids attenuates contaminant transport in ground water. The left side of the diagram provides a cross-sectional view of the spatial distribution of the contaminant concentration in ground water and co-located aquifer solids for a site where sorption attenuates contaminant transport. The trend in aqueous and solid contaminant concentrations for this scenario is depicted in Panel (A) to the right. Panel (B) depicts the relationship between aqueous and solid contaminant concentrations for a site where sorption does not attenuate contaminant transport.*

concentrations for a site where sorption attenuates contaminant migration is depicted on the left side of the illustration. Anticipated relationships between aqueous and solid contaminant concentrations for sites with and without active contaminant attenuation via sorption are depicted on the right side of the illustration in Panels (A) and (B), respectively. Specifically, where sorption onto aquifer solids is occurring, there should be an increasing trend in solid phase contaminant concentrations as a function of increasing aqueous concentration. In contrast, no change in solid phase contaminant concentrations as a function of increasing aqueous concentration is indicative that attenuation is not occurring. Ultimately, sites that demonstrate ground-water plume expansion and a lack of contaminant sorption (for contaminants subject to sorption) would be eliminated from further consideration of MNA as part of the cleanup remedy.

IC.2   Tier II

The objective under Tier II analysis would be to eliminate sites where further analysis shows that attenuation rates are insufficient for attaining cleanup objectives established for the site within a timeframe that is reasonable compared to other remedial alternatives. (see USEPA, 1999c, pages 19-21, for a discussion of "reasonable timeframe for remediation".) Data collection and analysis performed for Tier II would indicate whether MNA processes are capable of achieving remediation objectives, based on current geochemical conditions at the site. This data collection effort would also be designed to support identification of the specific mechanism(s) controlling contaminant attenuation.

An estimate of attenuation rates for inorganic contaminants will typically involve calculation of the apparent transfer of mass from the aqueous to the solid phase, based on sampling of ground water and/or aquifer solids. It is recommended that these estimates be based as much as possible on field measurements rather than modeling predictions. A recommended approach is to identify hydrostratigraphic units for the site and develop a ground water flow model which can be used to estimate ground water seepage velocities in each of these units (Further information on ground water flow models is provided in Section I.D.) These seepage velocities can be combined with measured contaminant concentrations to estimate mass flux (mass per time per area) for each contaminant, in each hydrostratigraphic unit. The necessary data might include physical parameters such as hydraulic conductivities within the aquifer and hydraulic gradients. Changes in mass flux can then be used to estimate mass loss from the aqueous phase since the last sampling event, which is assumed to be the apparent attenuation rate. (Further information on estimating attenuation rates is provided in Section IIIA.5.)

Determination of attenuation mechanism will depend on collection of data to define ground-water chemistry, aquifer solids composition and mineralogy, and the chemical speciation of the contaminant in ground water and associated aquifer solids. This will entail a significant effort in the site-specific data collection effort, but provides the

underpinning for further evaluation of the performance of MNA to be addressed in subsequent stages of the site characterization process. The goal of this characterization effort is to identify the aqueous and solid phase constituents within the aquifer that control contaminant attenuation. This data collection effort may include collection of field water quality data (e.g., pH, dissolved oxygen, alkalinity, ferrous iron, and dissolved sulfide), laboratory measurements of ground-water and aquifer solids chemical composition, microbial characteristics and/or mineralogy of the aquifer solids (as relevant to degradation or immobilization), and the chemical speciation of the contaminant in ground-water and/or the aquifer solids. Contaminant speciation refers to both oxidation state characterizations [e.g., As(III) vs. As(V)] as well as specific associations with chemical constituents in aquifer solids (e.g., precipitation of Pb carbonate vs. adsorption of Pb to iron oxides). Evaluations of the subsurface microbiology may be necessary in situations where biotic processes play a direct or indirect role in governing contaminant attenuation. Indirect microbial influence on contaminant attenuation includes situations in which the predominant characteristics of the ground-water chemistry are controlled by microbial oxidation-reduction reactions. This situation may be more predominant in plumes in which readily degradable organic contaminants, such as hydrocarbons or chlorinated solvents, are also present. Ultimately, mechanistic knowledge of the attenuation process along with a detailed knowledge of the ground-water flow field provides the basis for subsequent evaluations to assess the long-term capacity of the aquifer to sustain contaminant attenuation.

IC.3   Tier III

The objective under Tier III would be to eliminate sites where site data and analysis show that there is insufficient capacity in the aquifer to attenuate the contaminant mass to ground-water concentrations that meet regulatory objectives or that the stability of the immobilized contaminant is insufficient to prevent re-mobilization due to future changes in ground-water chemistry. Possible factors that could result in an insufficient capacity for attenuation include:

1. changes in ground-water chemistry result in slower rates of attenuation,

2. insufficient mass flux of aqueous constituents that participate in the attenuation reaction, and/or

3. insufficient mass of solid constituents in aquifer solids that participate in the attenuation reaction.

These factors pertain to situations where either degradation or immobilization is the primary attenuation process. For immobilized contaminants, factors to consider relative to the long-term stability of the attenuated contaminant include changes in ground-water chemistry that could result in release of the contaminant from aquifer solids due to desorption from solid surfaces or dissolution of precipitates. For example, contaminant desorption could be caused by changes in ground-water pH, since the degree of adsorption is typically sensitive to this parameter. Alternatively, dissolution of a contaminant attenuated as a carbonate

precipitate may result from decreases in ground-water pH and alkalinity.

Assessment of attenuation capacity will depend on knowledge of the flux of contaminants and associated reactants in ground-water, as well as the mass distribution of reactive aquifer solids along ground-water flow paths. In order to conduct this type of evaluation, adequate information is needed on the heterogeneity of the ground-water flow field, and the spatial and/or temporal variability in the distribution of aqueous and solids reactants within the plume. For situations where ground-water chemistry is governed by microbial processes, seasonal variations may exert an indirect influence on the effective capacity within the aquifer at any point in time. 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 based on site-specific data. Exploring alternatives to minimize contaminant release from source areas may prove beneficial for sites that possess insufficient capacity to adequately attenuate the ground-water plume. Ultimately, this points to the critical importance of a detailed characterization of the system hydrology.

Assessment of the stability of an immobilized contaminant can be evaluated through a combination of laboratory testing and chemical reaction modeling within the context of existing and anticipated site conditions. Both analysis approaches can be developed based on the information gathered during Tier II efforts to characterize the specific attenuation process active within the ground-water plume. Through Tier II analysis, a specific attenuation reaction was defined that identified critical reaction parameters such as the identity of dissolved constituents that participated in the process. In addition, mechanistic understanding of the overall reaction provides the context for evaluating site conditions or dissolved constituents that may interfere with or reduce the efficiency of the attenuation reaction. For example, sites where the contaminant plume is reducing (e.g., sulfate-reducing conditions) while ambient ground-water is oxidizing may be susceptible to future influxes of dissolved oxygen. In this situation, the attenuation process may be due to precipitation of sulfides under sulfate-reducing conditions within the plume. Future exposure of these sulfides to oxygen may result in dissolution of the sulfide precipitate along with release of the contaminant back into ground water. Alternatively, sites where attenuation is predominated by contaminant adsorption onto existing aquifer solids may be sensitive to future influx of dissolved constituents due to land use changes that alter either the source or chemical composition of ground-water recharge. The sensitivity to contaminant re-mobilization can be assessed via laboratory tests employing aquifer solids collected from within the plume boundaries that can be exposed to solutions that mimic anticipated ground-water chemistries (e.g., ambient ground-water samples or synthetic solutions in which the concentrations of specific dissolved constituents can be systematically varied). A supplementary avenue to test contaminant stability could include use of chemical reaction models with adequate parameterization to replicate both the attenuation reaction as well as changes in water composition that may interfere with attenuation. The utility of this type of modeling analysis would be the ability to efficiently explore contaminant solubility under a range of hypothetical ground-water conditions in order to identify the ground-water parameters to which the attenuation reaction may be most sensitive.

It is feasible to consider implementation of MNA as a component of the ground-water remedy if the analysis conducted through the previous Tiers indicates that the aquifer within the plume boundaries supports natural attenuation processes with sufficient efficiency, capacity, and stability. The technical knowledge obtained through identification of the specific attenuation mechanism and the sensitivity of the attenuation process to changes in ground-water chemistry can then be employed in designing a monitoring program that tracks continued performance of the MNA remedy.

IC.4   Tier IV

The objective under Tier IV analysis is to develop a monitoring program to assess long-term performance of the MNA remedy and identify alternative remedies that could be implemented for situations where changes in site conditions could lead to remedy failure. Site data collected during characterization of the attenuation process will serve to focus identification of alternative remedies that best match site-specific conditions. The monitoring program will consist of establishing a network of wells: 1) that provide adequate aerial and vertical coverage to verify that the ground-water plume remains static or shrinks, and 2) that provide the ability to monitor ground-water chemistry throughout the zones where contaminant attenuation is occurring. It is recommended that the performance monitoring program include assessment of the consistency in ground-water flow behavior, so that adjustments to the monitoring network could be made to evaluate the influence of potential changes in the patterns of ground-water recharge to or predominant flow direction within the plume. In addition to monitoring ground-water parameters that track the attenuation reaction, periodic monitoring of parameters that track non-beneficial changes in ground-water conditions is also recommended. Monitoring the attenuation reaction will include continued verification of contaminant removal from ground water, but will also include tracking trends in other reactants that participate in the attenuation reaction (possible examples include pH, alkalinity, ferrous iron, and sulfate). For sites in which contaminant immobilization is the primary attenuation process, periodic collection of aquifer solids may be warranted to verify consistency in reaction mechanism. It is recommended that the selection of ground-water parameters to be monitored also include constituents that provide information on continued stability of the solid phase with which an immobilized contaminant is associated. Examples of this type of parameter might include ferrous iron or sulfate to track dissolution of iron oxides or sulfide precipitates, respectively. Non-contaminant performance parameters such as these will likely serve as "triggers" to alert site managers to potential remedy failure or performance losses, since the attenuation reaction will

respond to these changed conditions. Since increases in mobile contaminant concentrations may be delayed relative to changes in site conditions, these monitoring parameters may improve the ability of site managers to evaluate and address the potential for ground-water plume expansion.

In summary, the tiered analysis process provides a means to organize the data collection effort in a cost-effective manner that allows the ability to eliminate sites at intermediate stages of the site characterization effort. A general synopsis of the objectives along with possible analysis approaches and/or data types to be collected under each tier is provided in Table 1.1. The types of data collected early in the site characterization process would typically be required for selection of appropriate engineered remedies, including characterization of the system hydrology, ground-water chemistry, contaminant distribution, and the aqueous

speciation of the contaminant. These system characteristics can have direct influence on the selection of pump-and-treat or in-situ remedies best suited to achieve cleanup objectives for inorganic contaminants. This limits any loss on investment in site characterization for sites where selection of MNA as part of the ground-water remedy is ultimately determined not viable. The primary objective of progressing through the proposed tiered site analysis steps is to reduce uncertainty in the MNA remedy selection.

The remaining discussion in this section of Volume 1 will elaborate on two issues that have been introduced above, specifically the use of models in site characterization and general factors to consider for implementation of a long-term performance monitoring program. These topics are addressed at this juncture to allow greater focus to discussions later in this volume pertaining specifically to

Table 1.1 Synopsis of site characterization objective to be addressed throughout the tiered analysis process and potential supporting data types and/or analysis approaches associated with each tier.

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

attenuation processes (Volume 1, Section II) and the types of site characterization data needed for their identification (Volume 1, Section III). The following discussion provides perspective on the role of model applications in the site characterization process, the types of models that might be employed to help meet the objectives set forth under each tier, and potential limitations in the availability and adequacy of available model codes.

ID. Role of Modeling in the Tiered Analysis Approach

Design of the site characterization effort and analysis of site-specific data in support of assessing the suitability of MNA as a component of the ground-water remedy is dependent on development of a Conceptual Site Model (CSM) that identifies site conditions and processes that influence contaminant transport. The CSM also provides the underpinning for selecting and developing model applications that provide a set of tools for evaluating transport processes, reaction mechanisms, attenuation capacity within the aquifer, and the sensitivity of the attenuation process to changes in site conditions. The types of models that may be employed as part of the site characterization process include simple calculations, speciation models, reaction models, transport models, and reactive transport models. Most modeling undertaken in support of an application will be quantitative, involving computer programs that require special skills to run correctly. The contaminated natural system being modeled is physically-, chemically-, and biologically-complex, and the modeler must have a thorough knowledge of the processes that affect the specific contaminants of concern. Site-specific data collected to define the physical, chemical, and biological characteristics of the aquifer are required to calibrate components of the analytical models and test the validity of model predictions. Deriving meaningful modeling results is likely to require expenditure of significant amounts of time, and entail considerable expense. This planning 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.

To obtain the best results at the least expense, it is important to develop a valid modeling plan before beginning the modeling itself. Developing such a plan will likely require the combined talents of a group of specialists, including those familiar with the site and those with expertise in applying quantitative modeling of physical, chemical, and biological systems to real-world problems. This section is devoted to giving general perspective to the design and implementation of the modeling strategy. In addition to the following discussion, the reader is also referred to the document entitled "Documenting Ground-Water Modeling at Sites Contaminated with Radioactive Substances" (USEPA, 1996).

ID.1 Developing a Conceptual Model

Initially, the CSM is developed based on a general knowledge of ground-water hydrogeology, ground-water geochemistry, and known properties of the specific contaminant. With acquisition of data that maps out the spatial and temporal heterogeneity of the subsurface system, the CSM can be updated. In general, there are more physical, chemical, and biological processes operating in the subsurface of any given site than can reasonably be accounted for in a modeling study. The modeling effort begins with the careful identification of the processes that play significant roles in contaminant migration and attenuation at the site. In this way a conceptual model emerges that will eventually be coded into the input streams of the software packages that will produce the modeling results. If a correct and robust conceptual model is not derived, the modeling results, no matter how detailed or expensive, will contribute little to understanding the site, and will not be supportive of the MNA application.

While it is important to begin modeling with a well-planned conceptual model, the conceptual model may evolve as modeling and collection of site-specific data proceeds. The processes of observation and measurement and of modeling are, in practice, closely interconnected. Initial observation and measurement suggests a conceptual model, which supports development of quantitative models. The results from application of these quantitative models, in turn suggest additional important observations and measurements, which better constrain model design and implementation. In this way, the conceptual model is updated in an iterative fashion, as progressively more is learned about the site. The most significant step in developing a conceptual model of natural attenuation at the site is to identify the transport and reaction mechanisms that significantly affect the mobility of contaminants there. Once these mechanisms have been identified, the logical components that will comprise the conceptual model can be selected.

The evaluation of transport refers to analysis of the flow of ground-water through the aquifer. The rate and direction of ground-water flow will be governed by the physical characteristics of the aquifer solids as well as the factors controlling inputs of water into the aquifer. Spatial and temporal heterogeneity or variability in these factors determines details of the mathematical construction of analytical models used to evaluate fluid and contaminant migration through the aquifer. In characterizing transport, it is important to ask questions such as:

- Does groundwater migrate through the bulk aquifer matrix, through fractures or heterogeneities in the matrix, or both?

- Does solute diffusion from areas of rapid flow to those with stagnant conditions affect contaminant transport on a scale finer than the envisioned numerical gridding, so that a dual porosity model is required?

- Should the medium be considered homogeneous or heterogeneous on the scale envisioned for the nodal blocks in the numerical gridding?

- Are medium properties best assigned deterministically, or according to a stochastic algorithm?

- Is hydrodynamic dispersion described well in a Fickian sense (i.e., in terms of dispersivity, according to Fick's law), by differential advection through a numerical gridding, or in both ways?

- How can the model be calibrated to reflect as accurately as possible transport rates through the subsurface?

- What additional data need to be collected to characterize flow and calibrate the transport model? Such data might include the distribution of hydraulic head, the evolution of the contaminant plume through time, and the results of tracer tests.

Evaluation of contaminant migration in ground water relies on determination of the types of chemical reactions that control contaminant degradation or immobilization. Thus, determination of specific reaction mechanisms that may be active within a ground-water plume provides the basis for constructing analytical models employed to evaluate performance of the attenuation process and project contaminant transport into the future. To characterize the reaction mechanisms driving attenuation, it is necessary to ask questions such as:

- Does the contaminant adsorb to solid surfaces? If so, onto what surfaces, and as what type of surface complex? Does it desorb readily?

- Is the contaminant chemically oxidized or reduced? Is the reaction catalyzed by mineral surfaces, or promoted by microbial activity? If so, what is the catalyst or microbial species?

- Does the contaminant precipitate as a solid phase? If it does, what is the phase, and what is its solubility?

- Might complexation of the contaminant with chemical constituents in solution affect its mobility?

A conceptual model can be thought of as a combination of the logical components describing the various aspects of transport and reaction at a site. For example, choice of how to represent hydrodynamic dispersion, the equations to account for sorption of contaminant species onto solid surfaces, rate laws describing the kinetics of redox reactions, and equations defining rates of microbial metabolism all contribute to the conceptual model. Since a conceptual model is no more than the sum of its components, and an analytical model is simply the realization of a conceptual model, the final modeling results are no better than the components selected.

ID.2 Types of Models

There are several types of models that may prove useful for characterizing attenuation processes at a site. In general, in approaching a specific question, it is most expedient to begin working with the simplest applicable model, adding complexity to the study as necessary. It is wise to avoid the temptation to begin by constructing the "ultimate" model, one that accounts for all aspects of transport and reaction at a site. Highly complex models are difficult to work with, expensive to produce, and difficult to interpret. A more efficient strategy is to begin with simple models of various aspects of the system, combining these as necessary into progressively more complex models, until reaching a satisfactory final result, one that reproduces the salient aspects of the system's behavior without introducing unnecessary complexity.

ID.2.1 Simple Calculations

Simple calculations performed by hand or via computer applications may provide an important component to the overall modeling strategy. For purposes of this document, two modeling approaches that fall under this category include simplified calculation approaches to evaluate a range of process outcomes and specific mathematical formulas used to calculate input parameters needed for implementation of more complex transport or reaction models. An example of a simplified calculation approach would be the calculation of the mass of contaminant and the mass of reactant within a predefined volume of the aquifer for the purpose of assessing if sufficient reactant mass is available for an identified attenuation process. This type of calculation is simplified in the sense that one may assume that the rate of the reaction is unimportant. Thus, while this type of calculation provides a general sense of the relative degree to which the aquifer could support attenuation, it does not likely provide a sufficiently accurate representation of the actual efficiency of the attenuation process. However, the utility of this calculation approach is to provide some perspective as to the relative importance of investing resources to fully characterize reactant mass or flux. Several examples of the second category of this model type, specific mathematical formulas, are provided at the following USEPA website - http://www.epa.gov/athens/learn2model/part-two/onsite/index.html. This website provides on-line access to a suite of prepackaged tools (or "calculators") for performing site assessment calculations. Several examples relevant to site characterization advocated within this document include:

- "Hydraulic Gradient Calculation" for assessing the direction(s) of ground-water flow employing head measurements in wells spaced horizontally across the site;

- "Vertical Gradients" for assessing the potential for vertical water transport within the aquifer based on head measurements in closely-spaced, vertically nested wells with identical screen lengths;

- "Vertical Gradients with Well Screen Effects" for assessing the influence of variable screen lengths in vertically nested wells on the calculated vertical gradient; and

- "Average Borehole Concentrations" to illustrate the potential impact on contaminant concentrations measured for samples collected from a single long-screened well in an aquifer with a depth-varying concentration and a depth-varying hydraulic conductivity field.

These simplified models support analysis of the adequacy of the location and construction of ground-water wells, which underpins the adequacy of the monitoring design to provide samples and data reflective of the site-specific conditions. They may also be used to provide reasonable estimates for parameters needed as input to more complex mass transport or reactive transport models. Since both modeling approaches provide a means for preliminary assessment of site data and potentially improving design of the monitoring network, they play an important role in the site characterization effort.

ID.2.2 Mass Transport Models

Mass transport models seek to describe the flow of ground water at a site, and the transport of chemical species within the flow. Mass transport models are generally implemented as transient simulations in one, two, or three dimensions. Strictly speaking, a mass transport model considers the migration of non-reacting species. In reality, many mass transport codes can consider simple reaction scenarios, such as partitioning of a species onto the solid surface according to a constant partitioning factor. Mass transport models can seldom be relied upon for describing natural attenuation, because they lack sophisticated knowledge of chemical and biological processes, but are nonetheless valuable in evaluating a site's potential for MNA. The models are well developed and straightforward to run; they are useful tools for simulating the rate and pattern of groundwater flow at a site.

Mass transport modeling might be applied to figure the transit time of contaminants within the site, absent attenuating processes. The models find use in applying the results of tracer tests to calibrate the flow field. Some reactive transport models (described below) accept externally determined flow fields as input, so running a mass transport model may be a required preliminary to a full reactive transport model.

ID.2.3 Speciation 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 under which contaminants might be attenuated by sequestration, and those in which they are likely to be mobile in the ground-water 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. Or, 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 are implemented via the assumption that the modeled system is in chemical equilibrium or, more commonly, partial chemical equilibrium. A model can be configured to account for:

- Reactions among species in solution, including protonation-deprotonation, redox, and complexation reactions.

- Adsorption reactions onto solid surfaces, possibly including minerals and organic matter.

- Precipitation and dissolution reactions, to predict whether a mineral is saturated in solution, or undersaturated or supersaturated.

- Gas solubility reactions, to account for the dissolution of coexisting gases into solution, or the loss of gas species from solution.

Where redox reactions play a critical role in the attenuation reaction, it may be important to use a speciation model that can account for redox disequilibrium. Microbial respiration, for example, is driven by the transfer of electrons from donating to accepting chemical constituents, including the inorganic contaminant. It may be critical, therefore, to characterize the redox state of ground water at a site in an accurate and meaningful manner to fully evaluate redox-driven reactions that influence contaminant attenuation. Redox reactions in shallow ground water rarely attain a state of equilibrium (e.g., Lindberg and Runnells, 1984), which limits the utility of analytical models that describe the distribution of chemical species in ground water based on a single parameter such as dissolved oxygen (DO) concentration or Eh (e.g., as measured using a DO or platinum electrode, respectively). Geochemical models that describe redox in terms of a single parameter may be limited in their accuracy and/or flexibility in describing the redox characteristics of the ground-water system. An alternative approach to the model design would be to employ a flexible description of redox in a state of chemical disequilibrium (e.g., as discussed in Bethke, 1996, Chapter 6.). This type of modeling approach allows the user to specify for each element the mass found in the various possible redox states and reports the energy (i.e., the Nernst Eh) associated with the half reaction for each pairing of the element's oxidized and reduced states.

ID.2.4 Reaction Models

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. Like speciation models, it is commonly necessary to use a reaction model with a flexible description of redox disequilibrium, as well as suitable models to describe adsorption and precipitation reactions. Where appropriate, the model should be able to account for the kinetics of species sorption, redox reactions, mineral precipitation and dissolution, or microbial metabolism. Examples of the application of reaction models in an MNA application include:

- Sequestration of contaminants onto a mineral surface as the mineral forms, such as the complexation of heavy metals in mine drainage onto ferrihydrite.

- Precipitation of contaminant-bearing minerals, according to a kinetic rate law appropriate for the chemical conditions at the site.

- Immobilization of a contaminant by oxidation or reduction, according to a kinetic rate law.

- Biotransformation of a contaminant by microbial life, using a rate equation for fermentation or cellular respiration appropriate for conditions at the site.

ID.2.5 Reactive Transport Models

Reactive transport models, as the name suggests, are the coupling of reaction models to transport models. Unlike a reaction model, a reactive transport model predicts not only the reactions that occur in the ground-water flow, but the distribution of those reactions across the site through time. A reactive transport model of a site 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, variation in

pH conditions, or the differential development of microbial populations.

- The ability to describe evolution of a contaminant plume through space and time.

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, and because the calculation procedure may require a significant amount of computing time. 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. Such 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 model.

ID.3 Modeling and the Tiered Analysis Approach

As described in Section IC of this document, a tiered analysis approach is recommended for organizing the collection of site-specific data and providing a means for screening out sites inappropriate for selection of MNA as part of the ground-water remedy. Previously, possible applications of models of varying complexity throughout the tiered analysis process were provided in Table 1.1. The following discussion provides additional context for evaluating the potential role of model applications during the site characterization process.

ID.3.1 Tier I – Demonstration of Contaminant Removal from Ground Water

The application of models under Tier I pertains primarily to initial characterization of hydrology and evaluating whether measured ground-water characteristics may support immobilization processes. Assessment of hydrology may include calculation of horizontal or vertical gradients to assess the predominant direction(s) of ground-water flow. This information could be used to guide installation of monitoring points within the aquifer for collection of ground-water and aquifer solids samples. Evaluation of contaminant immobilization potential may involve use of chemical data collected from ground-water and/or aquifer solids samples as input into a speciation model to assess the potential for contaminant precipitation or adsorption onto aquifer solids. For example, speciation calculations based on measurements of alkalinity and dissolved lead within the ground-water plume may indicate saturation or oversaturation with respect to precipitation of lead carbonate. Conversely, measurements of ground-water chemistry and extractable iron concentrations in aquifer solids could serve as parameter inputs into a speciation model with the capability of describing contaminant adsorption onto iron oxides. It is recommended that these latter calculations be used as secondary lines of evidence in support of site-specific measurements that demonstrate active sorption of the contaminant onto aquifer solids within the plume.

ID.3.2 Tier II – Determine Mechanism and Rate of Attenuation

Modeling at this stage in the evaluation process should be closely integrated with observational study. In studying the mechanism of contaminant removal from ground water, careful attention should be paid to assuring collection of sufficient data to fully define the components of the conceptual model. For example:

- If a precipitating phase is identified by x-ray diffraction, spectroscopy, or electron microscopy, it will be necessary to characterize the phase's solubility.

- If reaction with solid surfaces is identified as an important attenuation process, it will be necessary to collect sufficient data to properly parameterize an adsorption model that describes the specific mechanism of adsorption, as described in Section IIIB.

- It may be necessary to establish a kinetic rate law describing precipitation of the contaminant into solid phases, or its adsorption onto solid surfaces, where these reactions may occur at different rates throughout the plume due to the concentrations of aqueous or solid reactants.

In determining the rate of the attenuation process, modeling may be used to describe chemical fluxes in the system and rate of species uptake or production during chemical reaction. Modeling might be specifically employed to estimate the time frame required to sequester the contamination sufficiently to meet cleanup objectives, where the attenuation reactions are kinetically controlled.

ID.3.3 Tier III – Demonstrate Capacity and Stability of Removal Mechanism

Model applications under Tier III would be directed toward assessment of the capacity of the aquifer to attenuate the mass of contaminant within the ground-water plume and the long-term stability of an immobilized contaminant. Reaction models and/or reactive transport models might be employed to evaluate the extent of contaminant removal throughout the plume. Use of these model types allows assessment of rate-dependent reactions and/or the influence of decreases in the flux of reactants due to changes in concentration or ground-water flow that might occur over time. These same models may be employed to evaluate ground-water conditions that may remobilize contaminants sorbed to aquifer solids. These evaluations may prove most useful for situations in which laboratory testing may be less practical. For example, model simulations may be employed to examine the stability of the attenuated contaminant for hypothetical situations not reflected in existing ambient ground water. For example, modeling might be applied for a number of specific purposes:

- To test the chemical feasibility of specific remobilization scenarios, such as infiltration of pristine groundwater, a shift in oxidation state (perhaps due to waterlogging), or a change in pH (due to soil acidification, for example).

- To figure reactant fluxes required to remobilize the contaminant.

- To evaluate the possible effects of chelating agents, such as organic acids, in the groundwater.

These model applications provide a means to project system behavior under conditions that do not currently exist, but could feasibly develop. They provide a source of information that further reduces the uncertainty of reliance on MNA as a permanent remedy.

ID.3.4 Tier IV – Long-Term Performance Monitoring

Under Tier IV of the analysis process, modeling provides a tool for designing a long-term monitoring plan, as well as a contingency remedy for cases where unanticipated changes in site conditions leads to failure of the MNA remedy. Modeling tasks that might be performed at this stage include:

- Optimizing the location of monitoring wells for long-term observation.

- Optimizing the frequency of sample collection events based on knowledge of ground-water flow dynamics at the site.

- Identifying critical chemical parameters to monitor based on model simulations to examine the sensitivity of attenuation process rate or capacity to changes in ground-water composition.

- Identifying critical parameters to monitor based on model simulations to evaluate conditions leading to contaminant re-mobilization.

These model applications provide a means for designing the monitoring program to best evaluate remedy performance and provide site managers with a context for evaluating possible decreases in the efficiency of the attenuation process.

ID.4 Choosing Modeling Software

Once a modeling strategy has been developed and a conceptual model defined, a computer software package (or packages) will be needed to compute the modeling results. A number of software packages exist for modeling physical, chemical, and biological processes in natural systems. No single package is best for all problems; one seeks the package or packages that best satisfies the objectives of the site characterization process. Significantly, software packages designed for analyzing problems of the MNA of organic contaminants (e.g., Bioplume III; USEPA, 1997) are generally not suitable for studying the fate of inorganic contaminants. The first step in selecting software involves identification of packages incorporating features needed to evaluate the conceptual model. The selection process should amount to more than compiling a checklist of features. It is important to determine if the features work well for the situation in question.

It is critical to consider the efficiency of the software, not only in computing time, but the time required to configure each run and render the modeling results in a suitable graphical form. One should, therefore, inspect carefully the documentation from potentially suitable packages, and run test cases. In evaluating a commercial package, insist on inspecting the documentation before buying. Avoid licensing software without being allowed a trial period, or a period during which the software may be returned for a full refund.

ID.4.1 Public Domain vs. Commercial Software

Modeling software falls into two categories, public domain and commercial. Public domain codes can generally be downloaded over the internet or purchased for a minimal charge; some codes are obtained by personal request addressed to the developer. A public domain code has a number of potential advantages: there is little or no up-front cost; the source code is in many cases available, allowing the modeler to correct bugs and add features; and there may be a body of experienced users available for consultation or troubleshooting at minimal or no charge. A commercial code also has potential advantages: it may be written by a group of professional programmers; there may be people assigned to support users, offer training, and fix bugs; documentation may be superior; there is more likely to be an intuitive user interface; the code may be easier to use than public domain alternatives; and it may offer superior graphics for rendering results. In general, distributors of commercial codes hope they can convince customers that the up-front costs of their product will be offset in the long run by quality and savings, principally by improving the productivity of the people involved in the modeling process, and by speeding project completion.

ID.4.2 Sources of Software

A considerable number of software packages that can be applied to the analysis of inorganic contaminant attenuation in ground water are available in the public domain and from commercial sources. Tables 1.2–1.4 list examples of various types of commonly applied packages and their sources. Additional packages may be found by searching the internet, and from software retailers such as Rockware, Inc. (www.rockware.com) and Scientific Software Group (www.scisoftware.com). New software packages appear frequently, others fall into disuse or are no longer supported and updated, and new releases of the various packages add features and fix bugs. As such, no attempt is made in this document to provide exhaustive listings of software packages applicable to MNA assessments, nor to judge the suitability or compile the features of various packages. In evaluating software, the reader will be well served by considering in light of his or her own needs only the most recent available information. The following discussion provides some issues to consider during selection of a software package.

Issues to consider during selection of a mass transport model and a representative list of commonly applied models (Table 1.2):

- Whether the model operates in two or three dimensions, or both.

- Whether the model can account for dispersion in the manner chosen.

- If the model accounts for saturated flow (flow below the water table), unsaturated flow (above the water table), or both.

- The deterministic or stochastic method or methods the model can use to represent heterogeneity in the properties of the medium (hydraulic conductivity, dispersivity, and so on) across the modeling domain.

Issues to consider during selection of a geochemical speciation model and a representative list of commonly applied models (Table 1.3):

- A flexible description of redox state. A disequilibrium scheme in which each redox couple can be set to its own redox potential is commonly required.

- The ability to account for sorption or surface complexation in a manner appropriate for the site.

Issues to consider during selection of a reaction model, in addition to those relevant for a speciation model, and a representative list of commonly applied models (Table 1.3):

- An accounting for the kinetics of redox reactions, whether occurring in the fluid phase, catalytically on mineral surfaces, or promoted by enzymes.

- The ability to account for the kinetics of mineral precipitation and dissolution reactions invoked as an attenuation mechanism, using appropriate rate laws.

- A model of microbial metabolism based on valid chemical principles. The metabolic model should treat the

Table 1.2 Example software packages for modeling groundwater flow and mass transport.

Software	Source
FEFLOW	Groundwater Modeling, Inc. www.ssg-int.com/
GMS	Environmental Modeling Systems, Inc. www.ems-i.com/GMS/gms.html
Modflow-2000	U. S. Geological Survey water.usgs.gov/nrp/gwsoftware/modflow.html
Visual Modflow	Waterloo Hydrogeology www.visual-modflow.com
GroundWater Vistas	www.groundwater-vistas.com

Table 1.3 Example software packages for speciation in inorganic geochemical systems. Each of these packages except Wateq4F also has at least some capability for modeling reaction processes.

Software	Source
Chess	Ecole des Mines de Paris chess.ensmp.fr/
Eq3/6	Lawrence Livermore National Laboratory www.llnl.gov/IPandC/technology/software/softwaretitles/eq36.php
Mineql+	Environmental Research Software http://www.mineql.com/
MinteqA2	U.S. EPA http://www.epa.gov/ceampubl/mmedia/minteq/
Phreeq-C	U.S. Geological Survey wwwbrr.cr.usgs.gov/projects/GWC coupled/phreeqc/index.html
The Geochemist's Workbench®	University of Illinois www.geology.uiuc.edu/Hydrogeology
Visual Minteq	KTH (Sweden) www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm
Wateq4F	U.S. Geological Survey water.usgs.gov/software/wateq4f.html

metabolism as a balanced chemical reaction, accounting for not only consumption of substrate species, but generation of product species. The software should also account for how the amount of energy available in the environment affects metabolic rate, and for the growth and decay of biomass.

Issues to consider during selection of a reactive transport model, in addition to the points raised above about mass transport, speciation, and reaction models, and a representative list of commonly applied models (Table 1.4):

- Whether the model can work in one, two, or three dimensions.

- Compatibility of the model with the mass transport and reaction models chosen. For example, can the reactive transport model import a flow field predicted by the mass transport model?

- Time to solution, since reactive transport modeling can require considerable amounts of computing time.

ID.4.3 Thermodynamic Data

Most software packages are configured to accept any external database, provided that it is presented in the proper format. A number of databases have been compiled for various purposes, and many of these are available already formatted to be read directly into one or more of the widely distributed geochemical models. A list of various internet sites from which thermodynamic data can be downloaded in various formats is provided in Table 1.5. Additional databases might be located by consulting web pages and the latest documentation for the various geochemical modeling packages, and by searching the internet. Since updates to posted databases may be conducted infrequently, it may be worthwhile to verify the database incorporates currently accepted thermodynamic data based on a review of the technical literature.

Table 1.4 Example software packages for modeling reactive transport in inorganic geochemical systems.

Software	Source
Crunch	Lawrence Livermore Laboratory www.csteefel.com/
HYTEC	Ecole des Mines de Paris www.cig.ensmp.fr/~vanderlee/hytec/index.html
PHAST	U. S. Geological Survey wwwbrr.cr.usgs.gov/projects/GWC coupled/phast/index.html
Phreeq-C	U.S. Geological Survey wwwbrr.cr.usgs.gov/projects/GWC coupled/phreeqc/index.html
The Geochemist's Workbench® Professional[1]	University of Illinois www.geology.uiuc.edu/Hydrogeology

[1] The "Xt" package in previous releases.

Table 1.5 Example internet sources of thermodynamic data useful in constructing geochemical models.

Source	URL
Ecole des Mines de Paris	ctdp.ensmp.fr/
Japan Nuclear Cycle Development Institute	migrationdb.inc.go.ip/
Murdoch University (Australia)	Íess.murdoch.edu.au/iess/iess_home.htm
National Institute of Standards and Technology	webbook.nist.gov/
Nuclear Energy Agency (France)	www.nea.fr/html/dbtdb/
University of Illinois	www.geology.uiuc.edu/Hydrogeology/hydro thermo.htm
University of Illinois at Chicago	tigger.uic.edu/~mansoori/TRL html

ID.5 Accounting for Uncertainty

For a model constructed in support of an MNA application, there are a number of sources of uncertainty, including:

- Error in chemical analyses. The accuracy and completeness of chemical analyses vary widely. Routine chemical analyses performed by commercial laboratories are in many cases of insufficient quality to support geochemical and reactive transport modeling. Several useful checks for internal consistency are available in the American Water Works Association "Standard Methods" volume (Clesceri et al., 1998), and computer programs (e.g., Aq•QA, www.aqqa.com) are available for performing these tests automatically. Geochemical modeling applications 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.

- Error in determining hydrologic parameters. Measuring representative values of hydrologic parameters such as hydraulic conductivity and dispersivity can be difficult, because these values may change with the scale on which they are observed. Laboratory measurements, therefore, may give different results than well tests (e.g., slug and bail tests, pumping tests), which may in turn differ from values representative of the site as a whole. Measured hydrologic parameters are important, but may need to be calibrated to observations from the site, including perhaps the rate of plume advance or the migration of a tracer injected into the subsurface.

- Sample choice and dataset size. Significant error can be introduced by sampling bias, although this bias is not always obvious or even avoidable. Laboratory measurements of hydrologic properties, for example, are commonly made on samples that can be recovered intact, even though the fractured or poorly consolidated portions of the medium, left unsampled, control flow. Fluid samples may be taken 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. Finally, the number of samples available or monitoring wells constructed is in some cases too small to comprise a statistically significant dataset.

- Incompleteness and inaccuracy of the thermodynamic database. To provide meaningful results, a geochemical or reactive transport model has to include each of the aqueous species, minerals, gases, and adsorbed species important at the site, and the data for these species need to be accurate. The thermodynamic databases available for geochemical study vary widely in breadth and accuracy.

- Error in model components. Each of the components of which the model is constructed is a potential source of error. Components likely to contribute to error include kinetic rate laws, surface complexation (sorption) models, and descriptions of the effects of microbial metabolism.

- Conceptual errors. Perhaps most significantly, model results can be affected by failure to conceptualize the problem completely and accurately. If an important process is not accounted for, or accounted for in an inaccurate fashion, the modeling results will likely be rendered useless.

The modeler accounts for uncertainty by experimenting with the model to discover which sources of uncertainty affect the results significantly. This uncertainty can subsequently be reduced, for example, by making new measurements or refining critical observations. Another source of uncertainty is the limited possibility to obtain measured site-specific values for some of the model parameters due to the complexity of the geochemical model. It is recommended that the results of uncertainty analysis be provided for the purpose of site decisions. This information would include the sources and potential ranges of all input data along with the origin of input data (i.e., review of technical literature, model calibration, field testing, or estimation).

ID.6 Model Calibration and Verification

Developing a quantitative model of contaminant attenuation in the subsurface may entail considerable uncertainty. Parameters needed to constrain the model are seldom known precisely, parameter inputs may not be available and require estimation, and the conceptual model itself may need refinement. Due to these uncertainties, it is necessary to calibrate the model to observations, and to verify that the model behaves in a manner that adequately describes the natural system. The processes of calibration and verification are closely related, since calibration brings the model into alignment with observed data. A model that (1) utilizes to the greatest extent possible parameter values specific to the site, and (2) is calibrated to the observed evolution and distribution of the contaminant plume, therefore, is most likely to be readily verified. It is recommended that steps taken to calibrate the model application be documented and provided for review in order to build confidence in the use of this assessment tool.

Model verification requires that the model predict an independent set of observations, i.e., a set separate from those used for calibration. For example, a model that predicts the attenuation of chromate by chemical reduction might be "fit" on the basis of a plume or section thereof, and subsequently used to predict the behavior of another plume at the same site. The initial fitting would presumably involve arriving at reasonably precise estimates of the most uncertain inputs – in this case reduction rates, electron donor loads, and so on. If the subsequent independent prediction accurately reflects field observations, this result would lend credence to the model. Here, "accurate reflection" of field predictions probably means predicting correctly the speed at which the plume is retreating and estimating the rate of overall contaminant mass reduction to within a factor no greater than five. Predictions that do not achieve this level of accuracy should prompt further refinement of the model.

This discussion has been intended to point out that models may serve as a useful tool that can be employed as part of the evaluation process for selection of MNA as a remedy.

However, the complexity of the modeling effort and the potential level of uncertainty associated with model predictions indicate that pursuit of more direct lines of evidence is critical to the tiered analysis process. The acquisition of these data will depend on establishing a network of monitoring locations throughout the aquifer. The site-specific data collected from these monitoring locations provide the means to identify the attenuation process and assess the performance characteristics of the MNA remedy. As with any technology used as part of a cleanup remedy, continued assessment of remedy performance is critical for ensuring attainment of cleanup goals. The following discussion provides context for the eventual design of the performance monitoring program leading to site closure for situations in which MNA provides a viable component to the ground-water remedy.

IE. Long-Term Performance Monitoring and Site Closure

The performance of the MNA remedy must be monitored to determine compliance with site-specific remedial objectives identified in remedy decisions. This long-term monitoring is often the largest expenditure incurred in the course of cleanup and, for this reason alone, should be considered at the earliest stages of remedial investigation. Because the time horizons for successful implementation of an MNA remedy are often expected to be long, it is critical that particular attention is paid to long-term monitoring plans. Detailed discussions of the performance monitoring framework and monitoring plan development have recently been published (USEPA, 2003). Although that discussion focuses on attenuation of common organic contaminants, the framework and many of the principles governing plan development are also applicable to inorganic constituents. However, there are conceptual differences with respect to the outcome of the MNA remedy for inorganic contaminants. With the exception of situations where degradation reactions transform harmful contaminants (e.g., nitrate or perchlorate) into innocuous constituents, contaminant mass is not reduced during MNA for inorganic contaminants. The MNA process results in relocation, dispersion, and ultimately chemical conversion of the original source zone. Therefore, the purposes of performance monitoring are to demonstrate degradation to innocuous materials and immobilization of contaminants. It is recommended that site closure be considered only after degradation and immobilization within the risk level specified in the remedy decision are demonstrated and shown to have long term stability.

Development of a performance monitoring plan is site specific in nature. Monitoring objectives and quantifiable performance criteria are developed to evaluate temporal and spatial remedy performance with respect to the site-specific remedial action objectives. Much of the monitoring to demonstrate performance of the MNA remedy will fall into three basic categories: 1) ambient monitoring to assess background contaminant levels and the status of relevant ambient geochemical indicators (e.g., E_H, pH); 2) process monitoring to assure the progress of chemical attenuation; and 3) monitoring to detect plume expansion.

Within this framework, the OSWER Directive 9200.4-17P (USEPA, 1999c) provides eight specific objectives to be met by the performance monitoring program of an MNA remedy (Table 1.6). The objectives usually will be met by implementing a performance monitoring program that measures contaminant concentrations, geochemical parameters, and hydrologic parameters (e.g., hydraulic gradients). Much of the monitoring will be focussed on ground water. However, periodic monitoring of aquifer solids, through soil coring, will be warranted in most situations. These data will be used to evaluate the chemical behaviour of the contaminant in the subsurface over time, including:

- Changes in three-dimensional plume boundaries,

- Changes in the redox state that may indicate changes in the rate and extent of natural attenuation,

- Reduction in the capacity of aquifer materials for contaminant immobilization, and

- Mobile contaminant mass and concentration reductions indicative of progress toward contaminant removal objectives.

Contaminant behavior can then be evaluated to judge the effectiveness of the MNA remedy and the adequacy of the monitoring program.

Table 1.6 Objectives for performance monitoring of MNA (USEPA, 1999c).

1)	Demonstrate that natural attenuation is occurring according to expectations,
2)	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,
3)	Identify any potentially toxic and/or mobile transformation products,
4)	Verify that the plume(s) is not expanding down gradient, laterally or vertically,
5)	Verify no unacceptable impact to down gradient receptors,
6)	Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy,
7)	Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors, and
8)	Verify attainment of remediation objectives.

IE.1 Duration and Monitoring Frequency

As stated in the OSWER Directive (USEPA, 1999c), 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. Typically, monitoring is continued for a specified period after remediation objectives have been achieved to ensure that concentration levels are stable and remain below target levels. In order to demonstrate stability, verification of the achievement of target levels under conditions where the aquifer geochemistry has reestablished a chemical steady state with respect to ambient ground-water geochemistry will be needed. The magnitude of the chemical gradient between the impacted and non-impacted portions of the aquifer provides a reference point for evaluating establishment of steady-state conditions. A monitoring strategy to verify the attainment of remedial objectives and provide for termination of monitoring and site closure generally should be formulated during the development of the performance monitoring plan and updated, as necessary, prior to implementation.

Monitoring frequency should be specified in the performance monitoring plan. In addition, the plan may specify an approach and technical criteria that could be used to increase or reduce the frequency as conditions change. Such criteria would scale monitoring frequency to match MNA performance and the level of understanding and confidence in the conditions that control attenuation at a given site. The most appropriate frequency for ground-water sampling is site specific and depends on several factors including:

- The rate at which contaminant concentrations may change due to ground-water flow and natural attenuation processes,

- The degree to which the causes of this variability are known,

- The types of evaluations to be performed and the importance of the type of data in question, and

- The location(s) of possible receptors relative to the plume.

In addition, the most appropriate frequency may vary in different areas of the site based on site-specific conditions and the intended use of the data. Similar principles are applied in determining the most appropriate frequency for sampling of aquifer solids.

With respect to the initial frequency of ground-water sampling under the performance monitoring program, quarterly monitoring may often be an appropriate frequency to establish baseline conditions over a period of time sufficient to observe seasonal trends, responses to recharge, and to confirm attenuation rates for key contaminants. Quarterly monitoring for several years provides baseline data to determine trends at new monitoring points and test key hypotheses of the conceptual site model.

More frequent monitoring of ground-water elevations may be warranted, particularly during the establishment of baseline conditions, to improve the characterization of ground-water flow patterns. In addition, more frequent monitoring may be needed to observe changes in ground-water flow patterns in response to other site activities, such as the start or cessation of ground-water extraction in off-site water supply wells, source control activities, and other significant changes in the hydrologic system.

IE.2 Monitoring of Aquifer Solids

The aquifer material may serve as the reactive media to which many inorganic contaminants become partitioned and immobilized. Therefore, periodic re-assessment of the capacity of aquifer materials for contaminant immobilization, including immobilization of radioactive contaminants and any harmful products of radioactive decay, often is a critical step in performance monitoring. There are three aspects to this solid-phase characterization to be addressed through collection of field data and laboratory testing:

- Determination of the chemical process(es) resulting in contaminant immobilization,

- Determination of the capacity of the un-reacted aquifer material for contaminant immobilization, and

- Determination of the stability of the reacted aquifer material with respect to contaminant release.

Characterization of aquifer material requires collection of core material within the existing contaminant plume and down gradient and side gradient to the plume. Characterization within the existing plume is used to identify the immobilization process(es) and capacity, while down gradient and side gradient characterization is used to re-assess the potential and capacity for immobilization in the event of plume expansion. In general, this characterization involves identification of the aquifer mineralogy to determine the abundance and spatial distribution of reactive solid component(s) and the distribution of the contaminant among the identified components.

The spatial extent and density of sampling points will be dictated by the degree of heterogeneity of the aquifer material both within and outside of the existing plume boundary. The frequency of sampling will be dictated by the rate of the immobilization process with respect to fluid transport and the dynamics of fluid flow and chemistry. In general, sampling frequency will be greater within the plume boundary where immobilization is active. The frequency of sampling outside of the plume boundary will be dictated by the proximity of receptors and the time frame for reaching remedial objectives relative to the rate of weathering processes that may change the composition or mineralogy of the aquifer material.

IE.3 Monitoring Types

The majority of the monitoring performed to determine the effectiveness of the MNA remedy may be classified under three general headings:

- Monitoring of conditions outside of the plume boundaries (ambient monitoring),

- Monitoring of natural attenuation processes (process monitoring), and

- Monitoring to detect plume expansion and verify the lack of impact to receptors (migration monitoring).

Other types of monitoring include periodic evaluations of the effectiveness of any institutional controls specified in the remedy decision documents and, ultimately, verification of the attainment of all remedial objectives.

Ambient monitoring should be performed outside of the boundaries (e.g., hydraulically up gradient, side gradient, and down gradient) of the contaminant plume. The purpose of this monitoring is to establish background conditions and to provide an indication of the potential for additional plume migration in situations where redox state and the capacity of aquifer materials for contaminant immobilization are dominant controls on migration. The extent and duration of ambient monitoring will be influenced by the sensitivity of aquifer chemistry to changes in recharge water quality and processes that may change its composition.

Process monitoring is used to verify that attenuation is occurring according to prediction. If process monitoring indicates that attenuation is not occurring as expected, a change in cleanup approach may be warranted. Process monitoring is contaminant-specific and might include, for example, measurement of ground-water redox state or pH to assure the existence of conditions favorable for natural attenuation via reduction-oxidation processes or pH-dependent sorption as well as the monitoring of contaminants. Process monitoring parameters are discussed in the contaminant-specific sections in Volumes 2 and 3 of this document. Process monitoring should also take into account any impacts of ongoing or prior active treatment on subsequent ambient attenuation processes. For example, such impacts may include gradual shifts in system redox as water levels and/or electron donor/acceptor levels change after, respectively, pump and treat or in situ bioremediation have been halted.

Monitoring to detect plume expansion (migration monitoring) and any impacts to receptors is another important aspect of the performance monitoring program. This monitoring objective may be met through multi-level monitoring performed at or near the side gradient and down gradient plume boundaries, beneath the plume, and near any other compliance boundaries specified in remedy decision documents in conjunction with monitoring of possible receptor locations (e.g., potable water wells or locations of ecological receptors) to directly verify the lack of impacts. Monitoring locations between the plume and compliance boundaries or possible receptors should be close enough to the plume that a contingency plan can be implemented before the contaminant can move past the point of compliance or impact receptors. Identifying locations for monitoring wells designed to detect migration ultimately relies on a site-specific assessment of contaminant migration and fate. Additional insight may be obtained from site-specific transport model predictions, where model use is conducted iteratively with the site characterization process so that model predictions are both tested and influence future data collection.

IE.4   Monitoring Locations

At many sites, the performance monitoring program will be three-dimensional in nature due in large measure to the effects of site-specific hydrogeology on contaminant migration. Typical target zones for monitoring a contaminant plume (Figure 1.3) include:

- Original source areas - within and immediately down gradient of source areas (Process Monitoring)

The monitoring objectives include the detection of any further contaminant releases to ground water that may occur and demonstration of reductions in contaminant concentrations in ground water over time. In situations where the original source is contained, increased contamination or new contaminants could be indicative of containment system failure.

- Transmissive zones with highest contaminant concentrations or hydraulic conductivity (Process Monitoring)

A change in conditions in these zones, such as an increase in contaminant mass, change in redox state, increased ground-water velocity, or exceedance of the aquifer capacity for immobilization, may lead to relatively rapid plume expansion.

- Distal or fringe portions within the plume (Process and Migration Monitoring)

These are areas where reduction of contaminant concentrations in ground water to levels required by remedial action objectives may be attained most rapidly or where plume expansion may be observed most readily.

- Outside the plume, including areas near plume boundaries and other compliance boundaries (Migration Monitoring)

Multi-level monitoring points, reflecting vertical differences in subsurface conditions, generally will be warranted at the side gradient, down gradient, and vertical plume boundaries; between these boundaries and possible receptors; and at any other compliance boundaries specified in remedy decision documents. Monitoring of receptor locations should also be included to directly verify that no impacts occur.

- Zones in which contaminant reductions in ground water appear to be less than predicted (Process Monitoring)

These are the areas where attaining cleanup standards within time frames specified in the remedy decision documents may be impeded due to site conditions (*e.g.,* higher than anticipated concentrations of residual source materials, redox conditions, or exceedance of the capacity for immobilization). Such areas, if present, will be delineated through evaluation of data obtained throughout the performance

Site (Map View)
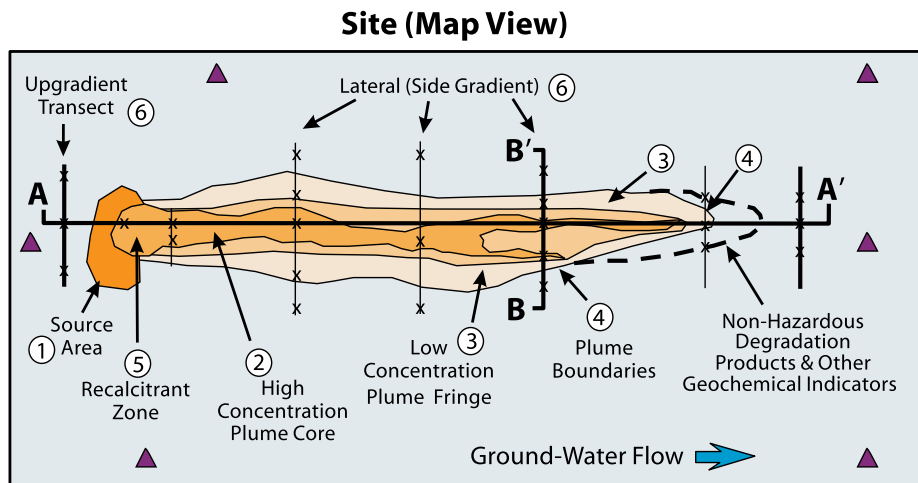
Target Monitoring Zones

1. Source area
2. Contaminated zones of highest concentrations and mobility
3. Plume fringes
4. Plume boundaries
5. Recalcitrant zone determined from historical trends
6. Upgradient and sidegradient locations

x   Monitoring well cluster

▲   Piezometer

×–×–×   Transect of well clusters
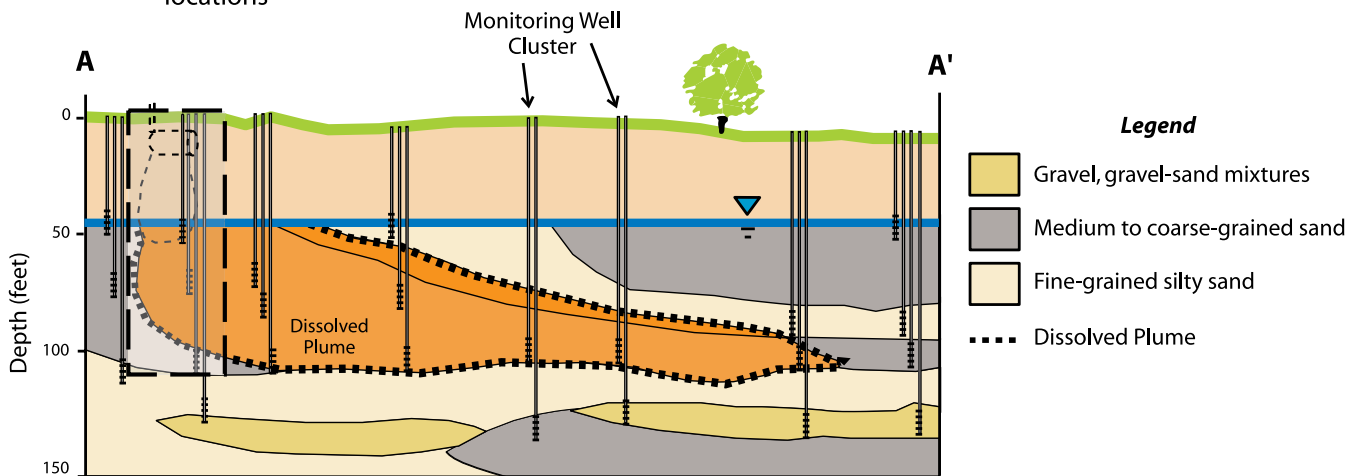
Figure 1.3 *Example of a network design for performance monitoring, including target zones for monitoring effectiveness with respect to specific remedial objectives.*

monitoring period. These areas may require additional characterization to determine if additional remedial actions are necessary to reduce contaminant concentrations to desired levels.

- Areas representative of uncontaminated settings (Ambient Monitoring)

Sampling locations for monitoring the redox state and immobilization capacity of aquifer materials include points that are adjacent to but outside the plume. Data from these monitoring locations will often be needed to assess the continuation of favorable conditions for attenuation. Since assumptions concerning the redox state and attenuation capacity affect interpretation of data from the plume, such assumptions should be periodically evaluated like other aspects of the conceptual site model. Therefore, multiple monitoring points generally should be used to determine the variability of these parameters outside the plume.

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- Areas supporting the monitoring of site hydrology

At some sites, monitoring of ground-water elevations at locations additional to those used for the monitoring of chemical parameters may be needed to determine if changes in ground-water flow rates and directions are occurring. Appropriate locations for placing piezometers will often include positions that are up gradient, side gradient, and down gradient of the contaminant plume, as well as in zones above and below the plume and near surface water bodies.

IE.5 Modification of the Performance Monitoring Plan

The monitoring plan should be a dynamic document that is modified as conditions change or the conceptual site model is revised to reflect new information. Decisions regarding remedy effectiveness and the adequacy of the monitoring program will generally result in either:

- Continuation of the monitoring program without modification;

- Modification of the monitoring program;

- Implementation of a contingency or alternative remedy; or

- Verification that remedial objectives have been met with subsequent termination of the monitoring program.

Continuation of the program without modification would be supported by contaminant concentrations behaving according to remedial expectations while ground-water flow and geochemical parameters remain within ranges indicative of continued contaminant immobilization. Modification of the program, including increases or decreases in monitoring parameters, frequency, or locations, may be warranted to reflect changing conditions or improved understanding of natural attenuation processes at the site. In addition, modification generally would be warranted whenever remedy modifications are implemented, such as implementation of additional source removal or hydraulic control for plume migration.

In situations where hydrologic and geochemical parameters are stable and the contaminant concentrations in ground water are decreasing as predicted, reductions in sampling frequency (e.g., semi-annual, annual, or less frequent) will often be warranted for process monitoring. For example, five years of quarterly monitoring showing predictable decreases in mobile contaminant concentrations might be the basis for decreasing the frequency to a semi-annual or annual basis at some sites. Ten years of semi-annual or annual monitoring that shows predictable decreases in mobile contaminant mass might likewise be the basis for additional decreases in frequency, depending on site conditions. Conversely, unexpected increases or lack of predicted decreases in contaminant concentrations may trigger additional characterization to determine the reasons for the behavior, increased monitoring of pertinent parameters, re-evaluation of the conceptual site model, and, potentially, the implementation of a contingent or alternative remedy.

Changes in the frequency of monitoring to detect plume expansion may also be warranted as process monitoring is modified. However, the frequency of such monitoring should not be decreased to the point where insufficient time would be available for implementation of an effective contingency plan in the event of MNA remedy failure.

Criteria for modifying the monitoring program, including the type and amount of data needed to support the evaluation, should be discussed and agreed to by stakeholders. Site-specific criteria should be developed to define conditions that indicate the appropriateness of increased or decreased monitoring, additional characterization, re-evaluation of the conceptual site model, implementation of a contingency or alternative remedy, and termination of performance monitoring.

Another reason for altering the monitoring program is the development of more advanced monitoring technologies. Because long-term monitoring costs are substantial, every advantage of technological advances in monitoring efficiencies should be considered. This might best be done by assessing monitoring technology every 3 to 5 years to identify "off-the-shelf" monitoring approaches/equipment that can improve accuracy and lower costs. National technology verification programs are often a good source of such information.

IE.6 Periodic Reassessment of Contaminant Removal Technologies

In addition to the routine monitoring of MNA remedy performance, it is recommended that periodic consideration be given to any technological advances in the efficiencies of source removal for inorganic contaminants. Implementation of more efficient technologies may result in reductions in the time frames for performance monitoring with associated reductions in cost as well as improvements in performance. Many sites may benefit from a Periodic Remedial Technology Assessment (PRTA) conducted at regular intervals (e.g., 5 years) throughout the performance monitoring program. The PRTA should consist of a rigorous literature search and engineering assessment of the field implementation of new technologies. It should involve a survey of cleanup efficiencies achieved by new technologies at sites similar to the one under consideration. The survey should rely on the results of national or state technology verification programs (e.g., USEPA Environmental Technology Verification Program, www.epa.gov/etv/; Interstate Technology & Regulatory Council, www.itrcweb.org). The PRTA should either indicate the absence of more suitable alternatives or suggest a faster path to site closure. The criteria for technology selection should be clearly stated during the development of the evaluation plan. The goal of this review should be identification of technologies that have a very high probability of achieving at least order-of-magnitude reductions in contaminant mass and/or achievement of MCLs in ground water by means acceptable to stakeholders. A reasonable metric should be successful implementation of the technology as judged by impartial bench marking criteria at several sites where site closure has been achieved.

1F.   References

Bethke, C.M. *Geochemical Reaction Modeling, Concepts and Applications*, Oxford University Press, New York, NY (1996).

Clesceri, L.S., A.E. Greenberg, and A.D. Eaton. *Standard Methods for the Examination of Water and Wastewater,* 20th Edition, American Public Health Association, Washington DC (1998).

USEPA. *Environmental Characteristics of EPA, NRC, and DOE Sites Contaminated with Radioactive Substances,* EPA 402-R-93-011, Office Radiation and Indoor Air, Washington DC (1993).

USEPA. *Common Chemicals Found at Superfund Sites,* EPA/OSWER No. 9203, Office of Solid Waste and Emergency Response, Washington DC (1994).

USEPA. *Contaminants and Remedial Options at Selected Metal-Contaminated Sites,* EPA/540/R-95/512, Washington DC (1995).

USEPA. *Documenting Ground-Water Modeling at Sites Contaminated with Radioactive Substances,* EPA/540/R-96/003, Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, Washington DC (1996). (http:// www.epa.gov/radiation/docs/cleanup/540-r-96-003.pdf)

USEPA. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water,* EPA/600/R-98/128, Office of Research and Development, Washington DC (1998). (http://www.epa.gov/ada/download/reports/protocol.pdf)

USEPA. *Understanding Variation in Partition Coefficient, Kd, Values: Volume I - Kd Model, Measurement Methods, and Application of Chemical Reaction Codes,* EPA 402-R-99-004A, Office of Radiation and Indoor Air, Washington DC (1999a).

USEPA. *Understanding Variation in Partition Coefficient, Kd, Values: Volume II - Geochemisry and Available Kd Values for Selected Inorganic Contaminants,* EPA 402-R-99-004B, Office of Radiation and Indoor Air, Washington DC (1999b).

USEPA. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites,* EPA/OSWER No. 9200.4-17P, Office of Solid Waste and Emergency Response, Washington DC (1999c).

USEPA. *Evaluation of the Protocol for Natural Attenuation of Chlorinated Solvents: Case Study at the Twin Cities Army Ammunition Plant,* EPA/600/R-01/025, Office of Research and Development, Washington DC (2001). (http://www.epa.gov/ada/download/reports/epa_600_r01_025.pdf)

USEPA. *Common Radionuclides Found at Superfund Sites,* EPA 540/R-00-004, Office of Radiation and Indoor Air, Washington DC (2002a).

USEPA. *Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration,* EPA/600/R-02/002, Office of Research and Development, Washington DC (2002b).

USEPA. *Understanding Variation in Partition Coefficient, Kd, Values: Volume III - Review of Geochemistry and Available Kd Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium,* EPA 402-R-99-004C, Office of Radiation and Indoor Air, Washington DC (2004).