Monitored Natural Attenuation of Inorganic Contaminants in Ground Water
Volume 1
Technical Basis for Assessment

**Evolution of Inorganic Contaminant Plume**

- **Time 1**: Mobile plume shrinkage due to degradation or immobilization onto aquifer solids
- **Time 2**: Immobilized inorganic contaminant still present on aquifer solids
- **Time 3**: Mobile contaminant
- **Original Plume Boundary**
- **Immobile Contaminant**
Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1 - Technical Basis for Assessment

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Notice

The U.S. Environmental Protection Agency through its Office of Research and Development managed the research described here under EPA Contract No. 68-C-02-092 to Dynamac Corporation, Ada, Oklahoma, through funds provided by the U.S. Environmental Protection Agency's Office of Air and Radiation and Office of Solid Waste and Emergency Response. It has been subjected to the Agency’s peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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.

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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-radiouclide 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).
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, strontrium (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 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).

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 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-
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 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 radionuclides (e.g., Am-241 and Np-237 from Pu-241) may be more toxic, have longer half-lives, and/or be more mobile than the parent in the decay series. Also, it is important that the near surface or

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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 radionuclides 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 specification 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

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**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 the discussion of specific site characterization approaches.

### Table 1.1

<table>
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<tr>
<th>Tier</th>
<th>Objective</th>
<th>Potential Data Types and Analysis</th>
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| 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 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 cornerstone 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 lead 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 remobilization.

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.scisoft.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.

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

<table>
<thead>
<tr>
<th>Software</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEFLOW</td>
<td>Groundwater Modeling, Inc. <a href="http://www.ssg-int.com/">www.ssg-int.com/</a></td>
</tr>
<tr>
<td>Visual Modflow</td>
<td>Waterloo Hydrogeology <a href="http://www.visual-modflow.com">www.visual-modflow.com</a></td>
</tr>
<tr>
<td>GroundWater Vistas</td>
<td><a href="http://www.groundwater-vistas.com">www.groundwater-vistas.com</a></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Software</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chess</td>
<td>Ecole des Mines de Paris chess.ensmp.fr/</td>
</tr>
<tr>
<td>Mineql+</td>
<td>Environmental Research Software <a href="http://www.mineql.com/">http://www.mineql.com/</a></td>
</tr>
<tr>
<td>The Geochemist’s Workbench®</td>
<td>University of Illinois <a href="http://www.geology.uiuc.edu/Hydrogeology">www.geology.uiuc.edu/Hydrogeology</a></td>
</tr>
<tr>
<td>Visual Minteq</td>
<td>KTH (Sweden) <a href="http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm">www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm</a></td>
</tr>
</tbody>
</table>
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>
<thead>
<tr>
<th>Table 1.4</th>
<th>Example software packages for modeling reactive transport in inorganic geochemical systems.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Software</strong></td>
<td><strong>Source</strong></td>
</tr>
<tr>
<td>Crunch</td>
<td>Lawrence Livermore Laboratory   <a href="http://www.csteefel.com/">www.csteefel.com/</a></td>
</tr>
<tr>
<td>The Geochemist's Workbench® Professional¹</td>
<td>University of Illinois   <a href="http://www.geology.uiuc.edu/Hydrogeology">www.geology.uiuc.edu/Hydrogeology</a></td>
</tr>
</tbody>
</table>

¹ The “Xt” package in previous releases.

<table>
<thead>
<tr>
<th>Table 1.5</th>
<th>Example internet sources of thermodynamic data useful in constructing geochemical models.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source</strong></td>
<td><strong>URL</strong></td>
</tr>
<tr>
<td>Japan Nuclear Cycle Development Institute</td>
<td><a href="http://migrationdb.inc.go.ip/">migrationdb.inc.go.ip/</a></td>
</tr>
<tr>
<td>Murdoch University (Australia)</td>
<td><a href="http://iess.murdoch.edu.au/iess/iess_home.htm">iess.murdoch.edu.au/iess/iess_home.htm</a></td>
</tr>
<tr>
<td>National Institute of Standards and Technology</td>
<td><a href="http://webbook.nist.gov/">webbook.nist.gov/</a></td>
</tr>
<tr>
<td>Nuclear Energy Agency (France)</td>
<td><a href="http://www.nea.fr/html/dbtdb/">www.nea.fr/html/dbtdb/</a></td>
</tr>
<tr>
<td>University of Illinois</td>
<td>[<a href="http://www.geology.uiuc.edu/Hydrogeology/hydro">www.geology.uiuc.edu/Hydrogeology/hydro</a> thermo.htm](<a href="http://www.geology.uiuc.edu/Hydrogeology/hydro">http://www.geology.uiuc.edu/Hydrogeology/hydro</a> thermo.htm)</td>
</tr>
<tr>
<td>University of Illinois at Chicago</td>
<td>[tigger.uic.edu/~mansoori/TRL html](<a href="http://tigger.uic.edu/~mansoori/TRL">http://tigger.uic.edu/~mansoori/TRL</a> html)</td>
</tr>
</tbody>
</table>
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., Eh, 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).

<table>
<thead>
<tr>
<th>Objective</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>Demonstrate that natural attenuation is occurring according to expectations,</td>
</tr>
<tr>
<td>2)</td>
<td>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,</td>
</tr>
<tr>
<td>3)</td>
<td>Identify any potentially toxic and/or mobile transformation products,</td>
</tr>
<tr>
<td>4)</td>
<td>Verify that the plume(s) is not expanding down gradient, laterally or vertically,</td>
</tr>
<tr>
<td>5)</td>
<td>Verify no unacceptable impact to down gradient receptors,</td>
</tr>
<tr>
<td>6)</td>
<td>Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy,</td>
</tr>
<tr>
<td>7)</td>
<td>Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors, and</td>
</tr>
<tr>
<td>8)</td>
<td>Verify attainment of remediation objectives.</td>
</tr>
</tbody>
</table>
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 groundwater 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 attainment at a given site. The most appropriate frequency for groundwater 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 to 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
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.

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


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


Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 2
Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium
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Notice

The U.S. Environmental Protection Agency through its Office of Research and Development managed portions of the technical work described here under EPA Contract No. 68-C-02-092 to Dynamac Corporation, Ada, Oklahoma through funds provided by the U.S. Environmental Protection Agency’s Office of Air and Radiation and Office of Solid Waste and Emergency Response. It has been subjected to the Agency’s peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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.
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.

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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 second 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 2, titled “Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium,” consists of individual chapters that describe 1) the natural processes that may result in the attenuation of the listed contaminants and 2) data requirements to be met during site characterization. Emphasis is placed on characterization of immobilization and/or degradation processes that may control contaminant attenuation, as well as technical approaches to assess performance characteristics of the MNA remedy. 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 rate and mechanism 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.

Where feasible, Agency-approved analytical protocols currently implemented for waste site characterization are identified, along with modifications that may be warranted to help insure the quality of site-specific data. In situations where Agency methods or protocols are unavailable, recommendations are made based on review of the existing technical literature. It is anticipated that future updates to these recommendations may be warranted with increased experience in the successful application of MNA as part of a ground-water remedy and the development of new analytical protocols.

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 supercede 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).
Cadmium
Richard T. Wilkin

Occurrence and Distribution
Cadmium is comparatively rare in the environment with an average abundance similar to other second- and third-row transition metals (e.g., silver and mercury). The median concentration of cadmium in soils and sediments ranges from about 0.04 to 1.8 mg kg\(^{-1}\) (Reimann and Caritat, 1998). Where cadmium concentrations are elevated, it is typically found in association with sulfide ores of zinc and sometimes with ores of copper and lead. The primary mineral associations of cadmium are with otavite (CdCO\(_3\)), greenockite (CdS), sphalerite (ZnS), smithsonite (ZnCO\(_3\)), and hemimorphite (Zn\(_4\)Si\(_2\)O\(_7\)(OH)\(_2\)-H\(_2\)O). Soil weathering can lead to release of the Cd\(^{2+}\) ion, which is generally soluble and mobile in water.

The primary industrial uses of cadmium are metal plating, production of Ni-Cd batteries, as a stabilizer in plastics, and as a pigment. According to Minerals Information statistics for 2001, approximately 75% of the U.S. apparent consumption of cadmium (a total of about 2.4 million pounds) went into production of Ni-Cd batteries (Wolke, 2003). The largest sources of cadmium contamination to ground water and surface water are from sewage sludge, mines (e.g., mine water, mine tailings leachate), metal smelters (process waters), battery recycling plants, and wastes from electroplating facilities.

Remedial Technologies
Treatment of cadmium and other heavy metals in industrial wastewater streams is often achieved by precipitation using lime, sodium carbonate, alkaline sulfides, or organosulfides. These treatment methods are generally unsuitable for drinking water. Ion exchange resins and adsorption substrates are in most cases used for treatment of drinking water contaminated with cadmium (Zhao et al., 2002; Lai et al., 2002). Technology classes suitable for remediation of cadmium-contaminated soils include containment, solidification/stabilization, and separation/concentration (USEPA, 1997). Containment technologies applied at metal contamination sites to minimize the transport of cadmium and co-contaminants out of source zones include caps and vertical barriers. Reactive barriers are appropriate for treatment of some cadmium and co-contaminant ground water plumes (e.g., Gibert et al., 2003; Wang and Reardon, 2001).

Regulatory Aspects
Cadmium and its compounds are very toxic to nearly all living organisms. The EPA has set the maximum contaminant level (MCL) for cadmium in drinking water at 0.005 mg L\(^{-1}\). Cadmium is fairly mobile and soluble in water at low to near-neutral pH. The main routes by which cadmium enters the human body are ingestion of plant-based food and inhalation of cadmium-bearing dusts. The kidney is the primary organ affected by exposure to cadmium. For non-potable water sources, ambient water quality criteria (AWQC) that are protective of aquatic life may serve as alternative cleanup goals. For cadmium, current statutes list both acute and chronic criteria for fresh waters as 0.002 mg L\(^{-1}\) and 0.00025 mg L\(^{-1}\), respectively, for a water hardness of 100 mg L\(^{-1}\) (USEPA, 2006; http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf). Adjustments to these criteria are to be applied for waters with different hardness. An example of where this criterion may apply is a site where contaminated ground water discharges to surface water.

Geochemistry and Attenuation Processes

Aqueous Speciation
Dissolved forms of cadmium are only present in the +2 valence state. Cadmium has a tendency to form aqueous complexes with both inorganic and organic ligands, although the uncomplexed Cd\(^{2+}\) ion is fairly stable. The most important inorganic cadmium complexes are with hydroxide, chloride, sulfate, bicarbonate, carbonate, cyanide, and ammonia. Complexation of cadmium with humic acids is important under conditions of high dissolved organic carbon (DOC) concentrations, but binding of cadmium with humic acids appears to be weaker when compared to lead (Abate and Masini, 2002; Christensen and Christensen, 1999; Dunnivant et al., 1992). In highly reducing systems, cadmium complexation with bisulfide is possible. It is likely that cadmium toxicity is related to its strong tendency to form bonds with thiol functional groups in certain enzymes which results in the displacement of biologically essential metals (Baes and Mesmer, 1976).

The fractional abundance of Cd-OH species in water as a function of pH is shown in Figure 1.1. The distribution diagram for cadmium hydroxy complexes indicates that Cd\(^{2+}\), Cd(OH)\(^{+}\), Cd(OH)\(_2\)\(^{2+}\) are the most significant species below...
pH 12. At low total concentrations of cadmium, hydrolysis of Cd$^{2+}$ becomes significant above about pH 9. Complexation of cadmium with chloride and ammonia becomes important as aqueous concentrations of these ligands exceed $10^{-2}$ molal and $10^{-3}$ molal, respectively (e.g., Lindsay, 1979).

Figure 1.1 Species distribution of Cd(II) in pure water as a function of pH at 25 °C.

Figure 1.2 shows the fractional abundance of cadmium species as a function of pH in an aqueous solution containing a mixture of chloride, sulfate, and inorganic carbon. Again the uncomplexed Cd$^{2+}$ ion dominates below pH 8.5. In general, complexation of cadmium with chloride and sulfate is most important at near-neutral to low pH; carbonate complexation is most important at pH 9 to 11; and, hydroxyl species dominate cadmium complexation at pH > 11 (Figure 1.2).

The identity of cadmium bisulfide complexes and their formation constants have been discussed by Daskalakis and Helz (1992) and Wang and Tessier (1999). Uncertainty persists regarding the stoichiometry of the most important cadmium complexes in sulfidic waters. This uncertainty mainly stems from the experimental approach that has been traditionally used to extract thermodynamic data, i.e., evaluation of CdS solubility over a range of total cadmium concentrations, total sulfide concentrations, and pH. Data presented in Wang and Tessier (1999) indicate that Cd(HS)$_2$ is the dominant species at $\Sigma S(-II)=10^5$ molal and over the pH range from 6 to 8, typically encountered in natural sulfidic waters. At lower total sulfide concentrations, CdHS$^+$ and Cd$^{2+}$ become increasingly important (Wang and Tessier, 1999).

**Solubility**

An Eh-pH diagram for cadmium is shown in Figure 1.3. Inspection of this diagram indicates that at the specified conditions Cd$^{2+}$ is the soluble form of cadmium at pH < 5 and at moderate to highly oxidizing redox potentials. At near-neutral to moderately alkaline pH (6 to about 12) cadmium carbonate (otavite) is stable, and at pH > 12.5 cadmium hydroxide is stable. In sulfidic environments, cadmium sulfide (greenockite) is stable over a wide pH range. Solubility expressions for cadmium carbonate and cadmium sulfide are given by:

\[
\text{CdCO}_3 + \text{H}^+ = \text{Cd}^{2+} + \text{HCO}_3^- \quad (\log K = -0.9)
\]

and

\[
\text{CdS} + \text{H}^+ = \text{Cd}^{2+} + \text{HS}^- \quad (\log K = -14.4)
\]

In natural deposits, cadmium often substitutes for zinc in the mineral structures of sphalerite (ZnS) and smithsonite (ZnCO$_3$). O’Day et al. (1998) suggest that as cadmium-substituted sphalerite weathers, cadmium is preferentially partitioned into the aqueous phase over zinc. Zinc was found to form various zinc hydroxides and/or zinc-iron oxyhydroxides depending on the total amount of iron in the system. Cadmium was not identified in the solid-phase products from weathering indicating its general tendency to be mobile in the aqueous phase (O’Day et al., 1998; Carroll et al., 1998).
Cadmium carbonates - Cadmium is known to form solid-solutions with calcium carbonate (calcite). The Cd$^{2+}$ and Ca$^{2+}$ ions are nearly the same size with crystal radii of 1.09 and 1.14 angstroms, respectively, assuming octahedral coordination. The formation of Ca-Cd carbonate solid solutions is environmentally significant because solid solutions are generally more stable and less soluble than endmember compositions. Cadmium uptake from aqueous solution by calcite has been widely studied (e.g., McBride, 1980; Davis et al., 1987; Papadopoulos and Rowell, 1988; Zachara et al., 1991; Stipp et al., 1992, 1993; Tesoriero and Pankow, 1996; Chiarello et al., 1997; Martin-Garin et al., 2003).

Cadmium uptake is thought to consist of two processes. The first process is rapid sorption and the second process is incorporation into the crystal lattice and formation of an otavite-calcite solid-solution. The latter process has been confirmed through determination of cadmium solid phase speciation during reaction with calcite (Bailey et al., 2005). Cadmium partitioning to carbonaceous materials has been applied by Wang and Reardon (2001) for the removal of cadmium from wastewater streams.

Cadmium phosphates - Santillan-Medrano and Jurinak (1975) observed the formation of cadmium phosphate precipitates in soil systems containing phosphorus. Precipitation of phosphate compounds over carbonate compounds was favored in phosphorous-containing systems at pH < 7.5. Substitution of cadmium into natural apatite has also been documented (Sery et al., 1996) and may be a more common route for partitioning to phosphate minerals at concentrations undersaturated with respect to precipitation of cadmium phosphate.

Cadmium hydroxides – Baes and Mesmer (1976) report the existence of three crystalline forms of Cd(OH)$_2$. At 25° C the stable form is $\beta$-Cd(OH)$_2$. This material is fairly soluble at circumneutral pH. Cadmium concentrations below the MCL of 0.005 mg L$^{-1}$ would only be approached at pH > 11 in systems saturated with respect to $\beta$-Cd(OH)$_2$.

Cadmium sulfides – It is well known that Cd$^{2+}$ and HS$^{-}$ react to form a very insoluble, yellow-colored precipitate. However, Daskalakis and Helz (1992) point out that under some conditions dissolved cadmium bisulfide complexes are very stable; consequently, the effectiveness of sulfide treatment for cadmium in wastewater has been overestimated in some cases due to uncertainty regarding the stability of cadmium bisulfide species.

Framson and Leckie (1978) examined the limit of coprecipitation of cadmium and ferrous monosulfide. Their experimental data suggest only limited coprecipitation, likely due to the size mismatch between the ferrous (~0.75 angstroms) and cadmium (~1.09 angstroms) cations. They suggest that in sulfidic systems, cadmium precipitates primarily through surface exchange with ferrous monosulfide substrates or as unsubstituted cadmium sulfide. Parkman et al. (1999) performed X-ray absorption spectroscopy experiments and also concluded that a CdS phase is formed as cadmium interacts with iron monosulfide. On the other hand, Coles et al. (2000) found up to 29% replacement of iron by cadmium in mackinawite (FeS). It is possible that this high percentage of replacement occurs at the surface of very fine-grained iron sulfide particles. Coles et al. (2000) found that the mixed ferrous-cadmium sulfides are more insoluble than pure mackinawite.

Adsorption

Adsorption/desorption behavior of cadmium is strongly a function of pH, and to a lesser extent a function of the solution concentration of cadmium and the concentration of competing cations or complexing ligands. At low concentrations of cadmium, sharp adsorption edges provide evidence that cadmium forms strong bonds with mineral surfaces. In general, the presence of calcium and magnesium reduces the extent of cadmium removal by aquifer solids. The presence or addition of zinc, which tends to be more strongly adsorbed, can reduce the amount of cadmium uptake by iron and aluminum oxides, indicating that zinc competes for similar adsorption sites and is preferentially adsorbed over cadmium (Benjamin and Leckie, 1980). It has also been observed that cadmium may preferentially adsorb to manganese oxides when they are present in sufficient quantities (Bellanca et al., 1996). Tonkin et al. (2004) have evaluated published cadmium adsorption data to determine surface complexation constants that may be employed to assess the potential extent of adsorption onto manganese oxides.

Ainsworth et al. (1994) examined the sorption behavior of cadmium on freshly prepared and aged hydrous ferric oxide (HFO). Their results indicate that HFO effectively removes cadmium from solution at pH above about 6.7. In general, the pH-dependent adsorption behavior parallels the change

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**Figure 1.3** Eh-pH diagram for cadmium (total Cd = $10^{-5}$ molal, total C = $10^{-3}$ molal, total S = $10^{-3}$ molal; all organic cadmium complexes are suppressed; activity coefficients for all species are set equal to 1).
in aqueous speciation from Cd$^{2+}$ to cadmium hydroxide species (see Fig. 1.1), although adsorption occurs at pH values where cadmium hydroxide species are unexpected in bulk solution. Aging times of up to 21 weeks showed little effect on the sorption behavior of cadmium onto HFO. HFO aged in the presence of Cd$^{2+}$ ions showed some desorption hysteresis suggesting that cadmium is incorporated into the metal oxide structure during recrystallization. Martínez and McBride (1998) suggest that coprecipitation of cadmium with amorphous iron oxides results in more reduced concentrations than can be achieved through surface adsorption alone. However, Ford et al. (1997) report that during long-term aging of hydrous iron oxides, cadmium desorbs or is released suggesting minimal incorporation of cadmium into the goethite or hematite structures.

Lai et al. (2002) investigated the adsorption characteristics of cadmium and humic acid onto iron oxyhydroxide-coated quartz sands. The adsorption of both cadmium and humic acid was highly pH dependent. Cadmium adsorption increased with pH, whereas humic acid adsorption decreased as pH increased. The presence of humic acid was found to result in increasing cadmium adsorption capacity in the pH range of 4-6.

**Redox Chemistry**

In natural systems cadmium is present in the +2 oxidation state. Therefore, the geochemical transport processes of cadmium are not directly tied to changes in redox conditions. Because cadmium forms stable precipitates and aqueous complexes with redox-sensitive elements such as sulfur and carbon, its mobility potential is indirectly tied to redox conditions. In sulfate-reducing systems, cadmium is expected to form insoluble CdS precipitates or coprecipitates with FeS (DiToro et al., 1990). In moderately reducing but non-sulfidic systems, however, reductive dissolution of hydrous ferric oxides with adsorbed cadmium could result in cadmium mobilization.

Several studies indicate that concentrations of dissolved cadmium increase when reduced systems are oxidized, such as when dredged sediments are land filled. This behavior may be due to oxidative dissolution of metal sulfides or due to the decomposition of organic materials that bind cadmium (e.g., Cooper and Morse, 1998; Simpson et al., 2000; Martínez et al., 2002).

**Colloidal Transport**

Transport of cadmium via colloids can be significant in ground water and surface water systems. Both mineral and organic particles can play a role in binding and transporting cadmium. Cadmium adsorbed to colloidal hydrous ferric oxides may subsequently desorb due to pH decreases or due to decreases in the oxidation-reduction potential.

**Site Characterization**

Cadmium mobility in ground water is governed by the total concentration of cadmium, the distribution of cadmium species in water, and the nature of cadmium partitioning in the solid phase. The development of site-conceptual models for predicting the long-term fate of cadmium at a contaminated site will require information on the distribution and concentration of cadmium in the aqueous phase and the solid phase. Table 1.1 indicates possible natural attenuation and mobilization pathways for cadmium. Details of the types of analytical measurements that may be conducted on sampled ground water and aquifer sediments to assist in identifying the attenuation mechanism(s) are discussed in the following paragraphs.

### Table 1.1 Natural Attenuation and Mobilization Pathways for Cadmium

<table>
<thead>
<tr>
<th>Attenuation Processes</th>
<th>Mobilization Processes</th>
<th>Characterization Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation of insoluble carbonates, sulfides, and hydroxides. In general, pH &gt; 8 will drive precipitation reactions resulting in Cd concentrations below the MCL.</td>
<td>Dissolution of carbonates at low pH; oxidative dissolution of sulfides at low to neutral pH and high Eh; degradation of organic matter; complexation/stabilization in the presence of DOC.</td>
<td>Evaluation of cadmium concentration in the aqueous phase. Determination of total Cd in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Evaluation of long-term storage capacity.</td>
</tr>
</tbody>
</table>
**Aqueous Measurements**

Quantitative measurement of cadmium concentrations in aqueous solutions is typically carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS), or atomic absorption spectroscopy (AAS). Input data to geochemical codes (e.g., MINTEQA2, PHREEQC, EQ3/6) for determining aqueous speciation also require, at a minimum, concentrations of major anions, major cations, dissolved organic carbon, temperature, and pH. In addition, while regulatory requirements stipulate that unfiltered ground-water samples be analyzed to support regulatory decisions at a contaminated site, it may be necessary to also collect filtered samples to help define the process(es) controlling contaminant mobility. The use of 0.45 μm pore size filters is common as an arbitrary cutoff point to differentiate between dissolved and particulate phases in water samples. However, caution is recommended when using this approach, particularly for Fe and Al and other elements that may be associated with Fe or Al particles (including Cd) that could pass through 0.45 μm filters. The use of filters with pore sizes less than 0.1 μm will generally provide a better assessment of the dissolved vs. particulate load in ground water.

**Solid Phase Measurements**

The implementation of an analytical approach to identify cadmium speciation in aquifer sediments is a challenging process. The accuracy of the analytical finding is dependent on the method of sample collection/preservation and the tools used to identify the mechanism of cadmium partitioning. It is recommended that the analytical protocol be designed to address the potential redox sensitivity of the solid phase(s) to which cadmium may be partitioned (e.g., sulfides in reduced sediments). Tools to evaluate the mechanism of cadmium solid phase partitioning range in complexity from relatively simple chemical extractions to advanced spectroscopic techniques.

The total concentration of cadmium in soils, sediments, and aquifer materials may be determined by X-ray fluorescence spectroscopy (XRF), or by ICP-AES after digestion in mineral acids. A variety of digestion or extraction methods can be found in the literature (Amacher, 1996). Neutron activation analysis is not commonly employed due to the scarcity of neutron sources required to irradiate the sample. X-ray fluorescence is the most attractive approach due to the relative ease of sample preparation, which may be conducted with the sample in its original state or following fusion with lithium metaborate. When combined with the determination of other major or trace elements in the solid sample, this provides an initial step for assessing possible association of cadmium with various solid phase components. This type of analysis can be conducted on the bulk sample as well as at a microscopic level using wavelength (electron microprobe) or energy dispersive spectroscopy coupled to a scanning or transmission electron microscope. Microscopic examination allows one to better differentiate whether cadmium may be distributed across a number of different mineral phases within the solid sample or primarily associated with a discrete phase. There are limitations to this approach (Pye, 2004), a significant one being that the analysis does not necessarily provide unique mineral identification necessitating the collection of supporting mineralogical and chemical data.

More detailed information on the specific partitioning mechanism(s) controlling cadmium solid phase speciation is typically required to adequately support site assessment for potential reliance on natural attenuation as part of a site remedy. There have been many applications of sequential extraction schemes to assess the speciation of solid phase cadmium (e.g., Tessier et al., 1979; Hickey and Kittrick, 1984; Pustišek et al., 2001; Buanaum et al., 2006). As discussed in the cited reports, sequential extraction methods provide a useful tool to assist in determining the chemical speciation of trace metals in soils/sediments, but essentially all documented methods show analytical limitations in selectively extracting cadmium and other metals associated with specific solid components. Where feasible, it is recommended that complimentary analytical techniques be employed to confirm the accuracy of cadmium speciation (e.g., O’Day et al., 1998; O’Day et al., 2000; Carroll et al., 2002; D’Amore et al., 2005) or the accuracy of the extraction of a targeted phase(es) for a given extractant (e.g., Shannon and White, 1991; Ngiam and Lim, 2001; Peltier et al., 2005). As an example, Peltier et al. (2005) have demonstrated that a common extraction method employed to target metals associated with easily reducible iron (hydr)oxides may also dissolve iron sulfides that may be present. The results from this analysis may lead to misidentification of a cadmium association with iron (hydr)oxides, resulting in the development of a conceptual site model that misrepresents the site-specific attenuation process. Under reducing conditions, it is also critical that aquifer sediments be sampled and processed in a manner that prevents exposure to oxygen prior to extraction in order to limit oxidation of reduced minerals (e.g., iron sulfides) that may host cadmium. Cadmium associated with a sulfide phase in sediments has been shown to repartition to more extractable phases upon oxidation (Saeki et al., 1993). Determination of the host mineral phase(es) dissolved for each extraction step is recommended, along with the use of surrogate Cd-bearing phases spiked into the sediment to confirm accuracy of the procedure (e.g., Rudd et al., 1988). The choice of appropriate cadmium surrogate phases would be governed by site-specific geochemical conditions or characterization of the mineralogy of the aquifer sediment.

**Long-Term Stability and Capacity**

The stability of attenuated cadmium will largely depend on the stability of site-specific geochemical conditions through time. For example, if cadmium attenuation follows a calcium carbonate coprecipitation pathway, then long-term stability of attenuated cadmium will depend, in part, on the persistence of pH conditions. If pH conditions were to shift significantly to low values, cadmium might be expected to release from the solid phase. It is therefore important to understand the attenuation mechanism(s) so that geo-

5
chemical triggers for mobilization can be anticipated and incorporated into evaluations of long-term monitoring data. For any proposed and identified attenuation mechanism, there will exist possible scenarios whereby remobilization could occur (i.e., changes in pH or Eh). It will be essential to explore the likelihood of such changes in site geochemistry and the sensitivity of the attenuation pathway to changes in the prevailing geochemical conditions.

Quantifying the attenuation capacity (as defined in Volume 1) will also require an understanding of the specific attenuation pathway(s). Attenuation capacity, for example, could be related to the extent that pH is buffered, the availability of sorptive sites in aquifer materials, or to the supply of electron donors needed to sustain microbially mediated redox conditions. For any proposed attenuation mechanism, there will be assumptions built into capacity estimations, so it is recommended that uncertainty analysis accompany capacity calculations.

**Tiered Analysis**

Determination of the viability of cadmium remediation via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. MNA may not be appropriate as a site remedy for cadmium contamination in acidic to circum-neutral pH, highly oxidizing, and/or DOC-rich environments. The goal of site assessment is to demonstrate the process(es) controlling cadmium sequestration onto aquifer solids and the long-term stability of solid phase cadmium as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

**Tier I** - Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate Cd partitioning to aquifer solids within the plume. Rapid movement of contaminants along preferred flow paths in the unsaturated and saturated zones can be induced by hydrologic events such as heavy rains. It will be important to determine that such hydrogeologic features do not result in contaminants bypassing zones where natural attenuation is occurring. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by a cadmium precipitate such as a carbonate/phosphate or sulfide phase. Identification of active sequestration to prevent cadmium migration in ground-water provides justification for proceeding to Tier II characterization efforts.

**Tier II** - Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume. This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation need to be identified under this stage of site characterization. This effort may require determination of the chemical speciation of aqueous and solid phase Cd, which may be approached according to the following scheme:

1) Determination of cadmium solution speciation via direct analytical measurements in combination with speciation calculations based on characterized ground-water chemistry;
2) Calculation of the saturation state of ground water relative to measured aqueous chemistry complimented by the possible isolation of discrete Cd mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;
3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Cd sorption (e.g., Amonette, 2002);
4) Identification of cadmium association(s) with the various solid phase components of aquifer solids through combination of chemical extractions with microscopic/spectroscopic confirmation of phase associations, and;
5) Demonstration of concurrence between the site conceptual model and mathematical model(s) that describe cadmium removal mechanism(s).

It is recommended that identification of cadmium chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the in-situ distribution of dissolved cadmium and mineralogy and prevents loss of cadmium from aqueous samples (e.g., due to oxidation and precipitation of ferrous iron in anoxic ground water). The demonstration of concurrence between conceptual and mathematical models describing cadmium transport will entail development of site-specific parameterization of the chemical processes controlling cadmium solid phase partitioning.

**Tier III** - Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Cd and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized Cd be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage.
For example, changes in ground-water pH can exert a significant influence on Cd adsorption or precipitate solubility. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of Cd mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for Cd uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that precipitation of Cd sulfide due to microbial degradation of organic compounds coupled with sulfate reduction occurs within the aquifer, then it is recommended that the mass distribution of organic carbon and sulfate to support this reaction within the aquifer be determined. This site-specific capacity can then be compared to Cd mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized Cd and sufficient capacity within the aquifer to sustain Cd attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction may be necessary.

**Tier IV** – Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated Cd. The specific chemical parameters to be monitored will include those identified under Tier III that may halt Cd partitioning to aquifer sediments and/or result in solubilization of either discrete Cd precipitates or aquifer minerals that sequester Cd from ground water. For example, solution phase parameters that could alter either Cd precipitation or adsorption include increases in soluble organic carbon in combination with changes in ground-water pH. In contrast, the concentration of dissolved iron or sulfate may indicate the dissolution of an important sorptive phase within the aquifer (e.g., reductive dissolution of iron oxides or oxidative dissolution of sulfides). Changes in these parameters may occur prior to observed changes in solution Cd and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of natural attenuation processes within the aquifer through the injection of soluble reactive components.

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USEPA. Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb, EPA/540/S-97/500, U.S. Environmental Protection Agency (1997).


Occurrence and Distribution

Lead is distributed in low concentrations in sedimentary rocks and soils. The average concentration of lead in shales, sandstones, and carbonate rocks is 20, 7, and 9 mg kg⁻¹, respectively (Turekian and Wedepohl, 1961). Kabatasp-Pendias and Pendias (1984) report background soil concentrations of 17-26 mg Pb kg⁻¹ in the U.S. Anthropogenic enrichment of lead in near-surface soils stems largely from airborne deposition of particles derived from fossil fuel combustion (e.g., gasoline and coal). Lead is a common metal contaminant at hazardous waste sites, especially at battery crushing and recycling facilities (USEPA, 1991). Indeed, lead is the most commonly recycled metal: roughly 50% of lead production is secondary lead. Approximately 70% of world-lead goes to lead-acid storage batteries. Natural lead enrichment occurs around hydrothermal deposits and base metal ores, most frequently as the mineral galena (PbS), but also as the oxidation products of lead sulfide ores such as anglesite (PbSO₄) and cerussite (PbCO₃).

Sources of lead contamination to surface waters and ground waters include: fall-out of atmospheric dust, industrial and municipal wastewater effluent, mineral fertilizers and pesticides, lead-based paints, and wastes from the mining, metallurgical, chemical, and petrochemical industries. Lead is a widely used non-ferrous metal in the petroleum and storage battery industries. In the early 20th century, lead was frequently used for constructing water pipes and for the solder used to seal pipe joints, and prior to 1978 lead carbonates and oxides were common pigment components in exterior and interior paints. From 1923 to the mid-1980's tetraethyl lead was used in the U.S. as an antiknock additive in gasoline, and lead derived from fuel combustion represented a dominant source of lead to the environment. Due to a better understanding of the health consequences stemming from lead exposure, as well as the introduction of catalytic converters, many countries have reduced or eliminated use of lead additives in gasoline. Most of the lead produced in the U.S. comes from mines in Missouri, with other major lead-producing mines in Alaska, Colorado, Idaho and Montana. The average annual consumption of lead in the U.S. from 1997 to 2001 was 1,690,000 metric tons.

Lead was ranked second on the CERCLA Priority List of Hazardous Substances in 1999 and 2001 (after arsenic - #1, and before mercury - #3, vinyl chloride - #4, and PCBs - #5). The priority list is prepared by the Agency for Toxic Substances and Disease Registry and EPA and is based on the frequency of occurrence of particular contaminants at National Priorities List (NPL) sites and their potential threat to human health. In absolute numbers, lead is by far the most common inorganic contaminant found at Superfund sites. For example, in 1996 lead contamination was found at 460 Superfund sites, compared to 306 with chromium contamination, 235 with arsenic, 226 with zinc, 224 with cadmium, 201 with copper, and 154 with mercury (USEPA, 1996).

Plume Characteristics

The fate of lead in the subsurface is controlled principally by adsorption at the solid-water interface, precipitation, and complexation with organic matter. Lead is strongly retained in soils and in most situations very little lead is transported to surface waters or ground water. Exceptions to this behavior are low pH systems or environments with high concentrations of dissolved organic carbon. Tetramethyl lead, a more soluble and volatile form of lead, may form as a result of microbial alkylation of inorganic lead in anaerobic environments. Remedial case studies at lead-contaminated Superfund sites primarily describe soil cleanup technologies (U.S. EPA, 1997). Fewer examples are found where remediation efforts have targeted lead contamination in ground water (Morrison and Spangler, 1993).

Remedial Technologies

Technology classes potentially applicable to the remediation of lead-contaminated soils include containment, solidification/stabilization, and separation/concentration (e.g., USEPA, 1997). Containment technologies applied at metal contamination sites include caps and vertical barriers to minimize the transport of lead and co-contaminants out of source zones. Solidification/stabilization technologies are treatment processes that mix reactive agents with contaminated material to reduce solubility or otherwise limit contact between the contaminated material and potential transport fluids. Amendments such as Portland cement or phosphate-based compounds are candidates for treatment of lead contamination in soils (e.g., USEPA, 1997). Separation/concentration methods have also been used for lead treatment, including ex-situ soil washing and in-situ soil flushing to physically or chemically reduce contaminant concentrations to meet site-specific cleanup goals. Ground-water remediation of lead using the permeable reactive barrier technology has been explored with some success in bench-top studies (e.g., Shokes and Möller, 1999).
Regulatory Aspects

Because of the highly toxic effects of lead on biological systems, treatment standards and concentration limits are stringent for the discharge of lead-bearing wastewaters and ground water. EPA has set the maximum contaminant level for lead at 0.015 mg L⁻¹. Generally, the predominant routes of exposure for lead are ingestion and inhalation of lead-bearing aerosols. As will be discussed below, lead is sparingly soluble in water over a wide range of chemical conditions. For non-potable water sources, ambient water quality criteria (AWQC) that are protective of aquatic life may serve as alternative cleanup goals. For lead, current statutes list both acute and chronic criteria for fresh waters as 0.065 mg L⁻¹ and 0.0025 mg L⁻¹, respectively, for a water hardness of 100 mg L⁻¹ (USEPA, 2006; http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf). Adjustments to these criteria are to be applied for waters with different hardness. An example of where this criterion may apply is a site where contaminated ground water discharges to surface water. Cleanup goals for lead in soils at Superfund sites range from 200 to 500 mg kg⁻¹ (USEPA, 1997).

Geochemistry and Attenuation Processes

Aqueous Speciation

Lead is known to form stable aqueous complexes with OH⁻, Cl⁻, CO₃²⁻, SO₄²⁻, and HS⁻. In pure water, lead is mainly present as Pb²⁺ below a pH of about 7. With increasing pH, the species PbOH⁺, Pb(OH)₂⁰, and Pb(OH)₃⁻ become dominant over Pb²⁺ (Figure 2.1). Lead carbonato complexes (PbCO₃⁰, Pb(CO₃)²⁻), lead chloride complexes (PbCl⁺, PbCl₂⁰), lead sulfate complexes (PbSO₄⁰, Pb(SO₄)²⁻), and lead sulfide complexes (PbHS⁺, Pb₂S₂) are typically considered in aqueous speciation modeling efforts (e.g., Hem and Durum, 1973; Hem, 1976; Marani et al., 1995; Pierrard et al., 2002; Rozan et al., 2003). In general, complexation of lead with chloride and sulfate is most important at near-neutral to low pH; carbonate complexation is most important at near-neutral to moderately alkaline conditions; and, hydroxyl species dominate lead complexation at high pH (Figure 2.2). Inorganic speciation of lead in site-specific water will depend on pH, total lead concentration, and the relative and absolute abundances of the major anions: chloride, sulfate, and carbonate.

Dissolved organic carbon (DOC) may also form stable complexes with lead and play an important role in governing lead mobility in ground-water systems; however, few data are available and comparatively few attempts have been made to assess the importance of lead interactions with DOC. In a recent study of landfill leachate-polluted ground water containing up to 180 mg DOC L⁻¹, more than 90% of the total lead in solution was present in DOC complexes (Christensen et al., 1999). This study also showed that the default database for MINTEQA2, which contains information for calculating metal complexation by DOC, was adequate for predicting the extent of lead complexation by DOC.

Reed et al. (1995) took advantage of lead partitioning to organic compounds in column-scale soil flushing studies. For soils contaminated with Pb(II) (500 mg kg⁻¹ from Pb(NO₃)₂), PbSO₄ (10,000 mg kg⁻¹), PbCO₃ (10,000 mg kg⁻¹), and Pb-naphthalene (400 mg kg⁻¹), they documented Pb recoveries of 100%, 100%, 100%, and 72%, respectively, using 0.01 M EDTA as the soil-flushing solution. These results demonstrate the degree to which lead can be mobilized by organic ligands such as EDTA.

![Figure 2.1](image)

*Figure 2.1* Pb(II) species distribution in pure water at 25 °C.

![Figure 2.2](image)

*Figure 2.2* Species distribution of lead in solution with 100 mg L⁻¹ chloride, 100 mg L⁻¹ sulfate, and 100 mg L⁻¹ total inorganic carbon, based on thermodynamic data in MINTEQA2 (Allison et al., 1990).

Solubility

An Eh-pH diagram for lead is shown in Figure 2.3. Inspection of this diagram indicates that at the specified conditions lead is stable in solids across the stability field of liquid water. At low pH and oxidizing conditions, lead sulfate is stable. At near-neutral to moderately alkaline pH, lead carbonates are stable, and at pH > 12.5 lead hydroxide is stable. In sulfidic environments, lead sulfide (galena) is stable over a wide pH range. The Pb(IV) phase, plattnerite, is stable at moderately alkaline to alkaline pH and at highly oxidizing redox potentials.
Solution pH plays a dominant role in governing lead solubility in aqueous solution. In general, the aqueous solubility of lead is low at near neutral to alkaline pH. Lead is expected to be mobile in low pH, oxidizing conditions. Hem and Durham (1973) found that at pH>7, the equilibrium solubility of lead was below 0.05 mg L⁻¹ when Pb(OH)₂ and PbCO₃ were assumed to be the solubility-controlling phases. Equilibrium solubility of greater than 1000 mg L⁻¹ lead was estimated at pH 4 in the absence of any sulfate. Lead is usually not a metal of concern at mining-related sites where acid mine drainage is produced. This is because the weathering of metal sulfides, in addition, to generating acidity also produces high concentrations of sulfate, which results in the precipitation of anglesite (Zänker et al., 2002).

For comparison purposes, the pH-dependent solubilities of lead carbonate, lead sulfate, and lead sulfide are shown in Figure 2.4. Lead carbonate is highly insoluble at pH>8, but can be highly soluble below pH 6. Consequently, acidification of a soil or sediment containing lead carbonate may result in lead mobilization. Lead sulfate solubility is pH-independent above pH of about 2 and the concentration of Pb(II) in equilibrium with lead sulfate varies inversely with the concentration of sulfate. Lead sulfide is highly insoluble even at low pH (Figure 2.4).

Important lead-bearing mineral phases include: lead hydroxide (Pb(OH)₂), cerussite (PbCO₃), hydrocerussite (Pb₃(CO₃)₂(OH)₆), anglesite (PbSO₄), galena (PbS), lead oxide (PbO), and chloropyromorphite (Pb₅(PO₄)₃Cl) in phosphate-bearing systems. In addition, plumbojarosite (Pb₀.₅Feₓ(SO₄)ₓ/₂(OH)₆) has been identified as an important secondary precipitate and lead sink in weathered mine wastes (e.g., Hochella et al., 1999). Thermodynamic data for most of these phases may be found in a variety of sources (e.g., see Pierrard et al., 2002, and references therein). In carbonate and sulfate systems the most favored mineral species appear to be anglesite, cerussite, and hydrocerussite (Lindsay, 1979; Marani et al., 1995).

Lead hydroxide and lead oxide, although predicted to be stable based on thermodynamic reasoning, seem to be kinetically hindered from precipitating at room temperature (Marani et al., 1995). In sulfate-reducing systems, galena precipitation is thermodynamically and kinetically favored over a wide range of pH and total sulfide concentrations (Uhler and Helz, 1984).

Marani et al. (1995) point out that the reliability of solubility predictions depends on the choice of the relevant solubility constants used in modeling studies. Unfortunately, such constants are wide ranging for lead. Reasonable agreement between solubility predictions from equilibrium modeling and filterable lead concentrations measured in aged soil-water systems was obtained only with a critical selection of solid phases in the modeling and by appreciating kinetic aspects of the Pb-H₂O system (Marani et al., 1995).
lead-contaminated soils. Reaction between labile lead phases and dissolved phosphate is rapid over a wide range of pH and P/Pb molar ratios and results in the formation of insoluble chloropyromorphite (Zhang and Ryan, 1999).

**Adsorption**

Adsorption of trace metals, such as lead onto oxide surfaces, has been well characterized in lab-based studies (e.g., Hayes and Leckie, 1986). Adsorption at mineral surfaces results from a set of chemical reactions between lead and various surface sites (Dzombak and Morel, 1990). Most of these reactions involve the release of H⁺ ions, which accounts for the strong dependence of adsorption on pH. Hydrous ferric oxide (HFO) is of particular interest because it is found at many contaminated sites and could play a major role in governing the mobility of lead, other metals, and metalloids (e.g., Trivedi et al., 2003; Dyer et al., 2003). Lead adsorbs more strongly onto HFO compared to most other divalent metal ions (Dzombak and Morel, 1990); the same is true for other ferric oxides, hydrous oxides, aluminum oxides, oxyhydroxides, clay minerals, and poorly ordered Fe- and Al-containing hydroxypolymer coatings on natural aquifer sediments (Sposito, 1984; Coston et al., 1995; O'Reilly and Hochella, 2003).

Long-term lab studies typically indicate that adsorption occurs in two steps: i) rapid initial surface sorption or exchange followed by, ii) continued but slow metal uptake. Ainsworth et al. (1994) reported on long-term aging studies of lead onto HFO. Consistent with previous investigations, they found that the adsorption of lead onto HFO increased sharply from 0 to 100% as pH increased from 3 to 6. The pH at which 50% of the lead was associated with the HFO surface was 4.7. The sorption behavior of lead onto HFO was found to be independent of time from 0 to 21 weeks of aging. In addition, desorption of lead from aged HFO exhibited no hysteresis with the adsorption pH edge developed from non-aged HFO. Ainsworth et al. (1994) concluded that the lead adsorption-desorption process is completely reversible with time and that there was no indication that lead was being incorporated into the HFO solid during aging. The process of recrystallization or aging may in fact result in the net loss of available sorption sites due to surface area reductions and may drive lead desorption (e.g., Ford et al., 1997).

Results of a series of laboratory experiments, which included studies of lead transport through columns packed with soil, were consistent with these concepts. Experiments showed that lead mobility decreased with increasing pH; lead adsorption resulted in decreases in pH, which, in turn, increased lead mobility; and, lead adsorption onto the soil was fast and reversible on the time-scale of transport (Papini et al., 1999).

Molecular studies of lead sorption onto hydrous ferric oxide show that Pb(II) ions associate with the iron hydroxide surface mainly as inner-sphere complexes (Trivedi et al., 2003). For most of the iron oxides, edge-sharing bidentate complexes are dominant at pH>5 over a wide range of adsorbate concentrations (e.g., Bargar et al., 1997; Manceau et al., 1992). Rouff et al. (2004) reached similar conclusions regarding lead sorption at the calcite-water interface. However, at higher initial concentrations of lead (4-12 mg L⁻¹), precipitation of lead carbonate dominates lead partitioning in the solid phase (Rouff et al., 2004).

Although lead adsorption in laboratory-based studies may be completely reversible, uptake of lead in natural systems is often substantially irreversible. Coughrey et al. (1986) reviewed soil measurements and suggested that only 50% of lead in soil was exchangeable. Others have noted substantially lower exchangeable fractions (see, e.g., Wang et al., 1995; Brady et al., 1999).

Adsorption of iron can influence the mobility of Pb even in the presence of strong complexing ligands like EDTA. Results of a transport experiment conducted in a mildly acidic, quartz-sand aquifer showed that Pb was displaced from EDTA complexes by Fe(III) dissolved from aquifer sediments over short transport distances (Davis et al., 2000). Even though Pb forms strong complexes with EDTA, strong adsorption of Pb at oxide surfaces enhances the thermodynamic driving force for displacement from EDTA complexes at mildly acidic pH values. However, decreasing solubility of Fe oxides with increasing pH decreases the affinity of the displacement reaction with increasing pH so that at pH values greater than 8 the reaction is unfavorable (Xue et al., 1995; Nowack et al., 2001). Lead was also displaced from EDTA complexes by Zn desorbed from Zn-contaminated sediments (Davis et al., 2000). These types of reactions may limit the extent to which complexing ligands enhance the transport of Pb in contaminated systems.

In reducing systems, adsorption of lead to iron sulfide surfaces is possible. Jean and Bancroft (1986) investigated the pH-dependent adsorption behavior of Pb on several iron sulfide minerals and found that the pH at which 50% of the lead was associated with the pyrite (FeS₂) surface was about 6.0. They suggested that the observed adsorption behavior is controlled by the hydrolysis of Pb²⁺ ions, whereby hydrolyzed species sorb directly on sulfide surface groups as a monolayer.

Lead adsorption onto or co-precipitation with amorphous FeS may be extensive in reducing systems. Experimental studies suggest that a significant fraction of the Fe in freshly precipitated FeS may be replaced rapidly by metal ions like Pb that form less soluble sulfides (Phillips and Kraus, 1965; Calecka et al., 1975; Coles et al., 2000).

**Redox Chemistry**

In natural systems lead is present in the +2 oxidation state over relevant conditions of pH and oxidation-reduction potential. Reduction of Pb²⁺ to metallic lead is expected to occur at redox potentials below the stability field of water at pH>6. The oxidized form of lead (Pb(IV)) is not expected in air-saturated solutions based on thermodynamic reasoning. However, the mineral platnerite (PbO₂) occurs in some natural systems and is associated with other oxidation products such as cerussite and pyromorphite (e.g., Yeates and Ayres, 1892; see Figure 2.3). In general, the geochemical transport processes of lead are not directly
Colloidal Transport

The transport of lead in particulate forms can be significant in ground water and surface water systems. Colloids are generally considered to be particles with diameters less than 10 micrometers (Stumm and Morgan, 1996). Colloidal particles can be present as mineral or organic forms. For the special case of lead sorbed to colloidal hydroxys ferric oxides, changes in geochemical regimes may either favor increased lead sorption or desorption. Increases in lead sorption may result from increases in pH or Eh. Conversely, decreases in pH or Eh may result in lead remobilization. Decreases in the ionic strength of the aqueous phase can enhance colloidal stability and promote lead transport, whereas increases in ionic strength can promote colloid aggregation and removal from the aqueous phase.

Site Characterization

Lead mobility in ground water is governed by the total concentration of lead, the distribution of lead species in water, and the nature of lead partitioning in the solid phase. The development of site-conceptual models for predicting the long-term fate of lead at a contaminated site will require information on the distribution and concentration of lead in the aqueous phase and the solid phase. Table 2.1 indicates possible natural attenuation and mobilization pathways for lead. Details of the types of analytical measurements that may be conducted on sampled ground water and aquifer sediments to assist in identifying the attenuation mechanism(s) are discussed in the following paragraphs.

Aqueous Measurements

Quantitative measurement of lead concentrations in aqueous solutions is typically carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS), or atomic absorption spectroscopy (AAS). Input data to geochemical codes (e.g., MINTEQA2, PHREEQC, EQ3/6) for determining aqueous speciation also require, at a minimum, concentrations of major anions, major cations, dissolved organic carbon, temperature, and pH. In addition, while regulatory requirements stipulate that unfiltered ground-water samples be analyzed to support regulatory decisions at a contaminated site, it may be necessary to also collect filtered samples to help define the process(es) controlling contaminant mobility. The use of 0.45 μm pore size filters is common as an arbitrary cutoff point to differentiate between dissolved and particulate phases in water samples. However, caution is recommended when using this approach, particularly for Fe and Al and other elements that may be associated with Fe or Al particles (including Pb) that could pass through 0.45 μm filters. The use of filters with pore sizes less than 0.1 μm will generally provide a better assessment of the dissolved vs. particulate load in ground water.

Solid Phase Measurements

The implementation of an analytical approach to identify lead speciation in aquifer sediments is a challenging process. The accuracy of the analytical finding is dependent on the method of sample collection/preservation and the tools used to identify the mechanism of lead partitioning. It is recommended that the analytical protocol be designed to address the potential redox sensitivity of the solid phase(s) to which lead may be partitioned (e.g., sulfides in reduced sediments). Tools to evaluate the mechanism of lead solid phase partitioning range in complexity from relatively simple chemical extractions to advanced spectroscopic techniques.

Table 2.1 Natural attenuation and mobilization pathways for lead.

<table>
<thead>
<tr>
<th>Attenuation Processes</th>
<th>Mobilization Processes</th>
<th>Characterization Approach</th>
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<tbody>
<tr>
<td>Precipitation of insoluble carbonates, sulfides, sulfates, and phosphates. In general, pH&gt;8 will drive precipitation reactions resulting in Pb concentrations below the MCL.</td>
<td>Dissolution of carbonates at low pH; oxidative dissolution of sulfides at low pH and high Eh; complexation/stabilization in the presence of DOC.</td>
<td>Evaluation of lead speciation in the aqueous phase. Determination of total Pb in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Evaluation of long-term capacity.</td>
</tr>
<tr>
<td>Sorption to iron hydroxides (reversible), organic matter, carbonates, sulfides (pH&gt;5).</td>
<td>Desorption at low pH; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides.</td>
<td>Evaluation of lead speciation in the aqueous phase. Determination of total Pb in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Batch and column testing to determine Pb uptake capacity of site-specific aquifer materials with variable geochemical conditions.</td>
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The total concentration of lead in soils, sediments, and aquifer materials may be determined by X-ray fluorescence spectroscopy (XRF), or by ICP-AES after digestion in mineral acids. A variety of digestion or extraction methods can be found in the literature (Amacher, 1996). Neutron activation analysis is not commonly employed due to the scarcity of neutron sources required to irradiate the sample. X-ray fluorescence is the most attractive approach due to the relative ease of sample preparation, which may be conducted with the sample in its original state or following fusion with lithium metaborate. When combined with the determination of other major or trace elements in the solid sample, this provides an initial step for assessing possible association of lead with various solid phase components. This type of analysis can be conducted on the bulk sample as well as at a microscopic level using wavelength (electron microprobe) or energy dispersive spectroscopy coupled to a scanning or transmission electron microscope. Microscopic examination allows one to better differentiate whether lead may be distributed across a number of different mineral phases within the solid sample or primarily associated with a discrete phase. There are limitations to this approach (Pye, 2004), a significant one being that the analysis does not necessarily provide unique mineral identification necessitating the collection of supporting mineralogical and chemical data.

More detailed information on the specific partitioning mechanism(s) controlling lead solid phase speciation is typically required to adequately support site assessment for potential reliance on natural attenuation as part of a site remedy. There have been many applications of sequential extraction schemes to assess the speciation of solid phase lead (e.g., Tessier et al., 1979; Harrington et al., 1998; Sutherland, 2002; Zänker et al., 2002; Buanum et al., 2006). As discussed in the cited reports, sequential extraction methods provide a useful tool to assist in determining the chemical speciation of trace metals in soils/sediments, but essentially all documented methods show analytical limitations in selectively extracting lead and other metals associated with specific solid components (e.g., Scheckel et al., 2003). Design and application of extraction procedures should take into account the chemical behavior of lead relative to potential analytical bias that may be introduced by the extraction chemistry. For example, due to its low solubility, lead carbonate would be anticipated to form during extractions conducted using solutions with pH buffered by an excess of dissolved bicarbonate-carbonate.

Where feasible, it is recommended that complimentary analytical techniques be employed to confirm the accuracy of lead speciation (e.g., O’Day et al., 1998; O’Day et al., 2000; Carroll et al., 2002; D’Amore et al., 2005) or the accuracy of the extraction of a targeted phase(es) for a given extractant (e.g., Shannon and White, 1991; Ngiam and Lim, 2001; Peltier et al., 2005). As an example, Peltier et al. (2005) have demonstrated that a common extraction method employed to target metals associated with easily reducible iron (hydr)oxides may also dissolve iron sulfides that may be present. The results from this analysis may lead to misidentification of a lead association with iron (hydr)oxides, resulting in the development of a conceptual site model that misrepresents the site-specific attenuation process. Under reducing conditions, it is also critical that aquifer sediments be sampled and processed in a manner that prevents exposure to oxygen prior to extraction in order to limit oxidation of reduced minerals (e.g., iron sulfides) that may host lead. Lead associated with a sulfidic phase in sediments has been shown to repartition to more extractable phases upon oxidation (Saeki et al., 1993; Cauwenberg and Maes, 1997). Determination of the host mineral phase(es) dissolved for each extraction step is recommended, along with the use of surrogate Pb-bearing phases spiked into the sediment to confirm accuracy of the procedure (e.g., Rudd et al., 1988). The choice of appropriate lead surrogate phases would be governed by site-specific geochemical conditions or characterization of the mineralogy of the aquifer sediment.

Pb Isotopes

Information about the source of lead contamination at a given site can be gained using isotopic analysis, particularly by examining the ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ (Emmanuel and Erel, 2002). As an example, Chow and Johnstone (1965) reported isotope ratios of lead extracted from gasoline (purchased in 1965). Their data demonstrated the similarity of the isotope compositions of lead in gasoline, airborne particles in Los Angeles, and snow from Lassen Volcanic Park. The study showed that lead in the air and snow in California in the 1960’s originated from fuel combustion exhaust. Gulson et al. (1981) analyzed the lead isotopic composition of soils in South Australia to identify the source of lead contamination. By analyzing and comparing isotope ratios they determined that orchard sprays, power stations, and smelters were not the principal source of lead contamination, rather lead contamination was again derived from tetraethyl lead in gasoline.

Long-term Stability and Capacity

The stability of attenuated lead will depend on the temporal stability of site geochemical conditions. For example, if lead attenuation follows a lead sulfide precipitation pathway, then long-term stability of attenuated lead may depend on the persistence of reducing conditions. It is therefore critical to understand attenuation mechanism(s) so that geochemical triggers for remobilization can be anticipated and incorporated into evaluations of long-term monitoring data. For any proposed and identified attenuation mechanism, there will exist possible scenarios whereby remobilization could occur (i.e., changes in pH or Eh). It will be essential to explore the likelihood of such changes in prevailing site geochemistry and the sensitivity of the attenuation pathway to changes in the prevailing geochemical conditions.

Quantifying the attenuation capacity (as defined in Volume 1) will also require an understanding of the specific attenuation pathway(s). Attenuation capacity, for example, could be related to the extent that pH is buffered, the availability of sorptive sites in aquifer materials, or to the supply of electron donors needed to sustain microbially mediated redox conditions. For any proposed attenuation mechanism,
there will be assumptions built into capacity estimations, so it is recommended that uncertainty analysis accompany capacity estimates.

**Tiered Analysis**

Determination of the viability of lead remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. MNA may not be appropriate as a site remedy for lead contamination in acidic to circum-neutral pH, highly oxidizing, and/or DOC-rich environments. The goal of site assessment is to demonstrate the process(es) controlling lead sequestration onto aquifer solids and the long-term stability of solid phase lead as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

**Tier I** - Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate Pb partitioning to aquifer solids within the plume. Rapid movement of contaminants along preferred flow paths in the unsaturated and saturated zones can be induced by hydrologic events such as heavy rains. It will be important to determine that such hydrogeologic features do not result in contaminants bypassing zones where natural attenuation is occurring. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by a lead precipitate such as a carbonate/phosphate or sulfide phase. Identification of active sequestration to prevent lead migration in ground-water provides justification for proceeding to Tier II characterization efforts.

**Tier II** - Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume. This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation need to be identified under this stage of site characterization. This effort may require determination of the chemical speciation of aqueous and solid phase Pb, which may be approached according to the following scheme:

1) Determination of lead solution speciation via direct analytical measurements in combination with speciation calculations based on characterized ground-water chemistry;
2) Calculation of the saturation state of ground water relative to measured aqueous chemistry complemented by the possible isolation of discrete Pb mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;
3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Pb sorption (e.g., Amonette, 2002);
4) Identification of lead association(s) with the various solid phase components of aquifer solids through combination of chemical extractions with microscopic/spectroscopic confirmation of phase associations, and;
5) Demonstration of concurrence between the site conceptual model and mathematical model(s) that describe lead removal mechanism(s).

It is recommended that identification of lead chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the in-situ distribution of dissolved lead and mineralogy and prevents loss of lead from aqueous samples (e.g., due to oxidation and precipitation of ferrous iron in anoxic ground water). The demonstration of concurrence between conceptual and mathematical models describing lead transport will entail development of site-specific parameterization of the chemical processes controlling lead solid phase partitioning.

**Tier III** - Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Pb and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized Pb be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage. For example, changes in ground-water pH can exert a significant influence on Pb adsorption or precipitate solubility. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of Pb mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for Pb uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that precipitation of Pb sulfide due to microbial degradation of organic compounds coupled with sulfate reduction occurs within the aquifer, then it is recommended that the mass distribution of organic carbon and sulfate to support this reaction within the aquifer be determined. This site-specific capacity can then be compared to Pb mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized Pb and sufficient capacity within the aquifer to sustain Pb attenuation, then the site characterization effort...
can progress to Tier IV. For cases where contaminant stabil-
ity is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction may be necessary.

**Tier IV** – Finally, under Tier IV a monitoring plan is estab-
lished along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated Pb. The specific chemical parameters to be monitored will include those identified un-
der Tier III that may halt Pb partitioning to aquifer sediments and/or result in solubilization of either discrete Pb precipi-
tates or aquifer minerals that sequester Pb from ground water. For example, solution phase parameters that could alter either Pb precipitation or adsorption include increases in soluble organic carbon in combination with changes in ground-water pH. In contrast, the concentration of dissolved iron or sulfate may indicate the dissolution of an important sorptive phase within the aquifer (e.g., reductive dissolution of iron oxides or oxidative dissolution of sulfides). Changes in these parameters may occur prior to observed changes in solution Pb and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of natural attenuation processes within the aquifer through the injection of soluble reactive components.

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 Nickel

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Occurrence and Distribution

Industrial activity and natural environmental conditions have led to the introduction of nickel into soil and aquatic environments as a result of anthropogenic and geogenic sources, respectively (Duke, 1980; Richter and Theis, 1980). Nickel is a relatively minor constituent of the earth’s crust having an average concentration of less than 0.01% by weight and ranking 24th in terms of abundance. Nickel is very heterogeneously distributed among crustal rocks ranging from less than 0.0001% in sandstone and granite to 4% in coveted ore deposits (Duke, 1980). Nickel can be found in igneous, sedimentary, and metamorphic rocks as well as nickel ores. In soils, nickel ranges from 5 – 500 mg kg\(^{-1}\) (Lindsay, 1979). Serpentine clay-rich soils are noted for natural geogenic abundance of nickel and have been the focus for use of hyperaccumulating plants to phytomine nickel (Chaney et al., 1995).

Nickel is one of the most mobile of the heavy metals in the aquatic environment. The mobility of nickel in the aquatic environment is controlled largely by competition between various sorbents to scavenge it from solution and ligands to form non-sorptive complexes. Although data are limited, it appears that in pristine environments, hydrous oxides and phyllosilicates control nickel mobility via co-precipitation and sorption. In polluted environments, the more prevalent organic compounds will keep nickel soluble by ligand complexation. In reducing environments, insoluble nickel sulfide may form. Nickel chloride is water-soluble and would be expected to release divalent nickel into the water. The atmosphere is a major conduit for nickel as particulate matter. Contributions to atmospheric loading come from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. Various dry and wet precipitation processes remove particulate matter as wash out or fallout from the atmosphere with transfer to soils and waters. Soil borne nickel may enter waters by surface runoff or by percolation into ground water. Once nickel is in surface and ground-water systems, physical and chemical interactions (complexation, precipitation/dissolution, adsorption/desorption, and oxidation/reduction) occur that will determine its fate and that of its constituents. The only gaseous nickel compound of environmental importance is nickel carbonyl. Under ambient conditions in moist air, it decomposes to form nickel carbonate. Thus, in the atmosphere at concentrations near the ppb level, it has a half-life of about 30 minutes. The removal of nickel carbonyl by precipitation or by adsorption on surfaces has not been documented. Since this compound is soluble in water, precipitation scavenging is possible. Nothing is known about its reaction with natural surfaces or its uptake by vegetation. Thus, dry deposition rates cannot be predicted until some experimental investigations have been conducted. Although nickel is bioaccumulated, the concentration factors are such as to suggest that partitioning into the biota is not a dominant fate process.

Production of nickel was 84.6 million pounds in 1986, down slightly from 90 million pounds reported in 1982. In 1986 it was estimated that industries consumed nickel as follows: transportation, 25%, chemical industry, 15%; electrical equipment, 9%; construction, 9%; fabricated metal products, 9%; petroleum, 8%; household appliances, 7%; machinery, 7%; and other, 11%. Nickel carbonate is used in nickel catalyst production for organic chemical manufacture, petroleum refining and edible oil hardening. Nickel oxide consumption in 1972 (representing over 30 million pounds containing nickel) is estimated to have been as follows: 60% for stainless and heat resisting steels, 27% for other steel alloys, 8% for other nickel alloys, 2% for cast irons, and 3% for other uses (USEPA, 1986). From 1987 to 1993, according to the Toxics Release Inventory nickel released to land and water totaled nearly 27 million pounds, of which most was to land. These releases were primarily from nickel smelting/refining and steelworks industries. The largest releases occurred in Oregon and Arkansas. The largest direct releases to water occurred in Maryland and Georgia (USEPA, 2003).

Plume Characteristics

The mobility of nickel in ground water will be controlled by partitioning reactions to aquifer sediments. Possible mechanisms influencing nickel partitioning to subsurface solids include direct adsorption to clay minerals, adsorption and/or coprecipitation with metal oxides, complexation with natural organic particles, ion exchange with charged surfaces, and direct precipitation as an hydroxide, carbonate or sulfide (Snodgrass, 1980). The chemical speciation of nickel in solution exerts a significant influence on the extent and mechanism(s) of partitioning to aquifer sediments, which may be influenced by acid-base reactions, oxidation-reduction reactions influencing the speciation of complexing inorganic solution species (e.g., aqueous sulfate vs. sulfide), and interactions with dissolved organic compounds. In general, inorganic/organic species that form dissolved complexes with nickel tend to enhance transport.
of nickel in soil profiles to subsurface water (e.g., dissolved organic carbon; Christensen et al., 1996; Warwick et al., 1997; Christensen and Christensen, 2000; Friedly et al., 2002). Field studies on transport in the subsurface illustrate several general conditions that are anticipated to result in expanding nickel plumes, including 1) acidic conditions (Kjoller et al., 2004), 2) manganese- and iron-reducing conditions (Larsen and Postma, 1997), and 3) the presence of mobile organic compounds that form soluble nickel complexes (Christensen et al. 1996; Kent et al., 2002).

**Remedial Technologies**

Possible engineered approaches that can be employed for remediation of a ground-water plume containing nickel include physical removal of contaminated soils or sediments that serve as a long-term source of nickel leached into ground water, extraction of the dissolved plume with some method of above-ground treatment, physical isolation of the dissolved plume, or in-situ treatment of a dissolved plume resulting in immobilization of dissolved nickel within the aquifer. Of these technologies, the use of permeable reactive barriers (PRBs) for the capture and immobilization of nickel plumes has been investigated and applied in field settings due to favorable performance and cost characteristics (Blowes et al., 2000). Both carbon- and metallic iron-based (or zero valent iron) reactive media have been employed for nickel removal from ground water. For carbon-based media, nickel removal is generally considered to occur through the precipitation of sulfide minerals, including nickel sulfides or coprecipitation of nickel with iron sulfides (e.g., Ludwig et al., 2002; McGregor et al., 2002). Reactive sulfide is generated in this type of PRB as a result of microbial sulfate reduction stimulated by degradation of an organic carbon substrate incorporated into the reactive barrier media. Zerovalent iron media have also been tested for the removal of nickel in ground water (e.g., Wilkin and McNeil, 2003). For this material, nickel removal may be achieved either through the stimulation of sulfate reduction with precipitation as a sulfide or through coprecipitation with or adsorption onto metallic iron corrosion products such as iron (hydr)oxides. There is also laboratory and field evidence that nickel immobilization can be enhanced through the addition of chemical amendments that promote nickel precipitation within soil or aquifer sediments (e.g., LaRocque and McBride, 1997; Boisson et al., 1999; Seaman et al., 2001). The applicability and performance of these technologies will depend on the geochemical characteristics within the ground-water plume in conjunction with the velocities of ground-water flow and the flux of beneficial and non-beneficial reactive components transported within the plume.

**Aqueous Speciation**

In ambient aqueous systems, nickel exists in the divalent oxidation state and is not subject to oxidation-state transformations under typical conditions. Nickel predominantly exists as a cationic species (Ni^{2+}) or various hydrolysis species (e.g., NiOH^+) at near-neutral pH (Baes and Mesmer, 1986). However, nickel may also form dissolved complexes in the presence of high concentrations of inorganic ions such as carbonate/bicarbonate and sulfate (Hummel and Curti, 2003; Chen et al., 2005) or organic ligands such as natural/synthetic carboxylic acids and dissolved humic compounds (Bryce and Clark, 1996; Baeyens et al., 2003; Strathman and Mynden, 2004). It is anticipated that nickel may form complexes with dissolved sulfate under sulfate-reducing conditions, although the current state of knowledge is insufficient to ascertain the relative importance of these species in aqueous systems (Thoenen, 1999). The formation of solution complexes, especially with organic ligands, may limit sorption of nickel to mineral surfaces in aquifer sediments (see Adsorption section below).

**Solubility**

Nickel may be immobilized within ground water through formation of pure nickel precipitates such as hydroxides, silicates, or sulfides (Merlen et al., 1995; Mattigod et al., 1997; Scheidegger et al., 1997; Thoenen, 1999; Scheinost and Sparks, 2000; Peltier et al., 2006) or through coprecipitation with other soil forming minerals such as silicates, iron oxides/sulfides, or carbonates (Manceau et al., 1985; Manceau and Calas, 1986; Huerta-Diaz and Morse, 1992; Ford et al., 1997; Scheidegger et al., 1997; Thoenen, 1999; Hoffmann and Stipp, 2001). Predicted nickel concentrations in the absence of sulfide for several potential pure nickel precipitates are shown in Figure 3.1. These data suggest that phyllosilicate and layered double hydroxide (LDH) precipitates (incorporating aluminum) may result in dissolved nickel concentrations below most relevant regulatory criteria over a pH range typical for ground water.
These data also point to the limited capability of pure nickel carbonates and hydroxides in controlling dissolved nickel concentrations to sufficiently low values except under very alkaline conditions. In the presence of dissolved sulfide, the precipitation of a nickel sulfide may plausibly control the concentration of dissolved nickel. The Eh-pH conditions under which these solubility-limiting phases may form is shown in Figure 3.2. According to these data, nickel-bearing phyllosilicate and/or LDH precipitates possess large stability fields indicating their relative importance to controlling nickel solubility under a range of conditions. These calculations point to the importance of dissolved aluminum and silicon concentrations in ground water relative to the potential sequestration of nickel via precipitation (Ford et al., 1999b; Scheinost et al., 1999). As discussed below (see Adsorption section), the formation of these nickel-bearing precipitates may be facilitated through initial adsorption onto clay minerals within the aquifer.

Figure 3.1  (a) Predicted solubility of various Ni precipitates that could form in aerobic ground water with concentrations of Al and Si controlled by the solubility of the clay mineral, kaolinite. (Note y-axis break to expand lower end of scale.) (b) Expansion of dissolved Ni data for equilibrium with Ni phyllosilicate; plotted on logarithmic scale. Nominal ground-water composition: 0.005 mole/L NaCl, 0.001 mole/L K₂SO₄, 0.001 mole/L MgNO₃, 0.001 mole/L CaCO₃, and 34 μmole/L Ni (2000 μg Ni/L). Model predictions using Visual MINTEQ Version 2.50 (Based on MINTEQA2 described in Allison et al. (1991); available at http://www.lwr.kth.se/English/OurSoftware/vminteq/) with solubility constants added for Ni phyllosilicate, Ni-Al-SO₄ LDH, and Ni-Al-CO₃ LDH (Peltier et al., 2006); total dissolved Ni concentrations modeled individually for each Ni solid phase by setting kaolinite as an ‘infinite’ solid and the Ni solid phase as a ‘possible’ solid for each pH titration.

Figure 3.2  Eh-pH diagrams for nickel at 25 °C. (a) System Ni-H₂O-Ca-Al-NO₃-HCO₃-SO₄ (2 mg Ni/L; 40 mg Ca/L; 3 mg Al/L; 6 mg NO₃/L; 60 mg HCO₃/L; 100 mg SO₄/L). Stability fields for solids are shaded green (Vaesite = NiS₂). (b) Same system plus 3 mg Si/L. Thermodynamic data for Ni₆₆Si₃Al₃(OH)₉(SO₄)₀.₁₂₅(OH)₀.₅ are from Peltier et al. (2006). [Note that the solubility of the Ni-Al-SO₄ LDH was adjusted to correct for charge imbalance for the chemical structure published in Peltier et al. (2006).]
Attenuation of nickel may also occur via coprecipitation during the formation of (hydr)oxides or sulfides of iron. These minerals have been observed to form at the boundaries between oxidizing and reducing zones within ground-water plumes. There are numerous laboratory and field observations that demonstrate the capacity of these precipitates for nickel uptake (Schultz et al., 1987; Huartadiaz and Morse, 1992; Coughlin and Stone, 1995; Ford et al., 1997; Ford et al., 1999a). Under these circumstances, the solubility of nickel will depend on the stability of the host precipitate phase. For example, iron oxide precipitates may alternatively transform to more stable forms (Ford et al., 1997), stabilizing coprecipitated nickel over the long term, or these precipitates may dissolve concurrent with changes in ground-water redox chemistry (e.g., Zachara et al., 2001).

**Adsorption**

Adsorption of nickel in soil environments is dependent on pH, temperature, and type of sorbent (minerals or organic matter), as well as the concentration of aqueous complexing agents, competition from other adsorbing cations, and the ionic strength in ground water. Nickel has been shown to adsorb onto many solid components encountered in aquifer sediments, including iron/manganese oxides, clay minerals (Dähn et al., 2003; Bradbury and Baeyens, 2005), and solid organic matter (Nachtegaal and Sparks, 2003). Sorption to iron/manganese oxides and clay minerals has been shown to be of particular importance for controlling nickel mobility in subsurface systems. The relative affinity of these individual minerals for nickel uptake will depend on the mass distribution of the sorbent minerals as well as the predominant geochemical conditions (e.g., pH and nickel aqueous speciation). For example, the pH-dependent distribution of nickel between iron and manganese oxides [hydror ferric oxide (HFO) and a birnessite-like mineral (nominally MnO₂)] for a representative ground-water composition is shown in Figure 3.3a. Based on the available compilations for surface complexation constants onto these two solid phases (Dzombak and Morel, 1990; Tonkin et al., 2004), one would project the predominance of nickel sorption to MnO₂ at more acidic pH and the predominance of HFO (or ferrihydrite) at more basic pH. With increasing mass of MnO₂, the solid-phase speciation of nickel will be progressively dominated by sorption to this phase. There are examples of the relative preference of nickel sorption to manganese oxides over iron oxides for natural systems (e.g., Larsen and Postma, 1997; Manceau et al., 2002; Kjoller et al., 2004; Manceau et al., 2006). As shown in Figure 3.3b, nickel adsorption may be inhibited (or nickel desorption enhanced) through the formation of solution complexes with organic ligands such as EDTA or natural organic matter (e.g., Bryce and Clark, 1996; Nowack et al., 1997). These dissolved compounds may be present as natural components within ground water or as co-contaminants within a contaminant plume (e.g., Means et al., 1978).

**Figure 3.3** (a) Nickel sorption as a function of pH in the presence of an hypothetical aquifer sediment with iron and manganese oxides reflective of the crustal abundance of these elements (Schulze, 2002; assumed 30% porosity with 185.0 g HFO/L and 1.66 g MnO₂/L). (b) Same conditions as in (a), but with 10 μM EDTA added. Nominal ground-water composition: 0.005 mole/L NaCl, 0.001 mole/L K₂SO₄, 0.001 mole/L MgNO₃, 0.001 mole/L CaCO₃, and 34 μmole/L Ni (2 mg Ni/L). Model predictions using Visual MINTEQ Version 2.50 (Based on MINTEQA2 described in Allison et al. (1991); available at http://www.lwr.kth.se/English/OurSoftware/vminteq/) with available surface complexation parameters derived from Dzombak and Morel (1990) and Tonkin et al. (2004); kaolinite set as an ‘infinite’ solid for pH titration.
As previously noted, adsorption of nickel onto mineral surfaces may serve as a precursory step to the formation of trace precipitates that reduce the potential for desorption with changes in ground-water chemistry. This may be realized through the nucleation and growth of surface precipitates on clay mineral surfaces due to continued uptake of nickel (Scheckel and Sparks, 2000; Scheckel et al., 2000; Dähn et al., 2002). This type of process may compete with other adsorption processes, such as ion exchange, depending on the prevailing ground-water chemistry and characteristics of the clay mineral (Elzinga and Sparks, 2001).

**Site Characterization**

**Overview**

Nickel mobility in ground water is governed by the total concentration of nickel, the distribution of nickel species in water, and the nature of nickel partitioning in the solid phase. The development of site-conceptual models for predicting the long-term fate of nickel at a contaminated site will require information on the distribution and concentration of nickel in the aqueous phase and the solid phase. Table 3.1 indicates possible natural attenuation and mobilization pathways for nickel. Details of the types of analytical measurements that may be conducted on sampled ground water and aquifer sediments to assist in identifying the attenuation mechanism(s) are discussed in the following paragraphs.

<table>
<thead>
<tr>
<th>Attenuation Processes</th>
<th>Mobilization Processes</th>
<th>Characterization Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation of Ni as carbonate, layered double hydroxide, or phyllosilicate phase in oxidized/reduced systems; precipitation of Ni as a sulfide in sulfate-reducing systems</td>
<td>Dissolution of Ni precipitates due to decreased pH; dissolution of NiS due to shift from reducing to oxidizing conditions.</td>
<td>Evaluation of dissolved Ni concentration in ground water. Determination of total Ni in the solid matrix and suspected components in Ni-bearing precipitate. Evaluation of mineral solubility relative to ground-water chemistry and published solubility constants.</td>
</tr>
<tr>
<td>Co-precipitation of Ni as a trace component in oxyhydroxides or sulfides of iron or manganese</td>
<td>Dissolution of host oxyhydroxide due to decrease in pH or shift from oxidizing to reducing conditions; dissolution of host sulfide due to shift from reducing to oxidizing conditions.</td>
<td>Evaluation of Ni concentration in ground water and in solid matrix. Evaluation of host precipitate formation relative to existing ground-water chemistry; determination of host mineral content in aquifer sediments via mineralogical characterization. Evaluation of Ni solid-phase partitioning using sequential extraction methodologies.</td>
</tr>
<tr>
<td>Adsorption of Ni to iron oxyhydroxides, iron sulfides, or other mineral surfaces</td>
<td>Desorption due to low pH, high competing cation concentrations, or high DOC concentrations for oxyhydroxides and sulfides. Reductive dissolution of iron oxyhydroxides or oxidative dissolution of iron sulfides.</td>
<td>Evaluation of Ni concentration in ground water and in solid matrix. Evaluation of Ni solid-phase partitioning using sequential extraction methodologies. Batch and column testing to determine Ni uptake behavior and capacity of site-specific aquifer materials under variable geochemical conditions.</td>
</tr>
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</table>

**Aqueous Measurements**

The total concentration of nickel in aqueous samples can be determined by an array of methods ranging significantly in sensitivity, detection limits, and accuracy. For aqueous systems, nickel can be measured by flame/graphite furnace atomic absorption (FAAS and GFAAS, respectively), inductively coupled plasma atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS), colorimetry, ion chromatography, and electrochemical methods (Stoeppler, 1980). The standard colorimetric method for nickel is the dimethylglyoxime (DMG) method (Amacher, 1996). Ion chromatography works well for nickel in determining total nickel in soil digestion solutions (Basta and Tabatabai, 1990). Electrochemical methods (e.g., anodic stripping voltammetry, platinum electrode differential oscillipolarography, or differential pulse polarography) are well suited for aqueous samples and often employ DMG-coated electrodes to concentrate nickel for better sensitivity (Stoeppler, 1980). Of the list above, FAAS, GFAAS, ICP-OES, or ICP-MS are the most common methods employed.

For ground water with elevated concentrations of dissolved organic carbon (e.g., landfill leachates) or known organic co-contaminants such as EDTA, it may be necessary to determine the chemical speciation of dissolved nickel. Geochemical speciation models (e.g., MINTEQA2, PHREEQC, EQ3/6) may be employed to assist in determining aqueous nickel speciation, but the...
accuracy of existing codes and/or associated geochemical databases for assessing complexion with dissolved organic carbon has been questioned (e.g., Christensen and Christensen, 2000). These computer speciation codes also require, at a minimum, the concentrations of major anions, major cations, total organic carbon (or specific species of organic compounds), temperature, and pH. Direct determination of the fraction of organic-complexed nickel may be accomplished through analytical fractionation of nickel using various exchange resins (e.g., Christensen and Christensen, 2000; Jian and Presley, 2002). As noted by Jiann and Presley (2002), the approach to sample preservation prior to separation may depend on whether fractionation can be conducted in the field or at a later time in the laboratory. Voltammetric measurements may also be employed to examine the relative distribution and stability of nickel complexes with dissolved organic compounds in water (e.g., Van den Berg and Nimmo, 1987; Bedsworth and Sedlak, 1999). Supporting data for these measurements would include determinations of total dissolved organic carbon along with specific organic constituents suspected in the ground-water plume. In addition, while regulatory requirements stipulate that unfiltered ground-water samples be analyzed to support regulatory decisions at a contaminated site, it may be necessary to also collect filtered samples to help define the process(es) controlling contaminant mobility. The use of 0.45 μm pore size filters is common as an arbitrary cutoff point to differentiate between dissolved and particulate phases in water samples. However, caution is recommended when using this approach, particularly for Fe and Al and other elements that may be associated with Fe or Al particles (including Ni) that could pass through 0.45 μm filters. The use of filters with pore sizes less than 0.1 μm will generally provide a better assessment of the dissolved vs. particulate load in ground water.

It has also been observed that nickel may be leached from certain grades of stainless steel well casing/screen materials under chemical conditions that may be encountered in contaminant plumes. Two published studies have provided detailed evaluation of the extent of nickel (and chromium) leaching that may occur for type 304 or 316 stainless steel screens (Hewitt, 1994; Oakley and Korte, 1996). Oakley and Korte (1996) provide a site-specific example of how elevated nickel concentrations derived from continuous leaching of well screen materials may be falsely identified as a component of a ground-water plume. This suggests that careful consideration should be given to the types of well screen materials and sampling protocols employed relative to the assessment of potential contaminants of concern within a plume.

**Solid Phase Measurements**

The implementation of an analytical approach to identify nickel speciation in aquifer sediments is a challenging process. The accuracy of the analytical finding is dependent on the method of sample collection/preservation and the tools used to identify the mechanism of nickel partitioning. It is recommended that the analytical protocol be designed to address the potential redox sensitivity of the solid phase(s) to which nickel may be partitioned (e.g., sulfides in reduced sediments). Tools to evaluate the mechanism of nickel solid phase partitioning range in complexity from relatively simple chemical extractions to advanced spectroscopic techniques.

Bulk solid phase nickel concentration can be determined directly on the solid sample by X-ray fluorescence spectrometry, neutron activation analysis, or following chemical digestion and analysis of nickel in the resultant liquid phase. A variety of digestion or extraction methods can be found in the literature (Amacher, 1996). Neutron activation analysis is not commonly employed due to the scarcity of neutron sources required to irradiate the sample. X-ray fluorescence is the most attractive approach due to the relative ease of sample preparation, which may be conducted with the sample in its original state or following fusion with lithium carbonate. When combined with the determination of other major or trace elements in the solid sample, this provides an initial step for assessing possible association of nickel with various solid phase components. This type of analysis can be conducted on the bulk sample as well as at a microscopic level using wavelength (electron microscope) or energy dispersive spectroscopy coupled to a scanning or transmission electron microscope. Microscopic examination allows one to better differentiate whether nickel may be distributed across a number of different mineral phases within the solid sample or primarily associated with a discrete phase. There are limitations to this approach (Pye, 2004), a significant one being that the analysis does not necessarily provide unique mineral identification necessitating the collection of supporting mineralogical and chemical data.

More detailed information on the specific partitioning mechanism(s) controlling nickel solid phase speciation is typically required to adequately support site assessment for potential reliance on natural attenuation as part of a site remedy. There have been many applications of sequential extraction schemes to assess the speciation of solid phase nickel (e.g., Tessier et al., 1979; Ryan et al., 2002; Peltier et al., 2005; Buanuam et al., 2006). As discussed in the cited reports, sequential extraction methods provide a useful tool to assist in determining the chemical speciation of trace metals in soils/sediments, but essentially all documented methods show analytical limitations in selectively extracting nickel and other metals associated with specific solid components. Where feasible, it is recommended that complimentary analytical techniques be employed to confirm the accuracy of nickel speciation (e.g., D’Amore et al., 2005; Manceau et al., 2006) or the accuracy of the extraction of a targeted phase(es) for a given reagent (e.g., Shannon and White, 1991; Ryan et al., 2002; Peltier et al., 2005). As an example, Peltier et al. (2005) have demonstrated that a common extraction method employed to target metals associated with easily reducible iron (hydr)oxides may also dissolve iron sulfides that may be present. The results from this analysis may lead to misidentification of a nickel association with iron (hydr)oxides, resulting in the development of a conceptual site model that misrepresents the site-specific nature of nickel contamination.
attenuation process. Under reducing conditions, it is also critical that aquifer sediments be sampled and processed in a manner that prevents exposure to oxygen prior to extraction in order to limit oxidation of reduced minerals (e.g., iron sulfides) that may host nickel. Determination of the host mineral phase(s) dissolved for each extraction step is recommended, along with the use of surrogate Ni-bearing phases spiked into the sediment to confirm accuracy of the procedure (e.g., Rudd et al., 1988). The choice of appropriate nickel surrogate phases would be governed by site-specific geochemical conditions or characterization of the mineralogy of the aquifer sediment.

**Long-term Stability and Capacity**

The stability of attenuated nickel will largely depend on the stability of site-specific geochemical conditions through time. For example, if nickel attenuation follows a pathway of coprecipitation with iron sulfide, then the long-term stability of attenuated nickel will depend, in part, on the persistence of reducing conditions. If ground-water redox conditions were to shift to oxidizing conditions, nickel might be expected to release from the solid phase. It is therefore important to understand the attenuation mechanism(s) so that geochemical triggers for mobilization can be anticipated and incorporated into evaluations of long-term monitoring data. For any proposed and identified attenuation mechanism, there will exist possible scenarios whereby remobilization could occur (i.e., changes in pH or Eh). It will be essential to explore the likelihood of such changes in site geochemistry and the sensitivity of the attenuation pathway to changes in the prevailing geochemical conditions.

Quantifying the attenuation capacity (as defined in Volume 1) will also require an understanding of the specific attenuation pathway(s). Attenuation capacity, for example, could be related to the extent that pH is buffered, the availability of sorptive sites in aquifer materials, or to the supply of electron donors needed to sustain microbially mediated redox conditions. For any proposed attenuation mechanism, there will be assumptions built into capacity estimations, so it is recommended that uncertainty analysis accompany capacity calculations.

**Tiered Analysis**

Determination of the viability of nickel remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. The goal of site assessment is to demonstrate the process(es) controlling nickel sequestration onto aquifer solids and the long-term stability of solid phase nickel as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

**Tier I** - Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate Ni partitioning to aquifer solids within the plume. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by a nickel precipitate such as phyllosilicate or sulfide phase. Identification of active sequestration to prevent nickel migration in ground-water provides justification for proceeding to Tier II characterization efforts.

**Tier II** - Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume. This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation need to be identified under this stage of site characterization. This effort may require determination of the chemical speciation of aqueous and solid phase Ni, which may be approached according to the following scheme:

1) Determination of nickel solution speciation via direct analytical measurements in combination with speciation calculations based on characterized ground-water chemistry;

2) Calculation of the saturation state of ground water relative to measured aqueous chemistry complemented by the possible isolation of discrete Ni mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;

3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Ni sorption (e.g., Amonette, 2002);

4) Identification of nickel association(s) with the various solid phase components of aquifer solids through combination of chemical extractions with microscopic/spectroscopic confirmation of phase associations, and;

5) Demonstration of concurrence between the site conceptual model and mathematical model(s) that describe nickel removal mechanism(s).

It is recommended that identification of nickel chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the in-situ distribution of dissolved nickel and mineralogy and prevents loss of nickel from aqueous samples (e.g., due to oxidation and precipitation of ferrous iron in anoxic ground water).
The demonstration of concurrence between conceptual and mathematical models describing nickel transport will entail development of site-specific parameterization of the chemical processes controlling nickel solid phase partitioning.

**Tier III** - Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Ni and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized Ni be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage. For example, changes in ground-water pH can exert a significant influence on Ni adsorption or precipitate solubility. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of Ni mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for Ni uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that precipitation of Ni sulfide due to microbial degradation of organic compounds coupled with sulfate reduction occurs within the aquifer, then it is recommended that the mass distribution of organic carbon and sulfate to support this reaction within the aquifer be determined. This site-specific capacity can then be compared to Ni mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized Ni and sufficient capacity within the aquifer to sustain Ni attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction may be necessary.

**Tier IV** – Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated Ni. The specific chemical parameters to be monitored will include those identified under Tier III that may halt Ni partitioning to aquifer sediments and/or result in solubilization of either discrete Ni precipitates or aquifer minerals that sequester Ni from ground water. For example, solution phase parameters that could alter either Ni precipitation or adsorption include increases in soluble organic carbon in combination with changes in ground-water pH. In contrast, the concentration of dissolved iron or sulfate may indicate the dissolution of an important sorptive phase within the aquifer (e.g., reductive dissolution of iron oxides or oxidative dissolution of sulfides). Changes in these parameters may occur prior to observed changes in solution Ni and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of natural attenuation processes within the aquifer through the injection of soluble reactive components.

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Copper

Richard T. Wilkin

Occurrence and Distribution
Copper is a minor element in the earth’s crust, ranking 25th in abundance and having an average concentration of 25 mg kg⁻¹ (Wedepohl, 1995). Crustal copper concentrations vary as a function of lithologic type and proximity to hydrothermal deposits of copper and other base metals. Mafic and ultramafic rocks such as basalts are usually more enriched in copper compared to rocks that make up continental crust such as granites and rhyolites. Median concentrations of copper reported in a survey of sediments and soils range from 7 to 35 mg kg⁻¹ (Reimann and Caritat, 1998). Ores of copper are highly diverse and range from: native copper deposits hosted in sulfur-poor basaltic and andesitic rocks; copper sulfides hosted in layered mafic intrusions, altered porphyritic rocks, and submarine massive sulfide bodies; and, copper oxides, carbonates, and sulfates formed in supergene deposits through the weathering of primary sulfide deposits (Guilbert and Park, 1986).

It is believed that the ancient civilizations of Mesopotamia (region of modern Iraq) made use of native copper and gold, possibly as far back as ca. 8700 BC. Indeed the exploitation of natural deposits of copper and gold, which are soft metals that can be hammered into shape without heat, marked the transition from the Stone Age to more modern ways of life (Diamond, 1997). Typical copper-bearing minerals include native copper, sulfides (chalcopyrite, CuFeS₂; bornite, Cu₁FeS₄; chalcocite, Cu₂S; covellite, CuS; digenite, Cu₉S₅), sulfosalts (tetrahedrite, Cu₁₂Sb₄S₁₃), carbonates (malachite, Cu₂(OH)₂CO₃; azurite, Cu₂(OH)₂(CO₃)₂), and oxides (tenorite, CuO). In the US, the principal copper mining states are Arizona, Utah, and New Mexico. In 2004, domestic mine production of copper was about 1.16 million tons, or about 8% of world mine production. While the US is the world’s second-largest producer of copper, it is the world’s largest copper-consumer. The principal modern use of copper is as an electrical conductor. Alloys of copper (e.g., brass and bronze) are used in jewelry, sculptures and for minting coins. Copper also has broad uses as an agricultural poison and as an algacide in water purification.

Plume Characteristics
Copper has five possible oxidation states (0, +1, +2, +3, and +4). Under most conditions, copper is present in aqueous solution as the divalent cation, Cu²⁺, or as Cu(II) hydroxide or carbonate complexes. However, copper is not especially mobile in aquatic environments due to the relatively low solubility of Cu(II)-bearing solids and high affinity of copper for mineral and organic surfaces. Certain organic compounds are able to keep copper soluble by ligand complexation. Hence, copper does not typically enter ground water except under conditions of low pH or high ligand concentrations. Where present, copper contamination in soils and ground water stems primarily from mining activities, metal production, wood production, fertilizer production, and combustion of fossil fuels and wastes (e.g., Bochenska et al., 2000; Zagury et al., 2003). Copper is not included on the CERCLA Priority List of Hazardous Substances, which is based on the frequency of occurrence of specific contaminants at National Priorities List (NPL) sites and their potential threat to human health. An internet search showed, however, that in 2005 copper was listed as a potential contaminant of concern (COC) in ground water at 287 NPL sites in EPA Regions 1-10.

Remedial Technologies
The primary techniques for dealing with copper-contaminated soils involve immobilization and/or extraction. Immobilization involves binding copper or other heavy metals to the soil matrix by solidification or stabilization. In this way, contaminated soils become less soluble, and hazardous compounds are prevented from entering ground water or surface water. Extraction involves a combination of processes to actually remove heavy metals from soil, for example, soil washing whereby metals are transferred into solution via solubilization by acids, bases, or chelating agents. In contrast to soils remediation, there are comparatively few examples of ground-water remediation demonstrations that focus on copper. In situ bioremediation to promote bacterial sulfate-reduction and consequent precipitation of insoluble copper sulfides has been proposed (Dvorak et al., 1992; Steed et al., 2000; Tabak et al., 2003). Permeable reactive barriers that are designed to intercept and treat contaminated ground water could be appropriate for dealing with copper contamination. Woinarski et al. (2003) discuss the application of a natural zeolite (clinoptilolite) in reactive barriers for removing copper via ion exchange (see also Inglezakis et al., 2003 and Park et al., 2002). Other reactive media explored in laboratory studies for treating copper include zerovalent iron (Wilkin and McNeil, 2003) and municipal compost (Waybrant et al., 1998).
**Regulatory Aspects**

The USEPA has set the Maximum Concentration Limit Goal (MCLG) of copper in drinking water at 1.3 mg L\(^{-1}\) (USEPA, 2006a; http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf). Copper is a trace element essential for good human health. It is part of the prosthetic groups of many proteins and enzymes and thus is essential to their proper function. Potential health effects from ingesting water with high concentrations of copper include gastrointestinal distress, and potential damage to the liver and kidneys. For non-potable water sources, ambient water quality criteria (AWQC) that are protective of aquatic life may serve as alternative cleanup goals. For copper, current statutes list both acute and chronic criteria for fresh waters as 0.016 mg L\(^{-1}\) and 0.011 mg L\(^{-1}\), respectively, for a water hardness of 100 mg L\(^{-1}\) (USEPA, 2006b; http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf). Adjustments to these criteria are to be applied for waters with different hardness. An example of where this criterion may apply is a site where contaminated ground water discharges to surface water.

**Geochemistry and Attenuation Processes**

**Aqueous Speciation**

Copper complexes are possible in the +1, +2, +3, and +4 valence states. Copper(III) and (IV) complexes are rare and unstable in water. Cu(I) complexes are present under reducing conditions but in general cuprous ions are highly insoluble in water. Cu(II) is the main oxidation state for soluble complexes of copper in aquatic environments. Cu(II) forms complexes with both hard (e.g., CO\(_3\)^{2-}, SO\(_4\)^{2-}, OH\(^-\), and Cl\(^-\)) and soft (e.g., S\(^2\), I\(^-\)) bases (Stumm and Morgan, 1996). The stereochemistry of Cu(II) principally involves distorted tetragonal (coordination number 4) or octahedral (coordination number 6) configurations. Cu(II) complexes are subject to the Jahn-Teller effect that acts to stabilize species with the d\(^{9}\) electronic configuration that are present in tetragonal or octahedral coordination.

In pure water, Cu\(^{2+}\) is the predominant ion below pH 7. Above this pH, the species CuOH\(^+\), Cu(OH)\(_2\)^{0}, and CuO\(_2\)^{2-} become increasingly important. Because of uncertainties in the estimates and measurements of the thermodynamic constants for copper complex formation, the speciation of copper in natural waters is not known in detail (e.g., Boyle, 1979; Leckie and Davis, 1979; Baes and Mesmer, 1976). Most models, however, predict that Cu\(^{2+}\) is a small fraction of the total copper concentration in freshwater and seawater systems and that complexed forms of copper are dominant.

A survey of references that report hydrolysis constants for Cu\(^{2+}\) shows considerable variability in species identified and in their formation constants (see e.g., Baes and Mesmer, 1976; Leckie and Davis, 1979 and references therein). Figure 4.1 shows the pH-dependent distribution of Cu\(^{2+}\) hydrolysis species based on the Lawrence Livermore National Laboratory thermodynamic database (thermo.com.v8.r6+), along with the pH-dependent solubility of tenorite (CuO) and the metastable solid, Cu(OH)\(_2\), based on data in Hidmi and Edwards (1999). Both CuO and Cu(OH)\(_2\) are insoluble at neutral to alkaline pH. Below pH of 6 to 7, dissolution of these phases would yield Cu\(^{2+}\) concentrations above the MCL of 1.3 mg L\(^{-1}\) (10^{-4.7} molal). Stable complexes of Cu\(^{2+}\) with SO\(_4\)^{2-} (CuSO\(_4\)^{0}) and CO\(_3\)^{2-} (CuCO\(_3\)^{0}) may contribute significantly to total copper at anion concentrations typically encountered in ground water. In environments with high ammonia concentrations, copper can be significantly bound to ammonia at pH>6.

Copper may be strongly complexed by dissolved organic matter (e.g., Smolyakov et al., 2004). Low molecular weight, dissolved organic complexes are generally highly mobile and able to transport copper in aquifer materials and soils (Han and Thompson, 2003; Christensen et al., 1999). Christensen et al. (1999) report that >85% of total copper was bound to dissolved organic carbon complexes in leachate with comparatively low dissolved organic carbon concentrations of <40 mg C L\(^{-1}\).

![Figure 4.1 Solubility of copper oxide and copper hydroxide as a function of pH in the system Cu-O-H at 25 °C.](image)

**Solubility**

An Eh-pH diagram for copper is shown in Figure 4.2. Inspection of this diagram indicates that at the specified conditions Cu\(^{2+}\) is the soluble form of copper at pH<6 and in moderately to highly oxidizing systems. Consequently, upon weathering, copper is likely to be more mobile under acidic rather than alkaline conditions (see, e.g., Paulson and Balistrieri, 1999). Copper hydroxycarbonate (malachite) has a narrow stability field at near-neutral pH and at moderately to highly oxidizing conditions. With increasing inorganic carbon concentrations, the malachite stability field...
would expand. At neutral to alkaline pH (>7) copper oxides are stable. With progressively more reducing conditions, cuprous oxide and elemental copper develop broad stability fields. Finally, in highly reducing and sulfidic environments, copper sulfides (chalcolite and covellite) are stable over a wide pH range. Aquifer materials usually contain some organic matter as well as sulfate from ground water. Microbial degradation of organic matter can be coupled to sulfate reduction with the production of hydrogen sulfide. Because of the extreme insolubility of copper sulfides, no complexing ligand can compete with hydrogen sulfide or metal sulfide surfaces for copper (Rose, 1989). In addition, there are several fairly common copper-iron-sulfur minerals such as chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄), and cubanite (CuFe₂S₃). Note that in solutions with high chloride concentrations (>1 M), the field of soluble copper in Figure 4.2 expands substantially due to the very strong nature of copper chloride complexes.

Cavallaro and McBride (1980) found that in alkaline soils copper was present as Cu(OH)₂ and with progressive aging, copper solubility decreased consistent with the formation of Cu₂(OH)₂CO₃. In general, they concluded that Cu²⁺ solubility in soil is highly correlated to pH. Dudley et al. (1991) proposed the formation of CuO in soil reacted with an extract of acid mine waste. In both the studies of Cavallaro and McBride (1980) and Dudley et al. (1991), proposed copper phase associations are based on a comparison of observed pH-dependent copper concentrations with solubility estimates based on thermodynamic data. Indeed, Leckie and Davis (1979) suggest that in most soil environments malachite and tenorite are the most important copper-bearing phases, with Cu(OH)₂ present as a metastable precursor to malachite and tenorite.

The stability relationships between copper hydroxycarbonates and oxides are shown in Figure 4.3 in terms of pH and CO₂ fugacity. Note that at high pH and CO₂ fugacity, aqueous copper carbonate complexes predominate over hydroxyl complexes. The diagram illustrates that over the pH and CO₂ conditions in most ground water systems, tenorite and malachite are the expected stable copper minerals.

**Adsorption**

McBride and Bouldin (1984) examined the solid-phase properties of copper in copper-contaminated soil. They concluded that long-term reaction of copper with calcareous soil failed to convert copper into a form unavailable to plants. Chemical extraction tests suggested that copper was present as an inorganic form in the soil, possibly tightly adsorbed on surfaces as hydroxyl or hydroxycarbonate species. Greater than 99.5% of the copper in the soil solution was complexed, probably with soluble organic compounds (McBride and Bouldin, 1984). In contrast, Cavallaro and McBride (1978) found that low pH soils are less effective in retaining Cu²⁺ compared to neutral soils and calcareous soils. They concluded that this behavior was in part related to increased competition at low pH for organic functional groups by aluminum and/or protons thus reducing the ability of Cu²⁺ to be adsorbed onto solid organic matter.

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**Figure 4.2** *Eh-pH diagram for copper at 25 °C (total inorganic carbon = 10⁻² molal; total sulfur = 10⁻³ molal; total copper = 10⁻⁵ molal).*

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**Figure 4.3** *Solubility and speciation of copper as a function of pH and log fugacity of CO₂(gas) at 25 °C. Solid lines separate stable phases and dotted lines separate aqueous species (total copper = 10⁻⁵ molal). Diagram drawn using thermodynamic data from MINTEQA2.*
Based on the solubility and sorption behavior of copper, it is expected that over a wide range of geochemical conditions copper will be effectively stable in the solid phase of soils and sediment materials. Copper has a strong affinity for the surfaces of iron oxides and hydroxides (e.g., Benjamin and Leckie, 1981; Robertson and Leckie, 1998; Martínez and McBride, 1998), clays (e.g., Pickering, 1980; Farqhar et al., 1997; Morton et al., 2001), sulfides (e.g., Patrick et al., 1997; Parkman et al., 1999), and organic matter (e.g., Sauvé et al., 1997; Schilling and Cooper, 2004). As well as being less soluble, Cu$^{2+}$ is more strongly adsorbed to mineral substrates than Zn$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$.

Benjamin and Leckie (1981) examined the pH-dependent sorption of copper, zinc, and lead onto hydrous ferric oxide. For these metals and for a range of precipitate loadings, the adsorption edge position, the pH at which half the metal was sorbed and half the metal remained in solution, increased in the order Pb$^{2+}$<Cu$^{2+}$<Zn$^{2+}$<Cd$^{2+}$. In this study, the pH at which 50% of copper was taken up by the surface of the iron precipitates ranged from about 5.0 to 5.5. At pH>$6$, copper was essentially completely removed from solution. Khoaahir et al. (2000) observed nearly identical pH-dependent behavior for copper adsorption onto iron oxide coated sand grains. Martinez and Motto (2000) determined the pH at which metal amended soils began to release copper via an acid titration method. Interestingly, they found that copper was released at about pH 5.5 ± 0.2 which is in good agreement with the adsorption studies, and further reinforces the notion of reversible sorption processes and potential copper mobility at low pH.

**Redox Chemistry**

Equilibrium between cupric and cuprous ions can be represented by the equation:

\[
\text{Cu}^{2+} + e^- = \text{Cu}^{+} \quad (\log K = 2.72)
\]

In natural systems the stable solid in very reducing conditions is expected to be cuprous sulfide (Cu$_2$S, chalcocite, see Figure 4.2). As the Eh increases there is a narrow window in which cupric sulfide (CuS, covellite) becomes important. Further increases in Eh can lead to the formation of elemental copper. So in general the solubility and speciation of copper are determined by redox equilibria of sulfur and copper and the strength of available ligands. Experimental studies of Cu(I) complexation by chloride and bisulfide are presented in Xiao et al. (1998), Thompson and Helz (1994), Mosselmans et al. (1999), and Mountain and Seward (1999, 2003). Luther et al. (2002) show that the reduction of Cu(II) to Cu(I) occurs in sulfidic solutions prior to the precipitation of copper sulfides.

**Colloidal Transport**

Recent studies are consistent in demonstrating that copper in ground water is frequently associated with colloids that appear to be organic in nature (Sañudo-Wilhelmy et al., 2002; Jensen et al., 1999; Freedman et al., 1996; Pauwels et al., 2002). The association between metals and ground water colloids is evident both in uncontaminated ground water (e.g., Sañudo-Wilhelmy et al., 2002) and in contaminated landfill leachates and in ground water impacted by mining districts (e.g., Jensen et al., 1999; Pauwels et al., 2002). Jensen et al. (1999) found that 86-95% of total copper in landfill leachate was associated with small-size colloidal matter and organic molecules. They concluded that most metals, including copper, present in the colloidal forms would have been sampled in the dissolved fraction if the commonly employed filter size of 0.45 μm had been used, since only negligible amounts of metal were found with colloids >0.40 μm. Pauwels et al. (2002) found that the mobility of copper in ground water impacted by the oxidative dissolution of massive sulfide deposits in the Iberian Pyrite Belt (Spain) was especially enhanced due to complexation with organic matter and/or adsorption onto colloids. For example, measured concentrations of copper were 10$^6$ to 10$^9$ times greater than concentrations modeled assuming equilibrium with respect to sulfide minerals (e.g., chalcopyrite).

**Site Characterization**

Copper mobility in ground water and the risk of copper exposure to plants, animals, and/or humans is governed by the total concentration of copper, the distribution of copper species in water, and the nature of copper partitioning in the solid phase. The development of site-conceptual models for predicting the long-term fate of copper at a contaminated site will require information on the distribution and concentration of copper in the aqueous phase and the solid phase. Table 4.1 indicates possible natural attenuation and mobilization pathways for copper.

Quantitative measurement of copper concentrations in aqueous solutions is typically carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectroscopy (ICP-MS), or atomic absorption spectroscopy (AAS). Some of the unique features of determining copper concentrations in natural waters are discussed in Boyle (1980) and Sañudo-Wilhelmy et al. (2002). Input data to geochemical codes (e.g., MINTEQA2, PHREEQC, EQ3/6) for determining aqueous speciation also require, at a minimum, the concentrations of major anions, major cations, total organic carbon, temperature, and pH. The total concentration of copper in soils, sediments, and aquifer materials may be determined by X-ray fluorescence (XRF) spectroscopy, or by chemical analysis after digestion in mineral acids.

While regulatory requirements stipulate that unfiltered ground-water samples be analyzed to support regulatory decisions at a contaminated site, it may be necessary to also collect filtered samples to help interpret that process(es) controlling contaminant mobility. The use of 0.45 μm pore size filter paper is common as an arbitrary cutoff point to differentiate between dissolved and particulate phases in water samples. However, caution is recommended when using this approach, particularly for Fe and Al and other elements that may be associated with Fe or Al particles (including Cu) that could pass through 0.45 μm filter papers. The use of filter papers with pore sizes less than 0.1 μm will generally provide a better assessment of the dissolved vs. particulate load of a ground water or a surface water sample.
Hickey and Kittrick (1984) examined the chemical partitioning of copper in soils and sediments containing high levels of heavy metals using the selective extraction approach developed by Tessier et al. (1979). In this study, copper was assigned to five operationally defined geochemical fractions: exchangeable, bound to carbonates, bound to Fe- and Mn-oxides, bound to organic matter, and residual. This study concluded that copper was the metal most significantly associated with organic matter. Compared to other heavy metals considered in this study (nickel, and zinc), copper displayed a low potential for mobility and metal bioavailability (Hickey and Kittrick, 1984).

**Long-Term Stability and Capacity**

The stability of attenuated copper will largely depend on the fluctuation of site-specific geochemical conditions through time. For example, if copper attenuation follows a copper hydroxycarbonate precipitation pathway, then long-term stability of attenuated copper will depend, in part, on the persistence of pH conditions. If pH conditions were to shift significantly to more acidic values, copper might be expected to release from the solid phase. It is therefore important to understand the attenuation mechanism(s) so that geochemical triggers for remobilization can be anticipated and incorporated into evaluations of long-term monitoring data. For any proposed and identified attenuation mechanism, there will exist possible scenarios whereby remobilization can occur (i.e., changes in pH or Eh). It will be essential to explore the likelihood of such changes in site geochemistry and the sensitivity of the attenuation pathway to changes in the prevailing geochemical conditions.

Quantifying the attenuation capacity (as defined in Volume 1) will also necessitate an understanding of the specific attenuation pathway(s). Attenuation capacity, for example, could be related to the extent that pH is buffered, the availability of sorptive sites in aquifer materials, or to the supply of electron donors needed to sustain microbiologically mediated redox conditions. For any proposed attenuation mechanism, there will be assumptions built into capacity estimations, so that uncertainty analysis is recommended to support capacity calculations.

**Tiered Analysis**

Determination of the viability of copper remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. MNA may not be appropriate as a site remedy for copper contamination in acidic pH, highly oxidizing, and/or DOC-rich environments. The goal of site assessment is to demonstrate the process(es) controlling copper sequestration onto aquifer solids and the long-term stability of solid phase copper as a function of existing and anticipated ground-water chemistry. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

**Tier I** - Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate Cu partitioning to aquifer solids within the plume. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by copper hydroxide, sulfate, carbonate, phosphate,

**Table 4.1** Natural attenuation and mobilization pathways for copper.

<table>
<thead>
<tr>
<th>Attenuation Processes</th>
<th>Mobilization Processes</th>
<th>Characterization Approach</th>
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<tbody>
<tr>
<td>Precipitation of insoluble hydroxycarbonates, carbonates, sulfides, and phosphates. In general, pH&gt;6 will drive precipitation reactions resulting in Cu concentrations below the MCL.</td>
<td>Dissolution of carbonates, hydroxycarbonates, and oxides at low pH; oxidative dissolution of sulfides at low pH and high Eh; complexation/stabilization in the presence of DOC.</td>
<td>Evaluation of copper speciation in the aqueous phase. Determination of total Cu in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Evaluation of long-term sorption capacity/stability.</td>
</tr>
<tr>
<td>Sorption to iron hydroxides, organic matter, carbonates, and sulfides.</td>
<td>Desorption at low pH; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides.</td>
<td>Evaluation of copper speciation in the aqueous phase. Determination of total Cu in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Batch and column testing to determine Cu uptake capacity of site-specific aquifer materials with variable geochemical conditions.</td>
</tr>
</tbody>
</table>
or sulfide. This provides justification for proceeding to Tier II characterization efforts.

**Tier II** - Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be assessed via a well transect along the ground-water flow path. In addition, time-series data may be collected at one or more monitoring points within the plume. This information will allow assessment of the relative timescales for contaminant immobilization and fluid transport and determination of whether remediation objectives can be met within the required regulatory timeframe. In addition, the mechanism(s) for attenuation need to be identified under this stage of site characterization. This effort may require determination of the chemical speciation of aqueous and solid phase Cu, which may be approached according to the following scheme:

1) Determination of solution speciation via direct analytical measurements (e.g., Martinez et al., 2001; Sañudo-Wilhelmy et al., 2002) to aid differentiation of uncomplexed (i.e., Cu$^{2+}$) and complexed (e.g., CuCl$^-$, Cu-organic ligand complexes) forms of mobile Cu in combination with speciation calculations based on characterized ground-water chemistry;

2) Calculation of the saturation state of ground water relative to measured aqueous chemistry complemented by the possible isolation of discrete Cu mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;

3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Cu sorption (e.g., Amonette, 2002; Burton et al., 2005); and

4) Determination of Cu-sediment associations via chemical extractions designed to target specific components within the aquifer sediment (e.g., Lee et al., 2005).

This compilation of information will facilitate identification of the reaction(s) leading to Cu immobilization within the plume.

**Tier III** - Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Cu and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized Cu be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage. For example, changes in ground-water pH can exert a significant influence on Cu adsorption or precipitate solubility. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of Cu mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for Cu uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that precipitation of Cu sulfide due to microbial degradation of organic compounds coupled with sulfate reduction occurs within the aquifer, then it is recommended that the mass distribution of organic carbon and sulfate to support this reaction within the aquifer be determined. This site-specific capacity can then be compared to Cu mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized Cu and sufficient capacity within the aquifer to sustain Cu attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction may be necessary.

**Tier IV** – Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to re-mobilization of attenuated Cu. The specific chemical parameters to be monitored will include those identified under Tier III that may halt Cu partitioning to aquifer sediments and/or result in solubilization of either discrete Cu precipitates or aquifer minerals that sequester Cu from ground water. For example, solution phase parameters that could alter either Cu precipitation or adsorption include increases in soluble organic carbon or chloride in combination with changes in ground-water pH. In contrast, the concentration of dissolved iron or sulfate may indicate the dissolution of an important sorptive phase within the aquifer (e.g., reductive dissolution of iron oxides or oxidative dissolution of sulfides). Changes in these parameters may occur prior to observed changes in solution Cu and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates interventive strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of natural attenuation processes within the aquifer through the injection of soluble reactive components.

**References**


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