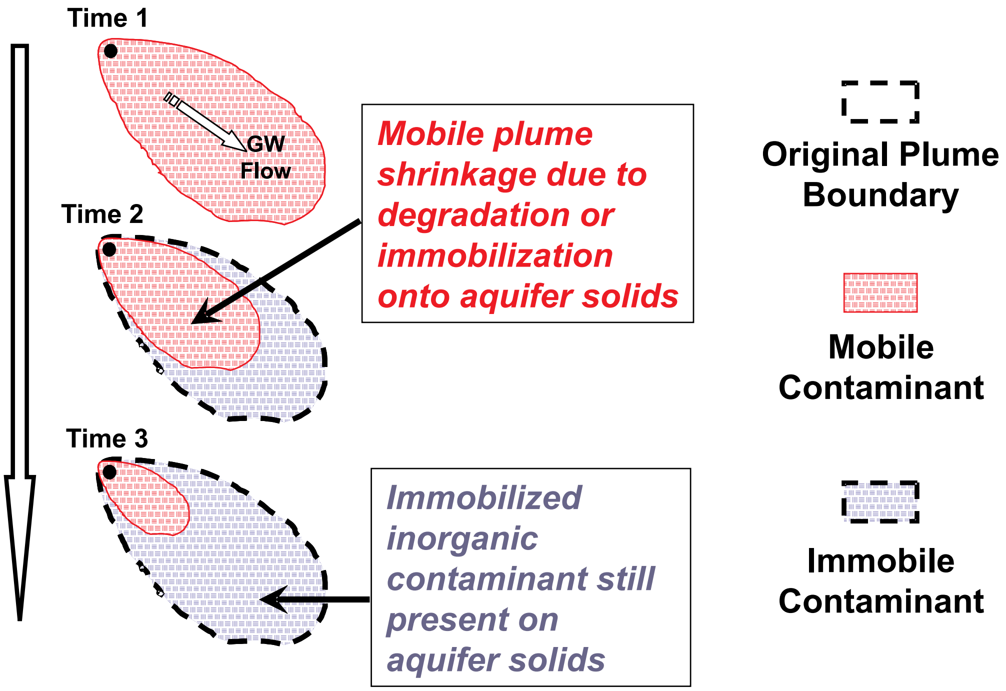
United States
Environmental Protection
Agency

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1

Technical Basis for Assessment

Evolution of Inorganic Contaminant Plume



EPA/600/R-07/139
October 2007

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 1 - Technical Basis for Assessment

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

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

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

Notice

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.

Stephen G. Schmelling

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

Contents

Section I - Conceptual Background for Natural Attenuation

Section II - Technical Basis for Natural Attenuation in Ground Water

Section III - Site Characterization to Support Evaluation of MNA

Figures

Tables

Acknowledgments

This document represents a collective work of many individuals with expertise in the policy and technical aspects of selecting and implementing cleanup remedies at sites with contaminated ground water. Preparation of the various components of this document was undertaken by personnel from the USEPA Office of Research and Development (ORD), Office of Superfund Remediation and Technology Innovation (OSRTI), and Office of Radiation and Indoor Air (ORIA), as well as technical experts whose participation was supported under USEPA Contract No. 68-C-02-092 to Dynamac Corporation, Ada, Oklahoma, through funds provided by ORIA and OSRTI. Contributing authors are listed below along with their affiliation:

Contributing Author	Affiliation
Richard T. Wilkin	USEPA/ORD, National Risk Management Research Laboratory, Ada, OK 74820
Kenneth Lovelace	USEPA/OSWER/OSRTI, Washington, DC 20460 (deceased)
Stuart Walker	USEPA/OSWER/OSRTI, Washington, DC 20460
Ronald Wilhelm	USEPA/OAR/ORIA, Washington, DC 20460
Steven Acree	USEPA/ORD, National Risk Management Research Laboratory, Ada, OK 74820
Steve Mangion	USEPA/ORD/OSP, Region 1, Boston, MA 02114
Robert W. Puls	USEPA/ORD, National Risk Management Research Laboratory, Ada, OK 74820
Ann Azadpour-Keeley	USEPA/ORD, National Risk Management Research Laboratory, Ada, OK 74820
Robert G. Ford	USEPA/ORD, National Risk Management Research Laboratory, Cincinnati, OH 45268
Patrick V. Brady	Sandia National Laboratories, Geochemistry Department (MS-0750), Albuquerque, New Mexico 87185
James E. Amonette	Pacific Northwest National Laboratory, Fundamental Science Directorate, Richland, WA 99352
Paul M. Bertsch	University of Kentucky, College of Agriculture, Lexington, KY 40506
Craig Bethke	University of Illinois, Department of Geology, Urbana, IL 61801
Douglas B. Kent	U.S. Geological Survey, McKelvay Building (MS-465), Menlo Park, CA 94025

Critical and constructive reviews were provided by Jim Weaver (USEPA/ORD National Exposure Research Laboratory, Athens, GA), George Redden (Idaho National Laboratory, Batelle Energy Alliance), and Sue Clark (Washington State University, Chemistry Department). Pat Bush (Ada, OK) is acknowledged for her technical editing to provide consistency in formatting and grammar. Martha Williams (Contract #68-W-01-032) assisted with final editing and formatting for publication. This effort is dedicated to the memory of Kenneth Lovelace, whose insight and patience made it a reality.

Executive Summary

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

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

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

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

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

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

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

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

Section I

Conceptual Background for Monitored Natural Attenuation

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

IA. Background and Purpose

IA.1 Document Organization

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

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

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

IA.2 Purpose of Document

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

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

---

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

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

This document is intended to provide an approach for evaluating MNA as a possible cleanup method for contaminated ground water. Although the focus of the document is on ground water, the unsaturated zone is discussed as a source of contaminants to ground water. Emphasis is placed on developing a more complete evaluation of the site through development of a conceptual site model[2] based on an understanding of the attenuation mechanisms, the geochemical conditions governing these mechanisms, the capacity of the aquifer to sustain attenuation of the contaminant mass and prevent future contaminant migration, and indicators that can be used to monitor MNA performance.

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

---

[2] *A conceptual site model is a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual model provides the basis for assessing potential remedial technologies at the site. "Conceptual site model" is* **not** *synonymous with "computer model"; however, a computer model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions.*

> *specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. (USEPA, 1999c, page 3.)*

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

> *"When relying on natural attenuation processes for site remediation, EPA prefers those processes that degrade or destroy contaminants. Also, EPA generally expects that MNA will only be appropriate for sites that have a low potential for contaminant migration." (USEPA, 1999c, page 3.)*
>
> *"MNA should not be used where such an approach would result in either plume migration or impacts to environmental resources that would be unacceptable to the overseeing regulatory authority.* ***Therefore, sites where the contaminant plumes are no longer increasing in extent, or are shrinking, would be the most appropriate candidates for MNA remedies."*** *(USEPA, 1999c, page 18.)*

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

> *"Control of source materials is the most effective means of ensuring the timely attainment of remediation objectives.* ***EPA, therefore, expects that source control measures will be evaluated for all contaminated sites and that source control measures will be taken at most sites where practicable.*** *At many sites it will be appropriate to implement source control measures during the initial stages of site remediation ("phased remedial approach"), while collecting additional data to determine the most appropriate groundwater remedy." (USEPA, 1999c, page 22.)*

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

> *MNA may, under certain conditions (e.g., through sorption or oxidation-reduction reactions), effectively reduce the dissolved concentrations and/or toxic forms of inorganic contaminants in groundwater and soil. Both metals and non-metals (including radionuclides) may be attenuated by sorption[3] reactions such as precipitation, adsorption on the surfaces of soil minerals, absorption into the matrix of soil minerals, or partitioning into organic matter. Oxidation-reduction (redox) reactions can transform the valence states of some inorganic contaminants to less soluble and thus less mobile forms (e.g., hexavalent uranium to tetravalent uranium) and/or to less toxic forms (e.g., hexavalent chromium to trivalent chromium). Sorption and redox reactions are the dominant mechanisms responsible for the reduction of mobility, toxicity, or bioavailability of inorganic contaminants. It is necessary to know what specific mechanism (type of sorption or redox reaction) is responsible for the attenuation of inorganics so that the stability of the mechanism can be evaluated. For example, precipitation reactions and absorption into a soil's solid structure (e.g., cesium into specific clay minerals) are generally stable, whereas surface adsorption (e.g., uranium on iron-oxide minerals) and organic partitioning (complexation reactions) are more reversible. Complexation of metals or radionuclides with carrier (chelating) agents (e.g., trivalent chromium with EDTA) may increase their concentrations in water and thus enhance their mobility. Changes in a contaminant's concentration, pH, redox potential, and chemical speciation may reduce a contaminant's stability at a site and release it into the environment. Determining the existence, and demonstrating the irreversibility, of these mechanisms is important to show that a MNA remedy is sufficiently protective.*
>
> *In addition to sorption and redox reactions, radionuclides exhibit radioactive decay and, for some, a parent-daughter radioactive decay series. For example, the dominant attenuating mechanism of tritium (a radioactive isotopic form of hydrogen with a short half-life) is radioactive decay rather than sorption. Although tritium does not generate radioactive daughter products, those generated by some radionulides (e.g., Am-241 and Np-237 from Pu-241) may be more toxic, have longer half-lives, and/or be more mobile than the parent in the decay series. Also, it is important that the near surface or*

---

[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:

---

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

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

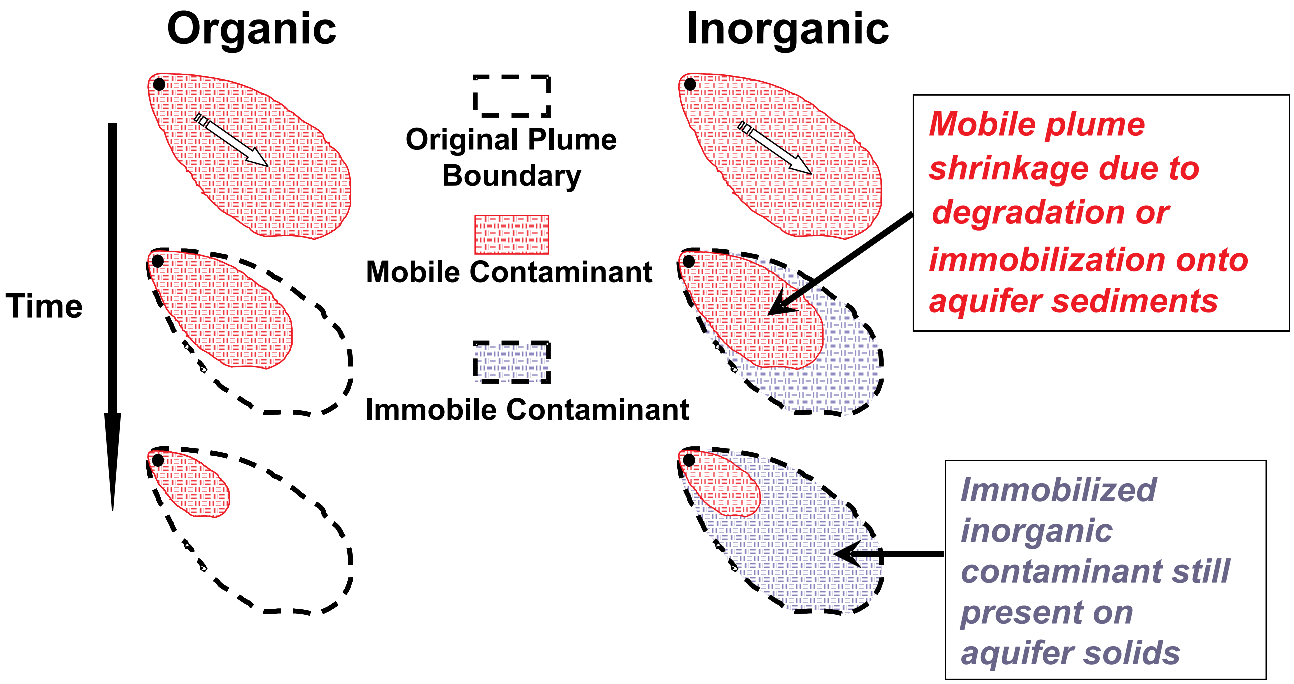
2) Demonstration of stabilization of the inorganic contaminant immobilized onto aquifer solids such that future re-mobilization will not occur to a level that threatens health of environmental receptors.

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

Site characterization to support evaluation of MNA as a remedial alternative will involve assessment of contaminant transport in the aquifer. In general terms, this process will include assessment of ground-water hydrology and the biogeochemical processes that control contaminant migration within the plume. Defining the processes that control contaminant immobilization (or degradation) along the paths of ground-water flow will necessitate collection of a range of data that define the dynamics of system hydrology, the chemical characteristics of ground water, and the properties of the aquifer solids. In order to screen out sites that are inappropriate for selection of MNA, it is recommended that collection of site-specific data be conducted in stages that serve to minimize expenditures while providing insight into the potential existence of natural processes that may attenuate contaminant migration. Description of a tiered analysis approach for organizing site characterization tasks is provided in the following section.

IC. Tiered Analysis Approach to Site Characterization

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



Mobile plume shrinkage due to degradation or immobilization onto aquifer sediments

Immobilized inorganic contaminant still present on aquifer solids

Figure 1.1 *Conceptual distinction between organic versus inorganic contaminant plume behavior where natural processes are active within the ground-water aquifer. Natural attenuation of inorganic contaminants is viable only if the immobilized contaminant remains stable and resistant to remobilization during changes in ground-water chemistry.*

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

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

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

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

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

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

IC.1 Tier I

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

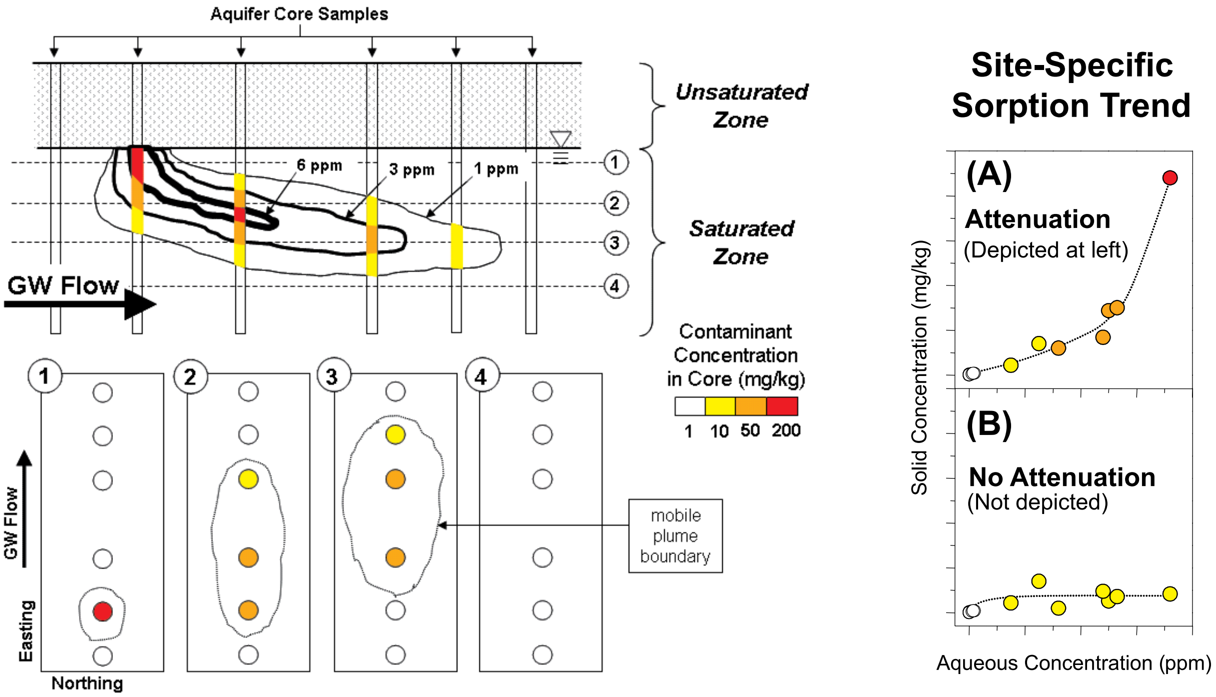


Figure 1.2 *Conceptual depiction of the data collection effort to demonstrate whether sorption to aquifer solids attenuates contaminant transport in ground water. The left side of the diagram provides a cross-sectional view of the spatial distribution of the contaminant concentration in ground water and co-located aquifer solids for a site where sorption attenuates contaminant transport. The trend in aqueous and solid contaminant concentrations for this scenario is depicted in Panel (A) to the right. Panel (B) depicts the relationship between aqueous and solid contaminant concentrations for a site where sorption does not attenuate contaminant transport.*

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

IC.2 Tier II

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

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

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

IC.3 Tier III

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

1. changes in ground-water chemistry result in slower rates of attenuation,
2. insufficient mass flux of aqueous constituents that participate in the attenuation reaction, and/or
3. insufficient mass of solid constituents in aquifer solids that participate in the attenuation reaction.

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

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

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

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

IC.4 Tier IV

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

In summary, the tiered analysis process provides a means to organize the data collection effort in a cost-effective manner that allows the ability to eliminate sites at intermediate stages of the site characterization effort. A general synopsis of the objectives along with possible analysis approaches and/or data types to be collected under each tier is provided in Table 1.1. The types of data collected early in the site characterization process would typically be required for selection of appropriate engineered remedies, including characterization of the system hydrology, ground-water chemistry, contaminant distribution, and the aqueous speciation of the contaminant. These system characteristics can have direct influence on the selection of pump-and-treat or in-situ remedies best suited to achieve cleanup objectives for inorganic contaminants. This limits any loss on investment in site characterization for sites where selection of MNA as part of the ground-water remedy is ultimately determined not viable. The primary objective of progressing through the proposed tiered site analysis steps is to reduce uncertainty in the MNA remedy selection.

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

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

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

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

ID. Role of Modeling in the Tiered Analysis Approach

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

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

ID.1 Developing a Conceptual Model

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

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

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

- Does groundwater migrate through the bulk aquifer matrix, through fractures or heterogeneities in the matrix, or both?
- Does solute diffusion from areas of rapid flow to those with stagnant conditions affect contaminant transport on a scale finer than the envisioned numerical gridding, so that a dual porosity model is required?
- Should the medium be considered homogeneous or heterogeneous on the scale envisioned for the nodal blocks in the numerical gridding?
- Are medium properties best assigned deterministically, or according to a stochastic algorithm?
- Is hydrodynamic dispersion described well in a Fickian sense (i.e., in terms of dispersivity, according to Fick’s law), by differential advection through a numerical gridding, or in both ways?

- How can the model be calibrated to reflect as accurately as possible transport rates through the subsurface?
- What additional data need to be collected to characterize flow and calibrate the transport model? Such data might include the distribution of hydraulic head, the evolution of the contaminant plume through time, and the results of tracer tests.

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

- Does the contaminant adsorb to solid surfaces? If so, onto what surfaces, and as what type of surface complex? Does it desorb readily?
- Is the contaminant chemically oxidized or reduced? Is the reaction catalyzed by mineral surfaces, or promoted by microbial activity? If so, what is the catalyst or microbial species?
- Does the contaminant precipitate as a solid phase? If it does, what is the phase, and what is its solubility?
- Might complexation of the contaminant with chemical constituents in solution affect its mobility?

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

ID.2 Types of Models

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

ID.2.1 Simple Calculations

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

- "Hydraulic Gradient Calculation" for assessing the direction(s) of ground-water flow employing head measurements in wells spaced horizontally across the site;
- "Vertical Gradients" for assessing the potential for vertical water transport within the aquifer based on head measurements in closely-spaced, vertically nested wells with identical screen lengths;
- "Vertical Gradients with Well Screen Effects" for assessing the influence of variable screen lengths in vertically nested wells on the calculated vertical gradient; and
- "Average Borehole Concentrations" to illustrate the potential impact on contaminant concentrations measured for samples collected from a single long-screened well in an aquifer with a depth-varying concentration and a depth-varying hydraulic conductivity field.

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

ID.2.2 Mass Transport Models

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

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

ID.2.3 Speciation Models

Speciation models seek to describe the distribution of chemical mass between solution, minerals, mineral surfaces, gases, and biomass. Models of this class are useful because they can predict the conditions under which contaminants might be attenuated by sequestration, and those in which they are likely to be mobile in the ground-water flow. For example, a speciation model might demonstrate that a contaminant is likely to adsorb to the surface of a component of the aquifer solids over the pH range of interest. Or, the model might show that the contaminant will tend to complex strongly with dissolved chemical species, leaving it mobile and resistant to attenuation.

Speciation models are implemented via the assumption that the modeled system is in chemical equilibrium or, more commonly, partial chemical equilibrium. A model can be configured to account for:

- Reactions among species in solution, including protonation-deprotonation, redox, and complexation reactions.
- Adsorption reactions onto solid surfaces, possibly including minerals and organic matter.
- Precipitation and dissolution reactions, to predict whether a mineral is saturated in solution, or undersaturated or supersaturated.
- Gas solubility reactions, to account for the dissolution of coexisting gases into solution, or the loss of gas species from solution.

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

ID.2.4 Reaction Models

Reaction models are similar to speciation models in that they consider the distribution of chemical mass, but have the additional ability of modeling the chemical evolution of the system. Like speciation models, it is commonly necessary to use a reaction model with a flexible description of redox disequilibrium, as well as suitable models to describe adsorption and precipitation reactions. Where appropriate, the model should be able to account for the kinetics of species sorption, redox reactions, mineral precipitation and dissolution, or microbial metabolism. Examples of the application of reaction models in an MNA application include:

- Sequestration of contaminants onto a mineral surface as the mineral forms, such as the complexation of heavy metals in mine drainage onto ferrihydrite.
- Precipitation of contaminant-bearing minerals, according to a kinetic rate law appropriate for the chemical conditions at the site.
- Immobilization of a contaminant by oxidation or reduction, according to a kinetic rate law.
- Biotransformation of a contaminant by microbial life, using a rate equation for fermentation or cellular respiration appropriate for conditions at the site.

ID.2.5 Reactive Transport Models

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

- The ability to account for heterogeneity at the site, such as an uneven distribution of a sorbing mineral, variation in pH conditions, or the differential development of microbial populations.

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

Reactive transport modeling is a relatively complex and time-consuming undertaking, since it combines the data needs and uncertainties inherent in modeling reaction as well as transport, and because the calculation procedure may require a significant amount of computing time. It may be the capstone of the modeling effort, but is seldom the best tool for initial scoping of the attenuation capabilities at a site. Such modeling, on the other hand, may play an important role in the site characterization effort, because it represents the integration of all of the components of the conceptual model.

ID.3 Modeling and the Tiered Analysis Approach

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

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

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

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

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

- If a precipitating phase is identified by x-ray diffraction, spectroscopy, or electron microscopy, it will be necessary to characterize the phase's solubility.
- If reaction with solid surfaces is identified as an important attenuation process, it will be necessary to collect sufficient data to properly parameterize an adsorption model that describes the specific mechanism of adsorption, as described in Section IIIB.
- It may be necessary to establish a kinetic rate law describing precipitation of the contaminant into solid phases, or its adsorption onto solid surfaces, where these reactions may occur at different rates throughout the plume due to the concentrations of aqueous or solid reactants.

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

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

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

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

- To figure reactant fluxes required to remobilize the contaminant.
- To evaluate the possible effects of chelating agents, such as organic acids, in the groundwater.

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

ID.3.4 Tier IV – Long-Term Performance Monitoring

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

- Optimizing the location of monitoring wells for long-term observation.
- Optimizing the frequency of sample collection events based on knowledge of ground-water flow dynamics at the site.
- Identifying critical chemical parameters to monitor based on model simulations to examine the sensitivity of attenuation process rate or capacity to changes in ground-water composition.
- Identifying critical parameters to monitor based on model simulations to evaluate conditions leading to contaminant re-mobilization.

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

ID.4 Choosing Modeling Software

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

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

ID.4.1 Public Domain vs. Commercial Software

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

ID.4.2 Sources of Software

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

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

- Whether the model operates in two or three dimensions, or both.
- Whether the model can account for dispersion in the manner chosen.

- If the model accounts for saturated flow (flow below the water table), unsaturated flow (above the water table), or both.
- The deterministic or stochastic method or methods the model can use to represent heterogeneity in the properties of the medium (hydraulic conductivity, dispersivity, and so on) across the modeling domain.

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

- A flexible description of redox state. A disequilibrium scheme in which each redox couple can be set to its own redox potential is commonly required.
- The ability to account for sorption or surface complexation in a manner appropriate for the site.

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

- An accounting for the kinetics of redox reactions, whether occurring in the fluid phase, catalytically on mineral surfaces, or promoted by enzymes.
- The ability to account for the kinetics of mineral precipitation and dissolution reactions invoked as an attenuation mechanism, using appropriate rate laws.
- A model of microbial metabolism based on valid chemical principles. The metabolic model should treat the

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

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

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

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

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

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

- Whether the model can work in one, two, or three dimensions.
- Compatibility of the model with the mass transport and reaction models chosen. For example, can the reactive transport model import a flow field predicted by the mass transport model?
- Time to solution, since reactive transport modeling can require considerable amounts of computing time.

ID.4.3 Thermodynamic Data

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

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

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

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

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

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

ID.5 Accounting for Uncertainty

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

- Error in chemical analyses. The accuracy and completeness of chemical analyses vary widely. Routine chemical analyses performed by commercial laboratories are in many cases of insufficient quality to support geochemical and reactive transport modeling. Several useful checks for internal consistency are available in the American Water Works Association "Standard Methods" volume (Clesceri et al., 1998), and computer programs (e.g., Aq•QA, www.aqqa.com) are available for performing these tests automatically. Geochemical modeling applications require complete chemical analyses, including not only the contaminants of interest, but the major ion chemistry, pH, and distribution of metals among their mobile redox states.
- Error in determining hydrologic parameters. Measuring representative values of hydrologic parameters such as hydraulic conductivity and dispersivity can be difficult, because these values may change with the scale on which they are observed. Laboratory measurements, therefore, may give different results than well tests (e.g., slug and bail tests, pumping tests), which may in turn differ from values representative of the site as a whole. Measured hydrologic parameters are important, but may need to be calibrated to observations from the site, including perhaps the rate of plume advance or the migration of a tracer injected into the subsurface.
- Sample choice and dataset size. Significant error can be introduced by sampling bias, although this bias is not always obvious or even avoidable. Laboratory measurements of hydrologic properties, for example, are commonly made on samples that can be recovered intact, even though the fractured or poorly consolidated portions of the medium, left unsampled, control flow. Fluid samples may be taken from monitoring wells completed in highly conductive layers, where they can be extracted rapidly, leaving unaccounted significant quantities of residual contamination in slightly less conductive layers. Finally, the number of samples available or monitoring wells constructed is in some cases too small to comprise a statistically significant dataset.
- Incompleteness and inaccuracy of the thermodynamic database. To provide meaningful results, a geochemical or reactive transport model has to include each of the aqueous species, minerals, gases, and adsorbed species important at the site, and the data for these species need to be accurate. The thermodynamic databases available for geochemical study vary widely in breadth and accuracy.
- Error in model components. Each of the components of which the model is constructed is a potential source of error. Components likely to contribute to error include kinetic rate laws, surface complexation (sorption) models, and descriptions of the effects of microbial metabolism.
- Conceptual errors. Perhaps most significantly, model results can be affected by failure to conceptualize the problem completely and accurately. If an important process is not accounted for, or accounted for in an inaccurate fashion, the modeling results will likely be rendered useless.

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

ID.6 Model Calibration and Verification

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

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

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

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

IE. Long-Term Performance Monitoring and Site Closure

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

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

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

- Changes in three-dimensional plume boundaries,
- Changes in the redox state that may indicate changes in the rate and extent of natural attenuation,
- Reduction in the capacity of aquifer materials for contaminant immobilization, and
- Mobile contaminant mass and concentration reductions indicative of progress toward contaminant removal objectives.

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

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

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

IE.1 Duration and Monitoring Frequency

As stated in the OSWER Directive (USEPA, 1999c), performance monitoring should continue until remediation objectives have been achieved, and longer if necessary to verify that the site no longer poses a threat to human health or the environment. Typically, monitoring is continued for a specified period after remediation objectives have been achieved to ensure that concentration levels are stable and remain below target levels. In order to demonstrate stability, verification of the achievement of target levels under conditions where the aquifer geochemistry has reestablished a chemical steady state with respect to ambient ground-water geochemistry will be needed. The magnitude of the chemical gradient between the impacted and non-impacted portions of the aquifer provides a reference point for evaluating establishment of steady-state conditions. A monitoring strategy to verify the attainment of remedial objectives and provide for termination of monitoring and site closure generally should be formulated during the development of the performance monitoring plan and updated, as necessary, prior to implementation.

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

- The rate at which contaminant concentrations may change due to ground-water flow and natural attenuation processes,
- The degree to which the causes of this variability are known,
- The types of evaluations to be performed and the importance of the type of data in question, and
- The location(s) of possible receptors relative to the plume.

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

With respect to the initial frequency of ground-water sampling under the performance monitoring program, quarterly monitoring may often be an appropriate frequency to establish baseline conditions over a period of time sufficient to observe seasonal trends, responses to recharge, and to confirm attenuation rates for key contaminants. Quarterly monitoring for several years provides baseline data to determine trends at new monitoring points and test key hypotheses of the conceptual site model. More frequent monitoring of ground-water elevations may be warranted, particularly during the establishment of baseline conditions, to improve the characterization of ground-water flow patterns. In addition, more frequent monitoring may be needed to observe changes in ground-water flow patterns in response to other site activities, such as the start or cessation of ground-water extraction in off-site water supply wells, source control activities, and other significant changes in the hydrologic system.

IE.2 Monitoring of Aquifer Solids

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

- Determination of the chemical process(es) resulting in contaminant immobilization,
- Determination of the capacity of the un-reacted aquifer material for contaminant immobilization, and
- Determination of the stability of the reacted aquifer material with respect to contaminant release.

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

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

IE.3 Monitoring Types

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

- Monitoring of conditions outside of the plume boundaries (ambient monitoring),
- Monitoring of natural attenuation processes (process monitoring), and
- Monitoring to detect plume expansion and verify the lack of impact to receptors (migration monitoring).

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

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

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

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

IE.4 Monitoring Locations

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

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

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

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

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

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

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

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

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

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

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

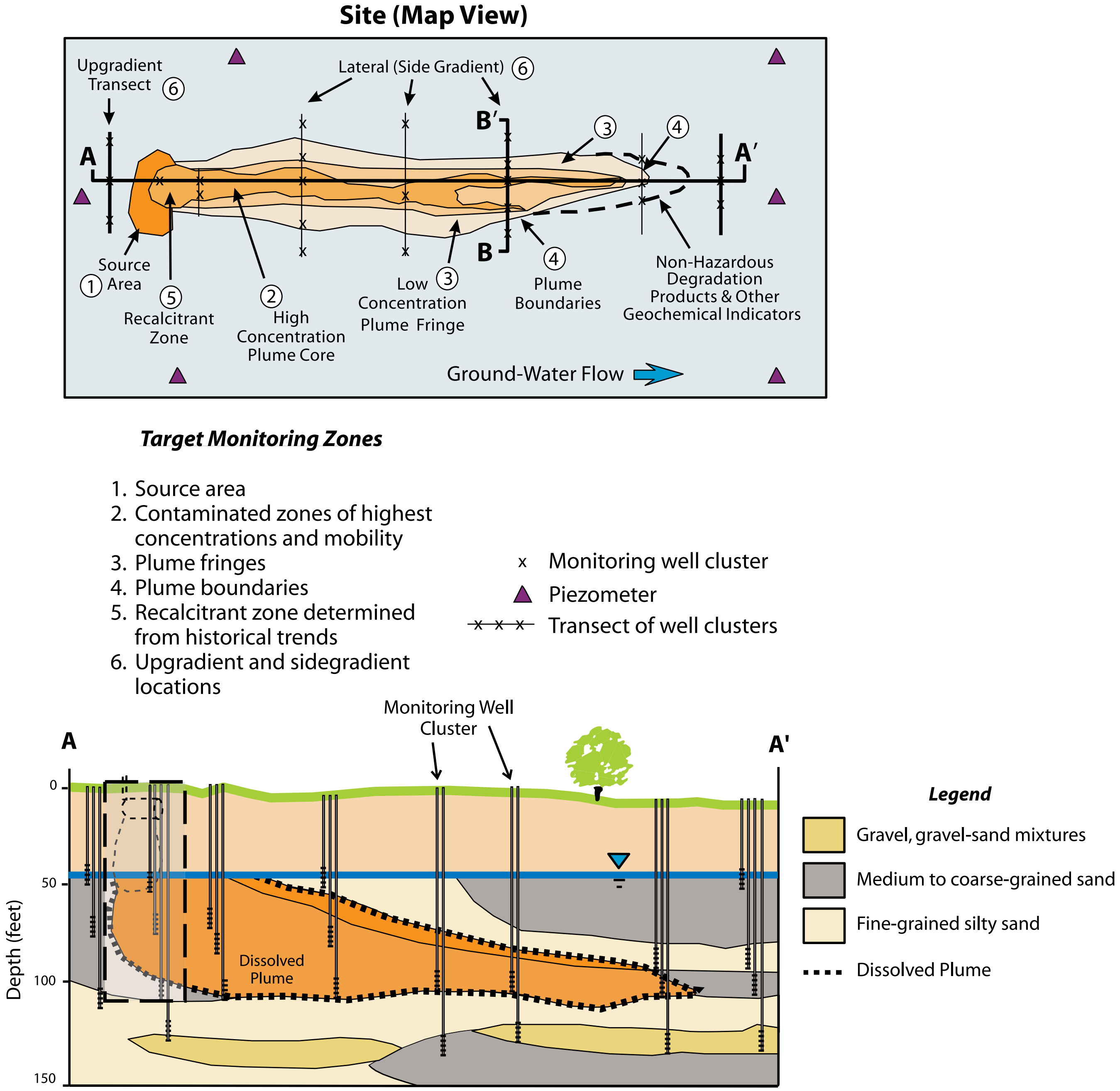


Figure 1.3 *Example of a network design for performance monitoring, including target zones for monitoring effectiveness with respect to specific remedial objectives.*

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

- Areas representative of uncontaminated settings (Ambient Monitoring)

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

- Areas supporting the monitoring of site hydrology

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

IE.5 Modification of the Performance Monitoring Plan

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

- Continuation of the monitoring program without modification;
- Modification of the monitoring program;
- Implementation of a contingency or alternative remedy; or
- Verification that remedial objectives have been met with subsequent termination of the monitoring program.

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

In situations where hydrologic and geochemical parameters are stable and the contaminant concentrations in ground water are decreasing as predicted, reductions in sampling frequency (e.g., semi-annual, annual, or less frequent) will often be warranted for process monitoring. For example, five years of quarterly monitoring showing predictable decreases in mobile contaminant concentrations might be the basis for decreasing the frequency to a semi-annual or annual basis at some sites. Ten years of semi-annual or annual monitoring that shows predictable decreases in mobile contaminant mass might likewise be the basis for additional decreases in frequency, depending on site conditions. Conversely, unexpected increases or lack of predicted decreases in contaminant concentrations may trigger additional characterization to determine the reasons for the behavior, increased monitoring of pertinent parameters, re-evaluation of the conceptual site model, and, potentially, the implementation of a contingent or alternative remedy. Changes in the frequency of monitoring to detect plume expansion may also be warranted as process monitoring is modified. However, the frequency of such monitoring should not be decreased to the point where insufficient time would be available for implementation of an effective contingency plan in the event of MNA remedy failure.

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

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

IE.6 Periodic Reassessment of Contaminant Removal Technologies

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

1F. References

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

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

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

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

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

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

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

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

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

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

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

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

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

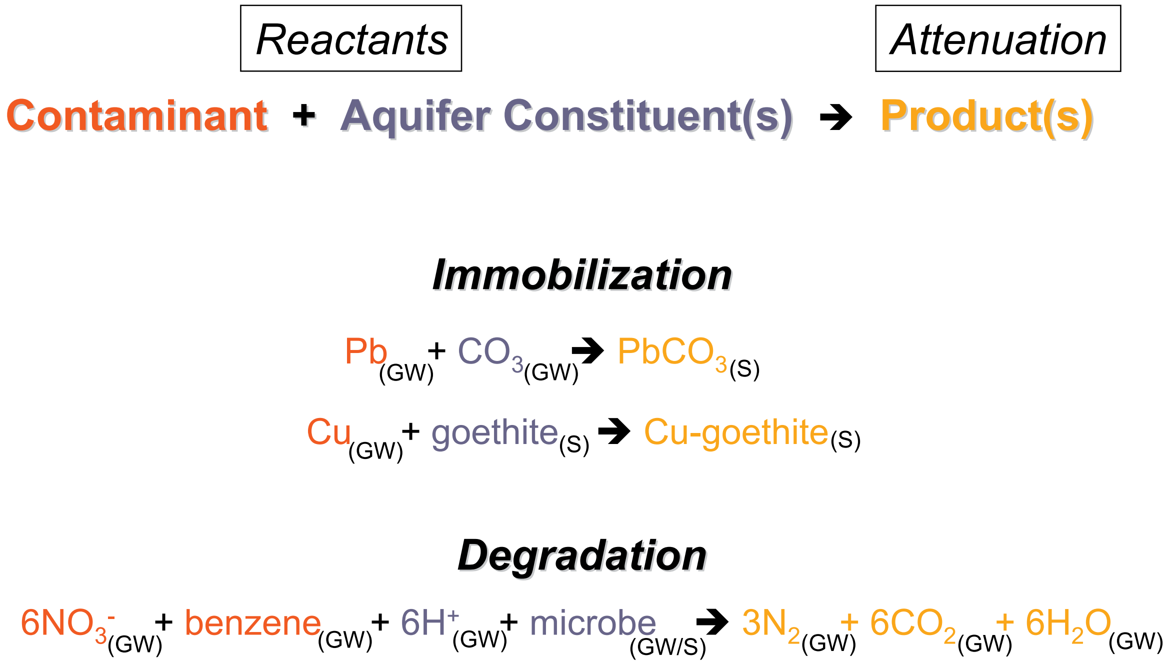
USEPA. *Understanding Variation in Partition Coefficient, Kd, Values: Volume III - Review of Geochemistry and Available Kd Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium,* EPA 402-R-99-004C, Office of Radiation and Indoor Air, Washington DC (2004).

Section II

Technical Basis for Natural Attenuation in Ground Water

Richard T. Wilkin, Steven Acree, Steve Mangion, Patrick V. Brady, Robert G. Ford, Robert W. Puls, Paul M. Bertsch, Douglas B. Kent, Ann Azadpour-Keeley, James E. Amonette, Craig Bethke

In determining whether MNA is applicable to a site, the properties of the site and the properties of the contaminant are analyzed in order to identify the specific process (or processes) causing contaminant attenuation. Inorganic contaminant transport in the subsurface will be governed by the site-specific characteristics of ground-water flow and the chemical interactions between the contaminant and aquifer solids along the path (or paths) of fluid flow. The overall extent of contaminant attenuation will be governed by the velocity of ground-water flow relative to the rates of chemical reactions that attenuate contaminant transport. The types and rates of chemical reactions that result in contaminant attenuation will be controlled by the availability of constituents within the aquifer that interact with the contaminant in a manner that results in contaminant immobilization or transformation. In simple terms, one can view the product of the reaction between the contaminant and aquifer constituents (or reactants) as the specific form of attenuation. Examples of possible attenuation reactions are provided in Figure 2.1 to illustrate this conceptual viewpoint and the types of processes that may be active at a given site. The reactants in the attenuation process may be present in dissolved form or associated with aquifer solids (e.g., aquifer minerals or microbes). Thus, assessment for MNA will necessitate collection of site-specific data that define the processes controlling contaminant transport. In order to provide context for the types of data that may be required to address this assessment objective, this section will provide a review of the physical and biogeochemical processes that govern contaminant transport in ground water.



$$Pb_{(GW)} + CO_{3(GW)} \rightarrow PbCO_{3(S)}$$

$$Cu_{(GW)} + goethite_{(S)} \rightarrow Cu\text{-}goethite_{(S)}$$

$$6NO_{3}^{-}{}_{(GW)} + benzene_{(GW)} + 6H^{+}{}_{(GW)} + microbe_{(GW/S)} \rightarrow 3N_{2(GW)} + 6CO_{2(GW)} + 6H_{2}O_{(GW)}$$

Figure 2.1 *Conceptual view of attenuation as the interaction of the contaminant with aquifer constituents to form a product resulting in attenuation. Subscript designations "(GW)" and "(S)" indicate, respectively, whether the reactant(s) and product(s) are in ground water or associated with immobile aquifer solids. For the degradation reaction,* N_2 *and* CO_2 *are likely present as dissolved gases; "goethite" is the name of a commonly occurring iron oxyhydroxide mineral in aquifers.*

IIA. Physical Transport Mechanisms

IIA.1 Basics of Ground-Water Flow and Solute Movement

Ground water is rarely static and moves from areas of ground-water recharge (i.e., high hydraulic head) to areas of discharge (i.e., low hydraulic head). In a porous medium, ground-water flow generally obeys Darcy's law with velocity proportional to the hydraulic conductivity and hydraulic gradient. In such settings, the average interstitial flow velocity, or seepage velocity (V_s), is the rate at which water moves through the pore spaces of the medium. Under natural conditions, ground-water movement is relatively slow with rates ranging from less than a foot per year to several feet per day (USEPA, 1991). Seepage velocities for the various aquifer materials at a site may often be estimated using:

$$V_s = Ki/n_e$$

where,

K = the hydraulic conductivity of the medium

i = the magnitude of the hydraulic gradient

n_e = the effective porosity or fraction of the medium occupied by interconnected pore space.

In general, the seepage velocity at most sites is expected to vary spatially due to heterogeneity in aquifer material properties and temporally due to fluctuations in hydraulic gradients.

The dominant processes that result in subsurface solute movement in this dynamic environment are advection and dispersion. Advection is the movement of a solute with the bulk movement of ground water (Freeze and Cherry, 1979) and generally is the primary solute transport mechanism at sites with moderate to high ground-water flow rates. Mechanical dispersion results in mixing of ground water during advection reducing dissolved solute concentrations within the plume and causing some solute molecules to travel faster and some to travel slower than the average ground-water velocity. A more detailed discussion of dispersion is provided by Gelhar (1993) and Gelhar et al. (1992). The result at the macro scale is that a solute will spread to occupy a larger portion of the flow field in the direction of ground-water flow and in transverse (perpendicular) directions than that due solely to advection. However, limitations in the ability to obtain direct measurements of dispersion relegate its determination primarily as a fitting parameter during calibration of a ground-water flow model for site-specific applications. At the field scale, stratification (with associated differences in the hydraulic conductivity of geologic materials) and fluctuations in hydraulic gradient often result in much greater differences in the movement of solutes relative to estimates based on the average ground-water flow velocity (Figure 2.2). Thus, relative to site-specific evaluation of contaminant transport, assessment of the degree of variability in the distribution of hydraulic conductivity within the aquifer and time-dependent changes in the magnitude and direction(s) of the hydraulic gradient most likely plays a more critical role under the site characterization effort.

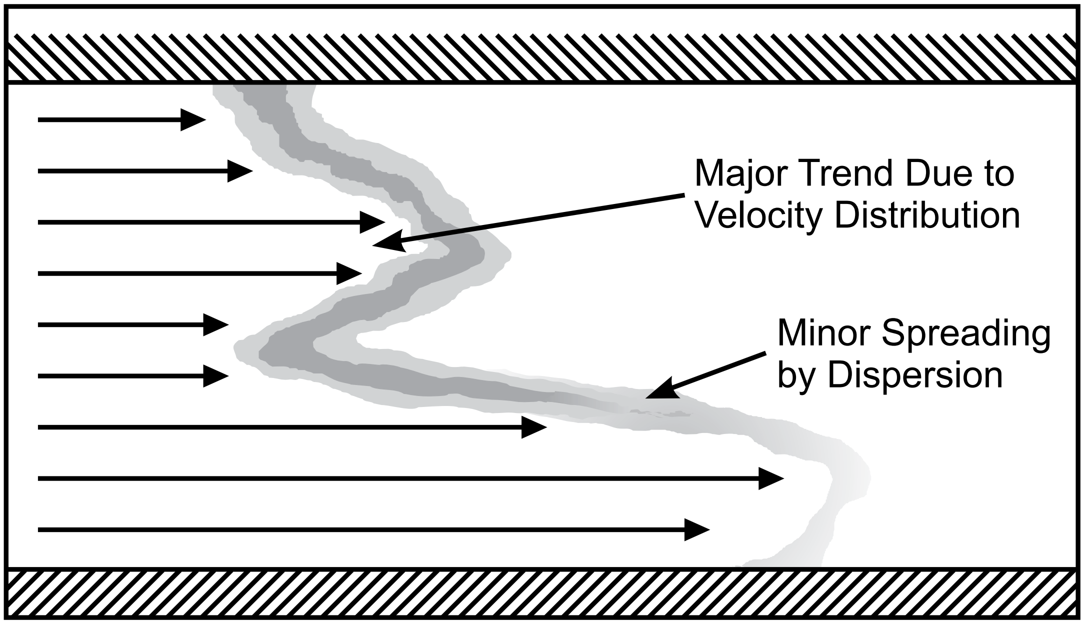


Figure 2.2 *Cross-sectional view of differences in solute migration due to differences in hydraulic conductivity with accompanying differences in ground-water velocity and the spreading of the solute front caused by dispersion (Keeley, 1989).*

IIA.2 Colloidal Transport of Inorganic Contaminants

The association of contaminants with suspended colloidal material in ground water is a possible transport mechanism and a complicating factor for accurate estimations of the natural attenuation of contaminants in subsurface systems. The mobile colloidal phase must be highly reactive, of sufficient quantity, and stable for periods of time (i.e., remain in suspension due to physical or chemical perturbations to the aquifer) to enable the transport of a significant mass of contaminants. Research to date indicates colloidal facilitated transport of contaminants in ground waters, surface waters and in the unsaturated zone. Evidence suggests that colloidal transport of contaminants may be significant for some species under some hydrogeological conditions. It is important therefore for sampling methods, transport models, and site assessments to consider and be sensitive to this transport mechanism.

Colloids are generally considered to be particles with diameters less than 10 microns (Stumm and Morgan, 1981). Based on theoretical considerations, Yao et al. (1971) and O'Melia (1980) have estimated that the most mobile colloidal particles in filtration studies in porous media may range from 0.1 to 1.0 µm. These include both organic and inorganic materials. Recent estimates of colloidal concentrations in ground water range as high as 63 mg L^{-1} (Buddemeier and Hunt, 1988), 60 mg L^{-1} (Ryan and Gschwend, 1990), and 20 mg L^{-1} (Puls and Eychaner, 1990). In addition to a high surface area per unit mass, colloidal particles such as organic carbon particles, clay minerals and iron oxides are also extremely reactive sorbents for inorganic contaminants. If mobile in subsurface systems, these colloids can effect the migration of contaminants for much larger distances than many transport models would predict, because sorbing contaminants spend a significant fraction of time associated with mobile rather than immobile solids, and because colloid transport can be primarily along large diameter, fast flow paths.

Colloidal material may be released from the soil or geologic matrix and transported large distances given favorable hydrological and geochemical conditions. Changes in solution chemistry resulting from environmental pollution or changes in ground water recharge chemistry can bring about changes in the aqueous saturation state in the subsurface leading to precipitation of new colloid-sized inorganic solids that are entrained within flowing ground water, or can cause the dissolution of matrix cementing agents, promoting the release of colloid-sized particles. In addition, changes in the concentrations of solutes that affect colloid surface charge, such as pH or organic anions, can change the stability of colloids. An excellent review of the mechanisms of colloidal release, transport, and stability was published by McCarthy and Zachara (1989). Reference to field and laboratory studies provide examples of situations representative of sites with subsurface contamination where periods of colloid mobilization may exist. For example, Gschwend and Reynolds (1987) demonstrated that submicron ferrous phosphate colloids were suspended and presumably mobile in a sand and gravel aquifer. The colloids were formed from sewage-derived phosphate and iron released from aquifer solids due to reduction and dissolution of ferric iron from the soil. Thompson et al. (2006) have also demonstrated that microbially-driven redox cycling of iron bound to soils may also lead to release of colloidal solids via indirect impacts on water chemistry. In this instance, the mobilized colloidal fraction was dominated by organic carbon solids.

However, field observations also point to the transience of colloid mobilization in the subsurface. Nightingale and Bianchi (1977) observed that ground-water turbidity may increase for periods of time due to mobilization of colloidal solids coincident with time-varying recharge events. These observed turbidity increases were abated with time as the aquifer returned to steady-state conditions. In addition, Baumann et al. (2006) observed high colloid concentrations in leachate from landfills, but colloid concentrations decreased rapidly in ground water down gradient from the landfill. Their observations suggested that the change of hydrochemical conditions at the interface, from a reducing, high ionic strength environment inside of the disposal sites to an oxidizing, low ionic strength environment in the ground water (together with physical filtration effects for the larger particles) was an effective chemical barrier for colloid migration. Thus, it appears that while colloid mobilization (along with associated contaminants) probably does occur, colloid migration is not likely to serve as a dominant mechanism for contaminant migration encountered at contaminated sites.

IIA.2.1 Implications for Natural Attenuation Assessment

Many studies have documented that colloidal transport can occur under some hydrogeological conditions. As noted above, very few studies have shown that transport of contaminants via colloidal transport in the subsurface accounts for the predominant mass of mobile contaminant at a site. Where colloidal transport may be significant from a human health standpoint is with highly toxic elements. From a site characterization perspective, assessing the significance of colloid-facilitated contaminant transport will depend on the adequacy of well installation materials and construction approaches, as well as the approaches to sampling ground water. Since well installation results in disturbance of the subsurface solids, initial development to removed fine-grained, disturbed aquifer materials from within and adjacent to the well screen is a critical step prior to initiating retrieval of ground-water samples. In addition, stabilization criteria employed as indicators of the retrieval of representative ground-water samples may need to be adjusted if it is important to rule out colloid transport as a contaminant migration method. For this situation, more strict limits may need to be placed on turbidity stabilization observations, resulting in longer pumping times and/or significantly lower pumping rates (e.g., Jensen and Christensen, 1999).

In addition, it is recommended that the chemical composition of the colloidal materials be identified at sites where field data suggests colloid-facilitated contaminant transport.

This step is warranted to rule out possible sources of sample contamination or artifacts resulting from sample collection or processing. For example, the presence of iron oxide colloids may be observed for reduced ground-water samples containing elevated concentrations of ferrous iron [e.g., >5 ppm Fe(II)] that are exposed to oxygen during collection or handling. In this case, the likely source of colloidal iron oxides is due to rapid oxidation and precipitation of ferrous iron after the ground water has been pumped from the subsurface. In general, the rigid and complex procedures needed to insure sample quality for identification of ground-water colloids may be difficult to implement within the overall characterization effort (e.g., Dai et al., 2002).

Ultimately, the resources expended to this effort need to be balanced with the effort to characterize site hydrology as well as the subsurface processes that may control contaminant degradation or sorption to aquifer solids. In order to provide context to the types of data that may be needed to identify specific sorption processes active within the plume, the following sections provide detail on the types of mechanisms that may result in contaminant immobilization.

As previously outlined in Section I, the processes leading to contaminant attenuation may include those that cause reduction of contaminant mass (i.e., degradation and radioactive decay) or cause immobilization of the contaminant via sorption to aquifer solids. For a majority of the inorganic contaminants encountered at contaminated sites, some form of immobilization will likely dominate the attenuation process. The following discussion will provide detail on the types of sorption processes that may result in contaminant attenuation. This discussion will illustrate the factors or parameters that are a component of the sorption reaction in order to provide context to the types of measurements needed to support identification of the site-specific attenuation process and its performance characteristics (discussed below in Section III of this volume). In addition, the impact that microbial processes exert on the subsurface geochemistry will be discussed in order to provide context to factors that may dictate site-specific conditions within a contaminant plume.

IIB. Contaminant Sorption to Aquifer Solids

The primary, and in most instances, the only process involved in the natural attenuation of inorganic contaminants is through partitioning to the solid phase. The process of contaminant transfer from the aqueous to the solid phase is generally referred to as *sorption* and involves three primary mechanisms (Sposito, 1986): *adsorption*, which is the accumulation of matter at the interface between the aqueous phase and a solid adsorbent without the development of a three-dimensional molecular arrangement; *precipitation,* which is the growth of a solid phase exhibiting a molecular unit that repeats itself in three dimensions; and *absorption*, which is the diffusion of an aqueous or adsorbed chemical species into a solid phase (Figure 2.3). From the standpoint of monitored natural attenuation, the mechanisms of most relevance will be dependent on contaminant and site specific characteristics, such as the surface reactivity, solubility, and redox sensitivity of the contaminant, as well as the type and abundance of reactive mineral phases and the ground-water chemistry.

More detailed discussion is provided below on the various sorption processes introduced in the preceding paragraph. As a point of reference, representative examples of sorption processes for specific contaminants are provided in Figure 2.4.

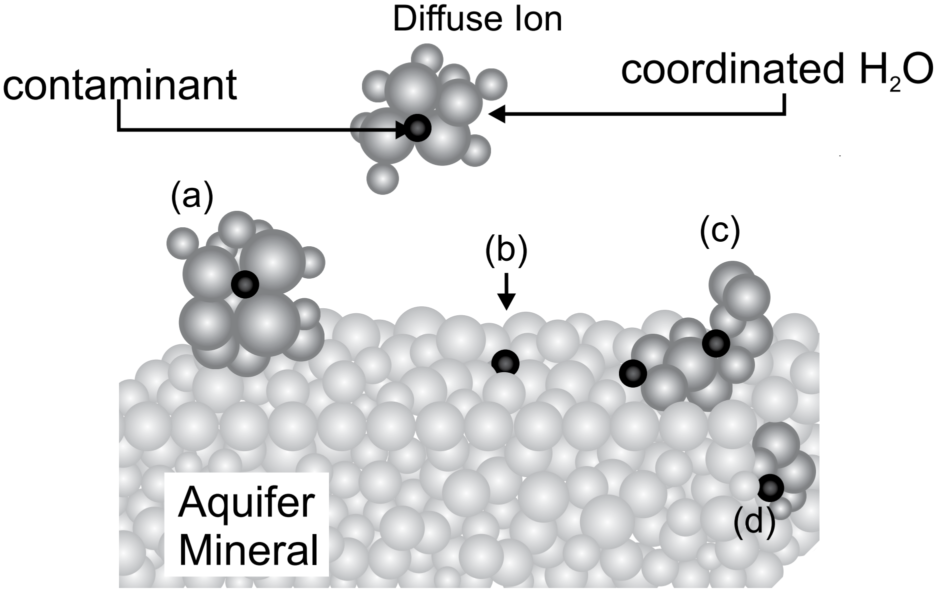


Figure 2.3 *Representation of an aquifer mineral surface with (a) an outer-sphere surface complex; (b) an inner-sphere surface complex; (c) a multinuclear surface complex or a surface precipitate; and (d) absorption, or solid state diffusion and substitution of the sorbate in the mineral structure (after Sposito, 1984).*

IIB.1 Adsorption

Adsorption processes are typically categorized by the relative binding strength of interaction between the adsorbate (species in solution) and the adsorbent (aquifer solid). There is a range of binding strength for contaminant adsorption that depends on characteristics of the adsorbate, sorbent, and ground-water chemistry. However, discussions of binding strength are generally couched in terms of "weak" or "strong" adsorption processes, albeit a common convention in chemistry would categorize both the covalent and electrostatic interactions involved in adsorption as 'strong' intermolecular forces (Israelachvili ,1994). One microscopic distinction borrowed from the characterization of soluble ion pairs that is commonly used to delineate weak and strong adsorption involves the solvation properties of the adsorbate (Westall, 1986; Stumm, 1992). If solvating water molecules are interposed between the cation or anion and the surface, the adsorption complex is referred to as *outer sphere* and is considered to be weak. Conversely, if upon adsorption the adsorbate loses waters of hydration such that there are no water molecules interposed between the cation or anion and the surface, the adsorption complex is referred to as *inner sphere* and is considered to be strong (Sposito, 1984). The propensity of a cation or anion to form either an inner-sphere or outer-sphere surface complex is a function of the adsorbate, the surface functional groups of the adsorbent, and aqueous phase chemistry (e.g., pH and ionic strength).

IIB.1.1 Reactive Mineral Phases Involved in Adsorption

Important adsorbent phases commonly found in the environment include phyllosilicate minerals, metal oxyhydroxide phases, sulfide phases, and natural organic matter (Dixon and Schulze, 2002). Many phyllosilicate minerals possess a permanent negative charge as a result of the substitution of lower valence cations, i.e., Mg(II), Fe(II), Li(I) for Al(III) in the octahedral layer and/or Al(III) for Si(IV) in the tetrahedral layer (referred to as isomorphic substitution). There are two main classes of phyllosilicate minerals based on layer structure (Figure 2.5). The 1:1 mineral layer type is comprised of one Si tetrahedral layer and one Al octahedral layer, which in soils and aquifers is commonly represented by the mineral kaolinite having the general formula $[Si_4]Al_4O_{10}(OH)_8 \bullet nH_2O$. Kaolinite and related minerals generally have insignificant degrees of cation substitution within their octahedral and tetrahedral layers, and, thus generally posses a very low permanent negative charge. The 2:1 mineral type is comprised of one Al octahedral layer interposed between two Si tetrahedral layers comparable to the mica structures (Figure 2.5). The 2:1 layer class is represented by a variety of minerals, which are classified based on the location (tetrahedral vs. octahedral layer) and relative amount of isomorphic substitution. The three major mineral classes within the 2:1 layer type are illite $(M_x[Si_{6.8}Al_{1.2}](Al_3Fe_{0.25}Mg_{0.75})O_{20}(OH)_4)$, vermiculite $(M_x[Si_7Al](Al_3Fe_{0.5}Mg_{0.5})O_{20}(OH)_4)$, and smectite $(M_x[Si_8]Al_{3.2}Fe_{0.2}Mg_{0.6}O_{20}(OH)_4)$, which display different levels

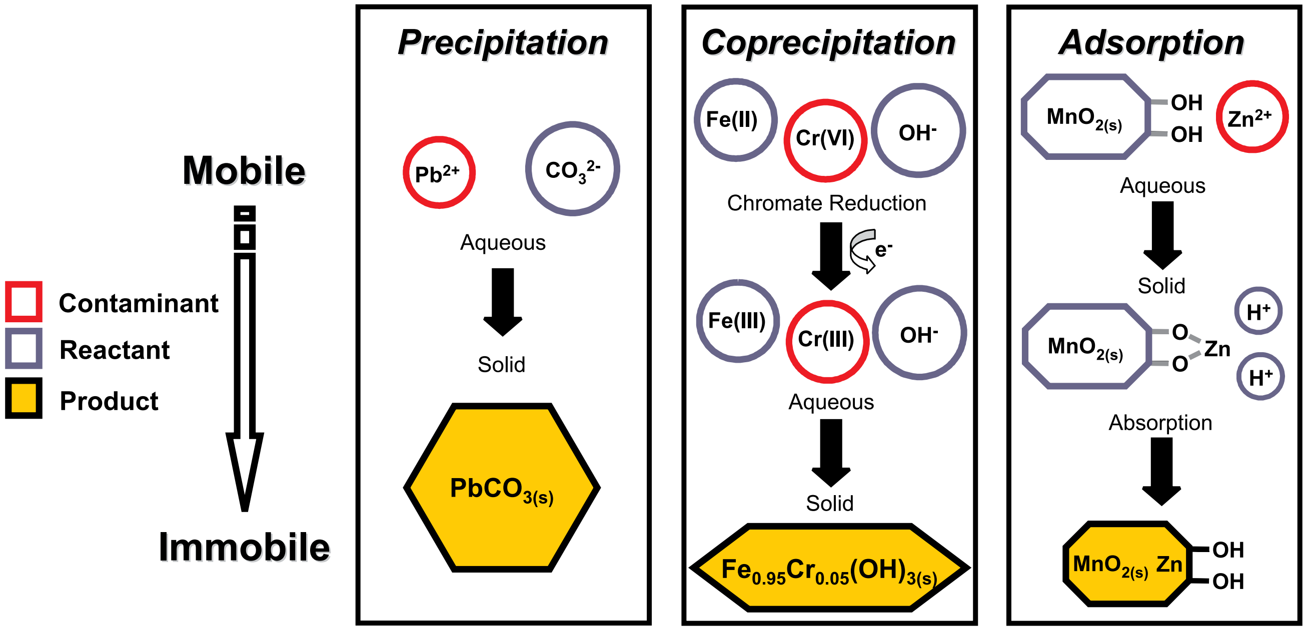


Figure 2.4 *Examples of contaminant-specific sorption processes that may lead to attenuation of the ground-water plume. Color coding is employed to distinguish the contaminant (red), aqueous or solid phase reactants (blue), and the product (yellow) of the reaction leading to contaminant attenuation. Absorption is illustrated as a possible sequential process that follows the adsorption of a contaminant onto a mineral component within aquifer solids.*

of cation substitution in their tetrahedral and octahedral layers. The permanent negative charge imparted to 2:1 clay minerals by isomorphic substitution is typically balanced through exchange reactions involving major cations in ground water (e.g., Na$^+$, K$^+$, Ca^{2+}, or Mg^{2+}; represented by "M$_x$" in the formulas listed above).

Contaminant sorption to phyllosilicates may occur via ion exchange or surface complexation with surface functional groups (see examples labeled "surface complex" and "ion exchange" in Figure 2.5). Due to differences in the levels of isomorphic substitution for the 1:1 and 2:1 clay mineral classes, ion exchange is usually only significant for 2:1 phyllosilicates. In addition to siloxane oxygen atoms along the basal plane, phyllosilicates possess two types of terminal ionizable OH groups, aluminol and silanol, protruding from the edge surface. These edge OH groups can form both inner- and outer-sphere complexes with metal cations and oxyanions depending on the pH of the bathing solution and on the specific characteristics of the cation or oxyanion (represented as "surface complex" in Figure 2.5).

The most important surface reactive phases for both cationic and anionic contaminants in many soil and subsurface systems are the metal oxyhydroxide phases. These phases are characterized by hexagonal or cubic close-packed O or OH anions with Fe$^{2+,3+}$, Al^{3+}, and/or Mn$^{3+,4+}$ occupying octahedral sites. These oxides are present as discrete phases and as complex mineral assemblages, being co-associated with phyllosilicates and primary minerals as coatings or with humic macromolecules. In soils and sediments the crystallinity of these phases typically varies from poorly ordered to well crystalline forms and grain size from the nanometer to micrometer scale. Among the most common Fe-oxyhydroxide phases found in soils and sediments are the poorly ordered phase ferrihydrite ($Fe_2O_3 \cdot nH_2O$), and the moderate to well crystalline phases, goethite (α–FeOOH), and hematite (α-Fe_2O_3). The most common Al oxyhydroxide phase found in soils and sediments is gibbsite (γ-$Al(OH)_3$). Additionally, poorly ordered aluminosilicates can be important reactive phases in certain soils and these include the very poorly ordered allophanes (Si/Al ratios 1:2 to 1:1) and the paracyrstalline phase, imogolite ($SiO_2 \cdot Al_2O_3 \cdot 2H_2O$). While Mn oxyhydroxides are less prevalent than Fe- and Al-oxyhydroxides in soils and sediments they are very important phases in terms of surface mediated redox reactions and because of their propensity for high metal sorption. The mineralogy of Mn is complicated by the range in Mn-O bond lengths resulting from extensive substitution of of Mn^{2+} and Mn^{3+} for Mn(IV). Thus, there exists a continuous series of stable and metastable compositions from MnO to MnO$_2$ forming a large variety of minerals. Among the more common Mn-oxyhydroxides are pyrolusite (β-MnO_2), the hollandite-cryptomelane family (α-MnO_2), todorokite, and birnessite (σ-MnO_2).

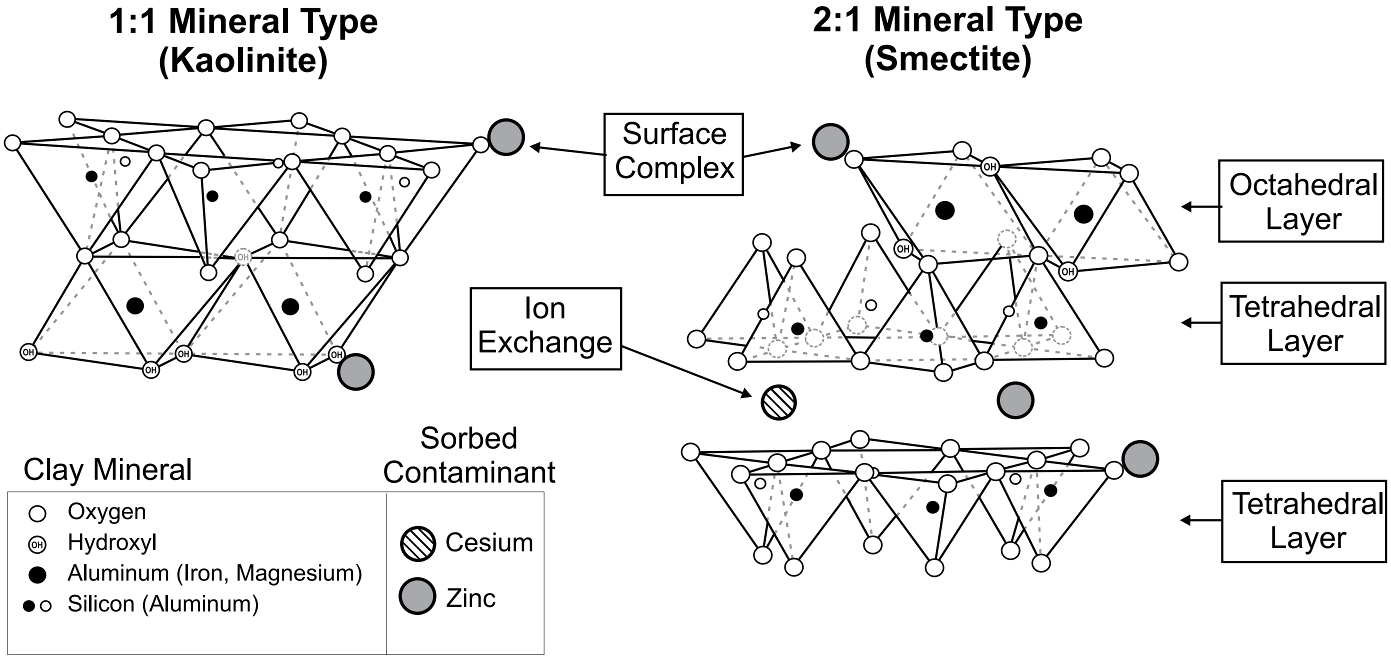


Figure 2.5 *Diagrammatic sketch of the structure of 1:1 and 2:1 phyllosilicate minerals. Also shown are hypothetical sorption reactions for zinc and cesium (ion exchange represented as 'M$_x$' in structural formulas for 2:1 phyllosilicates shown in text).*

IIB.1.2 Surface Functional Groups on Aquifer Solids and the Impact on Surface Charge

The reactive surface functional group for all of the metal oxyhydroxide phases is the inorganic OH moiety exposed on the outer periphery of these minerals. The reactivity of a specific metal oxyhydroxide is dependent on the surface area (S_A), surface-site density (N_S), the degree of coordination of the OH group to the bulk structure, and the point of zero charge (PZC). The charge on the mineral surface may impose either attractive or repulsive contributions to the overall adsorption reaction, depending on the type of charge possessed by the adsorbate. The properties of the sorbent that impact adsorption are controlled by both the grain size and specific structure of the oxyhydroxide phase.

The surface charge of oxyhydroxide minerals and edge sites on phyllosilicates is derived from the protonation and ionization of exposed surface hydroxyl groups, represented by $\equiv SOH_n^{n-1}$, where S represents the structural metal cation (e.g., Fe, Al, Mn) over a stoichiometric range from n= 0, 1, or 2. Thus, as a function of pH, the surface functional groups can be generally described with the following idealized nomenclature: $\equiv SOH_2^+$, $\equiv SOH^0$, and $\equiv SO^-$. The exact charge associated with the various surface functional groups is difficult to measure, so the main purpose of employing this nomenclature is to illustrate that surface charge varies as a function of ground-water chemistry. The gradual change in surface charging with pH for some common minerals is illustrated in Figure 2.6 and a discussion of surface site charging is provided below.

Natural organic matter comprised of complex polymers called humic substances, represents another very important reactive phase in aquifer solids. A variety of functional groups are present in humic substances, and, like OH functional groups of the inorganic metal oxyhydroxides, these also are characterized by pH dependent charging mechanisms. The primary functional groups associated with humic substances in terms of surface charge are carboxyl and phenolic groups, however the less abundant amino, imidazole, and sulfhydryl groups may play an important role in the sorption of certain contaminant metals when present at trace levels (Table 2.1).

Based on the previous discussion, it is apparent that the charge on aquifer solids can be grouped into two classes associated with the mechanisms that give rise to electrical charge associated with mineral surfaces or with organic functional groups. These two classes are commonly referred to as permanent (or constant) charge and variable charge.

- Constant charge - Constant charge is the predominant charge in phyllosilicate clays. Because, for the most part, these isomorphic substitutions occur during mineral formation, this charge deficit is fixed in the lattice structure and is hence unaffected by changes in electrolyte concentration or pH of the soil solution.
- Variable (pH dependent) charge - Variable charge is the predominant charge for oxyhydroxide minerals such as hematite, goethite, and gibbsite, as well as for humic substances. The metal ions in the vicinity of the surface of metal oxyhydroxide minerals are coordinatatively unsaturated, i.e. they are lewis acids, and coordinate with water molecules, which subsequently dissociate a proton leading to a surface layer of metal hydroxide functional groups. This process also occurs at the edges of phyllosilicate clays giving rise to SiOH (silanol) and AlOH (aluminol) functional groups. These surface hydroxyl groups can become positively or negatively charged by binding or dissociating a proton (i.e., protonation-deprotonation reactions):

$$S—OH + H^+ \leftrightarrows S—OH_2^+$$

$$S—OH \leftrightarrows S—O^- + H^+$$

Thus, the prevalent surface charge in aquifer solids will be dependent on the pH of ground water and the types and concentrations of ions that balance the permanent charge association with phyllosilicates. The extent to which

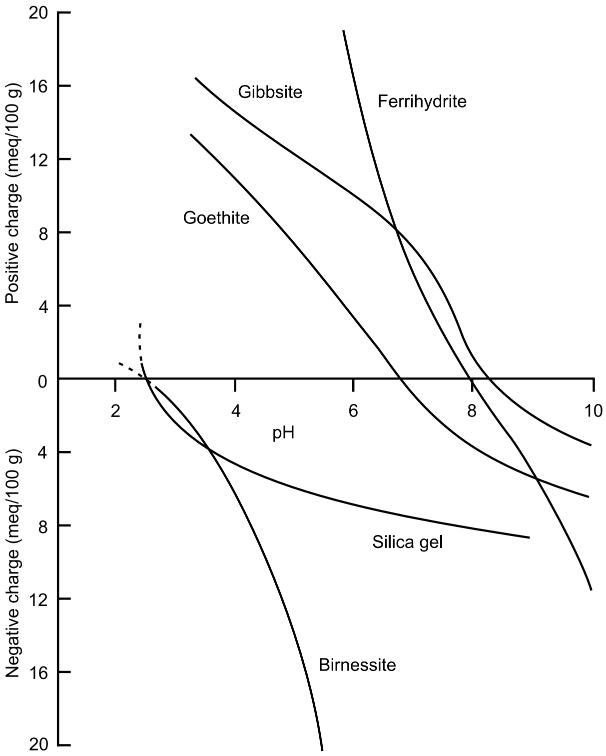
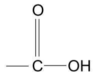
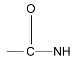
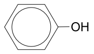
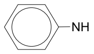


Figure 2.6 *Surface charge of some hydroxides from pH 2 to 10 measured in different electrolyte solutions shown in parentheses; positive and negative surface charge shown above and below the x-axis, respectively. Ferrihydrite [$Fe(OH)_3 \cdot nH_2O$] (0.001 M $NaNO_3$) from Hsi and Langmuir (1985); gibbsite [$Al(OH)_3$] and silica gel [$SiO_2 \cdot nH_2O$] (1.0 M CsCl) based on Greenland and Mott (1978); goethite [α-FeOOH] (0.005 M CsCl) based on Greenland and Mott (1978) (see also Hsi, 1981); birnessite (σ-MnO_2] (0.001 M $NaNO_3$) based on Catts and Langmuir (1986).*

Table 2.1 Important functional groups in humic substances that impact surface charging behavior and contaminant binding.

Functional Group	Structural Formula
Amino	$-NH_3$
Carboxyl	 $-C(=O)-OH$
Carbonyl	 $-C(=O)-NH$
Alcoholic hydroxyl	-OH
Phenolic hydroxyl	
Imidazole	
Sulfhydryl	-SH

protonation or deprotonation occurs is also a function of the metal ion and the local binding environment of the metal hydroxide surface group. The highly electropositive Si^{4+} in silanols precludes the protonation of the surface hydroxyl and this functional group can only dissociate a proton under pH conditions generally encountered in ground water. Aluminols, on the other hand, can be either positively or negatively charged. Various types of hydroxyls of differing reactivity have been identified spectroscopically at the surface of metal oxides.

The charge of aquifer minerals is always electrically balanced by interactions with ions of an opposite charge (counter-ions). We can define two broad classes of weak and strong interactions (outer and inner-sphere) that act to neutralize the charge developed at soil mineral surfaces.

IIB.1.3 Weak and Strong Adsorption Regimes

Weak adsorption regime - Within the weak adsorption regime, simple ion exchange is the most common mechanism and involves the electrostatic attraction of an ionic species by a negative or positive charge emanating from a mineral surface or from functional groups associated with humic substances (Sposito, 1981). Long before the structures of reactive soil minerals were determined, it was observed that, under certain circumstances, there was a reversible and stoichiometric (based on charge) replacement of major cations in soils equilibrated with concentrated neutral salt solutions according to the reaction:

$$Na_2\text{-}X_s + Ca^{2+}_{aq} \leftrightarrow Ca\text{-}X_s + 2Na^+_{aq}$$

Soil and sediment materials are typically characterized by their cation exchange capacity (CEC), which is defined as the quantity of cations reversibly adsorbed per unit weight of mineral and typically expressed as cmol kg^{-1}. The cation exchange capacity of 2:1 phyllosilicate clays tends to be constant over a wide pH range, since ionizable edge groups are relatively minor on a surface area basis compared to the permanent charge associated with planar sites. For 2:1 phyllosilicates, cations hydrated to differing degrees are located in the interlayer space and can be displaced by other competing cations through ion exchange reactions (see Figure 2.5). In principle, cation exchange reactions involve both inner and outer sphere complexation with planar sites, although except for the special case discussed below for large weakly hydrated monovalent cations, such as K^+ and Cs^+, both are readily reversible. Both inner and outer sphere complexes can also form with O functional groups associated with organic macromolecules and O and OH atoms associated with metal oxyhydroxides, but only the outer sphere complexes are considered weak adsorption. The major difference between phyllosilicates having substantial isomorphic substitution and metal oxyhydroxides and humic substances, is that the CEC is highly pH dependent, increasing with increasing pH. Since reactive mineral phases in soils and sediments are a composed of complex assemblages of phyllosilicates, oxyhydroxides, and humic substances, CEC is always a pH dependent property.

Strong adsorption regime - As discussed above, simple ion exchange is the predominant adsorption mechanism for phyllosilicate clays. A major exception to this is the inner-sphere sorption of larger unhydrated cations, such as K^+ and Cs^+ to oxygen atoms of two opposing siloxane ditrigonal cavities of collapsed layers of weathered micaceous minerals, such as illite, which can be classified as an 'irreversible' adsorption or as an absorption process.

At this point it is important to discuss the concept of the reversibility of adsorption. From the perspective of chemical thermodynamics, the definition of a 'reversible' process is one where the initial state of the system can be restored with no observable effects in the system *and* its surroundings (Holman, 1980). The use of the term 'irreversible' from the standpoint of adsorption mechanisms is relative and does not strictly adhere to the thermodynamic (or chemical) definition in all cases. The fixation of Cs^+ in illitic minerals is conceptually thought to proceed via an initial ion exchange reaction followed by an interlayer collapse (fast) or through the slower migration into interlayer sites in collapsed layers (absorption). Once Cs^+ is fixed within the interlayer of the clay mineral, its release is not readily reversible via displacement with competing solutes, i.e., through ion exchange mechanisms. Thus, the release of fixed Cs^+ is subsequently controlled by a process such as mineral dissolution. In this sense, the original fixation process is irreversible, since contaminant release would result from a mechanism other than the reversal of the original adsorption mechanism.

The formation of a chemical bond between an adsorbate and a functional group on the adsorbent also falls within the category of a strong adsorption regime. In general, breaking chemical bonds requires more energy than overcoming electrostatic interactions. Metal adsorption to OH functional groups of oxyhydroxide phases through surface complexation can be illustrated by the following surface reaction (Stumm, 1992; McBride, 2000):

$$=Fe\text{-}OH^{-1/2} + M(H_2O)_6^{n+} \Rightarrow =Fe\text{-}O\text{-}M(H_2O)_5^{(n-3/2)+} + H_3O^+$$

Thus, specific adsorption of cations increases the positive charge at the mineral surface when $n > 1$, which is generally the case for transition elements, and results in the net release of H^+ ions to the soil solution. Adsorption of anions from solution occurs by ligand exchange of a OH or H_2O at the surface functional group according the following reaction (solution anion represented by A^{n-}):

$$=\text{Fe-OH} + A^{n-} \Rightarrow \text{S-}A^{(n-1)-} + OH^-$$

Anion adsorption is favored by low pH, which leads to protonation of surface functional groups and makes them better leaving groups in the ligand exchange reaction.

IIB.2 Precipitation

Mineral-water reactions occur as ground water moves through porous media. These reactions may result in the removal of aquifer components due to mineral dissolution or result in the buildup to oversaturation and consequent precipitation of secondary minerals. As an outcome of mineral-water reactions along a flow path, fluid compositions and the mineralogical makeup of the solid phase will continuously evolve towards a stable or equilibrium state. Mineral precipitation processes in aquifer systems are an important group of immobilization mechanisms for inorganic contaminants in ground water.

Full treatment of precipitation processes, including coverage of relevant thermodynamic and kinetic concepts, is outside the scope of this document. The reader is referred to numerous standard textbooks in geochemistry, soil science, and aquatic chemistry (e.g., Lindsay, 1979; Stumm, and Morgan, 1981; Drever, 1982; Sposito, 1989; Stumm 1992; Morel and Hering, 1993; McBride, 1994; Sparks, 1995; Langmuir, 1997; Lasaga, 1999). The purpose of this section is to introduce key concepts and issues regarding the potential impact precipitation reactions may exert on contaminate attenuation. In general, mineral precipitation in relation to contaminant immobilization can be discussed in the context of four widely studied processes:

- Precipitation from solution: Nucleation and growth of a solid phase exhibiting a molecular unit that repeats itself in three dimensions. Homogeneous nucleation occurs from bulk solution and heterogeneous nucleation occurs on the surfaces of organic or mineral particles. Heterogeneous nucleation is thought to be more important in natural systems that are rich in reactive inorganic and biological surfaces. Precipitation may result in the formation of sparingly soluble hydroxides, carbonates, and, in anoxic systems, sulfides. Many precipitation reactions have a strong dependence on pH.

- Coprecipitation: Incorporation of an element as a trace or minor constituent within a precipitating phase. In this case, the contaminant substitutes for a more concentrated component in the crystal lattice (isomorphous substitution). This process is distinct from adsorption due to incorporation of the contaminant within the bulk structure of the major mineral phase. Examples of coprecipitation include Cr(III) in hydrous ferric oxide, Cd(II) in calcium carbonate, and As(III) in iron sulfide.

- Surface precipitation: A precipitation process intermediate between surface complexation and precipitation from bulk solution. Surface precipitation represents the continuous growth of particles formed via heterogeneous nucleation. Macroscopic studies of adsorption of some solutes, particularly di-valent and tri-valent cations, suggest that precipitation occurs at surfaces under conditions where the solid is apparently undersaturated based on solution concentrations (Dzombak and Morel, 1990).

- Mineral transformation: Adsorbed contaminants can become incorporated into minerals that form as a result of recrystallization or mineral transformation processes in soils and sediments. Transformation reactions may be accelerated or retarded by the contaminant, and in some cases mineral transformation may result in the exclusion of the impurity contaminant from the solid phase. Examples include incorporation of anions, such as As(V), into hydrous ferric oxide and transformation to Fe oxyhydroxides (e.g., Ford, 2002), coprecipitation of metals with iron monosulfide and transformation to iron disulfide (e.g., Lowers et al., 2007), and layered double hydroxides (typically with Al) as intermediates between adsorbed/surface precipitated metal ions like Ni and Zn, and metal-ion-containing aluminosilicates (e.g., Ford, 2007).

The relative importance of these processes will be determined by contaminant characteristics as well as site-specific characteristics of the plume ground-water chemistry and aquifer solids. These individual processes are discussed in more detail below.

IIB.2.1 Precipitation from Solution

Solution precipitation or crystallization can be divided into two main processes: nucleation and crystal growth. Nucleation occurs prior to growth of a mineral crystal. Both nucleation and growth processes require a system to be oversaturated in the new phase. The probability of nucleation occurring increases exponentially with the degree of oversaturation. Nucleation of a new phase is often facilitated in the presence of a surface (heterogeneous nucleation) compared to bulk solution (homogeneous nucleation). Because nucleation and growth are processes that compete for dissolved solutes, at high degrees of oversaturation the rate of nucleation may be so fast that all excess solute is partitioned into crystal nuclei. In contrast, lower levels of oversaturation can result in the growth of existing crystals without nucleation. Well-formed or euhedral crystals typically develop slowly via growth from solution at low degrees of oversaturation. During crystal growth various chemical reactions can occur at the surface of the growing mineral, such as adsorption, ion exchange, diffusion, and formation of surface precipitates. In general, the rate of crystal growth is controlled either by transport of solutes to the growing surface (i.e., transport controlled), by reactions at the surface (i.e., surface controlled), or a combination of these factors.

For the most abundant cations present in aquifers and soils, such as Al, Si, Fe, Mn, Ca, and Mg, precipitation of mineral forms is common and will in many cases control concentrations observed in solution. At contaminated sites, concentrations of ground-water contaminants are typically several orders of magnitude below the concentrations of the dominant solutes in water. At low concentrations, sorption, surface precipitation, or formation of a dilute solid solution (coprecipitation) may be the more probable removal processes for contaminant species (McBride, 1994). However, precipitation of iron-bearing or aluminum-bearing minerals, for example, can have an important affect on the transport and fate of metal and metalloid contaminants. Major mineral precipitate classes encountered in aquifers and soils are listed in Table 2.2.

The tendency for a system to support a specific precipitation or dissolution reaction can be evaluated through comparison of the equilibrium solubility constant for a given solid phase to the ion activity product calculated using ground-water chemical data. The relative magnitude of the values of the equilibrium solubility product and the calculated ion activity product provides a measure of the saturation state of ground water relative to mineral precipitation or dissolution. A conventional method for expressing the ground-water saturation state is by calculation of the saturation index, SI, which is given by (Stumm and Morgan, 1981):

$$\mathrm{SI} = \Delta G_r^0/RT + \ln Q = \ln Q/K_r$$

where ΔG_r^0 is the standard state free energy change of the reaction, R is the gas constant, T is temperature in degrees Kelvin, Q is the reaction quotient (or ion activity product), and K_r is the temperature- and pressure-dependent equilibrium constant of a reaction. Another term used frequently in place of the saturation index is the relative saturation, $\Omega = Q/K_r$. At chemical equilibrium, $\Delta G_r^0 = 0$, $Q = K_r$, and $\Omega = 1$. In this special case, the solution of interest is in equilibrium with the mineral and no dissolution or precipitation should take place. Where $\Delta G_r^0 < 0$, the mineral cannot precipitate from solution and the thermodynamic driving force is such that mineral dissolution should occur. Where $\Delta G_r^0 > 0$, the mineral will likely precipitate if there are no limiting kinetic factors (Table 2.3).

Table 2.2 Major mineral classes in aquifers and soils.

Mineral Class	Primary Mineral	Contaminant Precipitate
Hydroxides	$Al(OH)_3$, gibbsite $Fe(OH)_3$, hydrous ferric oxide FeO(OH), goethite FeO(OH), lepidocrocite	$Cu(OH)_2$ $Cr(OH)_3$ $Zn(OH)_2$
Oxides	Fe_3O_4, magnetite Fe_2O_3, hematite MnO_2, pyrolusite SiO_2, quartz	UO_2, uraninite
Carbonates	$CaCO_3$, calcite/aragonite $FeCO_3$, siderite $MnCO_3$, rhodochrosite	$CdCO_3$, otavite $ZnCO_3$, smithsonite $PbCO_3$, cerussite
Sulfates	$BaSO_4$, barite $CaSO_4 \cdot 2H_2O$, gypsum	$PbSO_4$, anglesite $RaSO_4$
Sulfides	FeS, mackinawite FeS_2, pyrite/marcasite	PbS, galena NiS, millerite HgS, cinnabar ZnS, sphalerite
Phyllosilicates	$Al_4(OH)_8Si_4O_{10}$, kaolinite $K_{1.5}Al_2(OH)_2Si_{2.5}Al_{1.5}O_{10,}$ illite	$Ni_3Si_2O_5(OH)_4$, nepouite $Na_{0.3}Zn_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$, sauconite

The ion activity product is a useful probe to evaluate the potential for contaminant precipitation. Some caution, however, is recommended in interpreting solution indicators as evidence for the presence of a particular precipitated solid within the plume. The observation that an ion activity product is equal to a corresponding solubility product is not unequivocal evidence that a given phase is at equilibrium or even present in the system (Sposito, 1984). Similarly, an ion activity product that is greater than a corresponding solubility product cannot be taken as confirmation that precipitation is occurring. To understand the state of a system with respect to precipitation and dissolution, it is recommended that the presence of the relevant solid phases be evaluated in addition to measuring the concentrations of solutes that participate in a precipitation reaction suspected to occur within the ground-water plume.

Table 2.3 Relationships among Q, K, and Ω.

Process	Saturation Index, log (Q/K_r)	Relative Saturation, Ω	Q, K_r
Mineral dissolution	Negative	< 1	$Q < K_r$
Mineral precipitation	Positive	> 1	$Q > K_r$
Equilibrium	0	1	$Q = K_r$

IIB.2.2 Coprecipitation

Contaminant plumes are often characterized by concentrations of dissolved solids in excess of that found in ambient ground water. These elevated dissolved solids may be derived as a component of the contaminant source or due to the dissolution of soil or aquifer solids during plume transport. Examples of these processes include interactions of acid wastes with aquifer solids leading to dissolution of aquifer minerals (e.g., carbonates or oxyhydroxides) or the development of reducing conditions driven by microbial degradation of organic contaminants that result in reductive dissolution of iron-bearing minerals. With downgradient transport, changes in ground-water chemistry or interaction with unimpacted aquifer solids may lead to precipitation of these major ground-water constituents out of solution. Contaminants may be removed from ground water at the location where precipitation of these major ground-water constituents occurs. This process is called coprecipitation, since the contaminant is sequestered within a newly formed precipitate, but only as a trace structural component within the precipitate. Examples of major precipitate classes with a coprecipitated contaminant include oxyhydroxides (e.g. $Fe_{1-x}Cr_x(OH)_{3(s)}$), carbonates (e.g., $Ca_{1-x}Cd_xCO_{3(s)}$), sulfides (e.g., $Fe_{1-x}Ni_xS_{2(s)}$), and phyllosilicates. The contaminant may be coprecipitated in a cationic or anionic form depending on ground-water chemistry and the nature of the precipitating phase.

For coprecipitates (or solid solutions) the concentration of the contaminant in ground water in contact with a precipitate may be reduced significantly below that observed for ground water in which the concentration of the contact is governed by the solubility of a precipitate in which the contaminant is a major structural component (e.g., $Ca_{1-x}Cu_xCO_{3(s)}$, coprecipitate vs. $CuCO_{3(s)}$, pure precipitate). For example, the partial molal Gibbs free energy of a binary mixture can be expressed as the sum of two components: a mechanical mixing term and a free energy of mixing term ($\Delta G_{mixture}$):

$$\bar{G}_{mixture} = \left(X_1\bar{G}_1 + X_2\bar{G}_2\right) + \Delta G_{mixture}$$

where X_1 and X_2 are the mole fractions of two components in a binary mixture. The $\Delta G_{mixture}$ term contains an ideal component that depends on X_1 and X_2 and a non-ideal component dependent on X_1, X_2, and activity coefficients in the solid phase (γ_1 and γ_2):

$$\Delta G_{mixture} = RT\left[X_1 \ln X_1 + X_2 \ln X_2\right] + RT\left[X_1 \ln \gamma_1 + X_2 \ln \gamma_2\right]$$

For an ideal solid solution, $\gamma_1 = \gamma_2 = 1$, so that $RT[X_1 \ln\gamma_1 + X_2 \ln\gamma_2] = 0$. Ideal mixing may be approached where the amount of substitution is very low (a dilute solid solution) or where the mixing cations are closely matched in size and charge. In this case, the $\Delta G_{mixture}$ function is a symmetrical parabola having a minimum at $X_1 = X_2 = 0.5$. Hence as a general rule, the free energy of binary mixtures is less than that of the pure, end-member components. It follows that the solubility of an ion can be lowered in a mixed ionic compound relative to the solubility of the pure compound.

Remobilization of a coprecipitated contaminant will be governed by the overall stability of the host precipitate, which may be controlled by ground water parameters such as pH and/or redox state. In most cases, the identification of a coprecipitation process cannot be made with a single line of evidence. Observations of decreased contaminant concentrations concurrent with decreases in the concentrations of major ground-water constituents such as Ca, Fe, or dissolved sulfide may be indicative of a coprecipitation event. It is recommended that this evidence be supplemented with solid phase characterization approaches, such as chemical extractions or microanalytical techniques, to confirm that coprecipitation is an attenuation mechanism.

IIB.2.3 Surface Precipitation

Surface precipitation may result when adsorption leads to high sorbate coverage at the mineral-water interface. Surface precipitation can be thought of as an intermediate stage between surface complexation and bulk precipitation of the sorbing ion in solution (Farley et al., 1985; Ford et al., 2001). At low concentrations of the sorbing metal at the mineral surface, surface complexation is the dominant process. As the concentration of the sorbate increases, the surface complexation concentration increases to the point where nucleation and growth of a surface precipitate occurs. Surface precipitation can be viewed as a special case of coprecipitation where the mineral interface is a mixing zone for ions of surface precipitate and those of the underlying substrate. It is generally believed that surface precipitation can occur from solutions that would appear to be undersaturated relative to precipitate formation based on considering solution saturation indices. The reason for this may be due in part to different equilibrium constants for surface precipitation versus precipitation from solution, or may be related to the way the mineral-water interface is modeled (Sverjensky, 2003). For example, the dielectric constant of water and therefore activity coefficients in bulk solution may be different from activity coefficients near a mineral surface. Again, the identification of a surface precipitation process cannot be made only with solution data. Solid phase characterization data, such as chemical extractions or microanalytical techniques, are needed to confirm that surface precipitation plays a role as an attenuation mechanism.

IIB.2.4 Mineral Transformation

In many cases the solids that precipitate in near surface environments are not the most thermodynamically stable phases. For example, hydrous ferric oxide, ferrihydrite, is metastable relative to the iron oxyhydroxide goethite. The preponderance of metastability in near surface environments is a consequence of the slowness of chemical reactions at temperatures typical of surficial environments. Kinetics, therefore, play an integral role in ground-water and soil geochemistry. Mineral transformation is one example of how metastable precipitates evolve toward more stable mineral phases within an aquifer. Ultimately, contaminants that are initially adsorbed onto or coprecipitated with these metastable precipitates are likely to become more resistant to remobilization if they are incorporated into the more stable transformation product.

The Ostwald Step Rule is often obeyed in low-temperature mineral formation. Precipitation of less stable and more soluble phases is followed by transformation to progressively more stable and less soluble phases. This behavior stems from the preferential formation of materials with fast precipitation kinetics over nucleation and growth of phases with slow kinetics (Stumm, 1992). Differences in precipitation kinetics are often tied to structural complexity of the precipitating mineral. Relatively simple structures are able to form rapidly whereas ordered structures, although more stable, require longer time periods to develop. Precursor phases are usually poorly crystalline and they may be chemically dissimilar to the final stable mineral. Examples that follow the Ostwald Step Rule include the precipitation of ferrihydrite and transformation to more stable iron oxyhydroxides (goethite) and iron oxides (hematite), the precipitation of mackinawite and transformation to pyrite, and the precipitation of amorphous aluminosilicates such as allophane and transformation to halloysite and kaolinite. Transformation pathways result from solution mediated processes or solid-phase transitions (Steefel and van Cappellen, 1990).

The iron monosulfide-to-iron disulfide transformation has been widely studied in the laboratory and in the field. In this example of a mineral transformation process, mackinawite ($Fe_{1+x}S$) precipitates as concentrations of dissolved sulfide and ferrous iron accumulate in pore water. It has been determined that in sulfate-reducing environments, pore water concentrations of ferrous iron and sulfide are controlled by the solubility of mackinawite. Mackinawite, however, is metastable with respect to the iron disulfides, pyrite and marcasite. The rate of transformation from mackinawite to pyrite or marcasite depends on pH and redox conditions. Metals that coprecipitate with mackinawite are likely incorporated into pyrite, which is more stable over a wide pH range and in anoxic conditions. The rate at which this transformation occurs will be governed by chemical conditions including the coprecipitation or adsorption of contaminants and other dissolved constituents from solution. Site characterization aspects relating to mineral transformation processes as an immobilization mechanism will involve determining the spatial concentration distribution of precursor phases and their more stable transformation products along with contaminant associations using mineralogical and wet chemical characterization tools.

IIB.3 Implications for Natural Attenuation Assessment

The sorption processes discussed in the preceding paragraphs may act in isolation or together to arrest contaminant migration within the aquifer. Factors that dictate which process is likely to dominate contaminant attenuation include chemical properties of the contaminant, chemical characteristics of the ground water, and properties of the aquifer solids. Due to the complexities of directly identifying the immobilized form of the contaminant, it is likely that multiple lines of evidence will be needed to adequately discern the controlling attenuation reaction. These lines of evidence will include the evaluation of patterns in ground-water chemistry that point to potential precipitation or coprecipitation reactions, evaluation of aquifer solids to determine patterns in contaminant and solid component associations, and the use of chemical speciation or reaction models to assess if ground-water and aquifer solid characteristics are consistent with observed contaminant attenuation. Additional perspective on possible sorption processes for specific contaminants is provided in the contaminant-specific chapters included in Volume 2 and 3 of this document.

IIC. Microbial Impacts on Inorganic Contaminant Attenuation

The chemical characteristics of ground water and properties of the aquifer mineral components are, in part, influenced by microbial reactions. Microbial activity within the aquifer may also play a more direct role in controlling contaminant speciation and migration. The influence of microbial reactions may be more pronounced in contaminant plumes that also contain degradable organic contaminants such as hydrocarbons or chlorinated solvents. In these instances, the plume geochemistry may differ significantly from that observed in ambient ground water at a site. If microbial reactions play a significant role in contaminant attenuation, it may be necessary to gather information on the degree that these reactions control the concentrations and distributions of reactants that participate in contaminant attenuation, as well as the capacity of the aquifer to sustain microbial activity within the plume. In order to provide perspective on the potential influence of the subsurface microbiology, the following discussion provides an overview of general characteristics of subsurface microbiology, the influence of microbial activity on the redox state within the plume, and the types of contaminant attenuation reactions that may be directly mediated by microorganisms.

IIC.1 Characteristics of Aquifer Microbiology

Microbial reactions can alter the geochemical structure of the subsurface (Newman and Banfield, 2002), and it is becoming increasingly important to characterize these processes in terms of the natural attenuation of inorganic contaminants. Microorganisms inhabiting the subsurface environment exhibit a remarkable array of metabolic capabilities enabling them to use organic or inorganic matter as energy sources and propagate under aerobic or anaerobic conditions. A large part of a microorganism's metabolism is devoted to the generation of adenosine triphosphate (ATP), an "energy currency" that is used by the microorganism for cell synthesis. Microorganisms derive energy through the oxidation of organic compounds or chemically-reduced inorganic ions and compounds. The electrons or hydrogen atoms resulting from oxidation are transferred in most microorganisms by an electron transport chain to an electron acceptor which, in the case of aerobic respiration, is oxygen. Some microorganisms are capable of anaerobic respiration, whereby the electron acceptor is not O_2 but chemically-reducible inorganic compounds such as NO_3^-, SO_4^{2-}, CO_2, Fe^{3+}, or iron/manganese oxyhydroxides. A third type of metabolism, called "fermentation," involves intra-molecular oxidation/reduction without an externally supplied terminal electron acceptor. Fermentation reactions are not considered here because they do not involve metal transformations.

The metabolic diversity manifested by microorganisms is key to their being agents of geochemical change in the subsurface (Ehrlich, 1995). Subsurface biota are usually categorized as either heterothropic or chemolithotrophic according to the following criteria:

- Heterotrophic microorganisms - Heterotrophs include bacteria (single- or multi-celled organisms lacking internal membrane structures), fungi (mycelial or single-celled organisms possessing a cell wall but no photosynthetic capability), protozoa (unicellular, microscopic animals such as amoebae), and archaebacteria (a newly discovered group of organisms possessing a unique cell envelope, membrane structure and ribosomal RNA, distinguishing them from all other microorganisms). Heterotrophs derive energy from the oxidation of organic compounds and obtain most of their carbon from these compounds. Some heterotrophs respire aerobically while others respire anaerobically, requiring the availability of oxygen or other reducible compounds to serve as electron acceptors.
- Chemolithotrophic microorganisms - Some genera of bacteria and archaebacteria are chemolithotrophs. These microorganisms derive energy from the oxidation of inorganic compounds (for example, Fe^{2+}, HS^-, and H_2) and obtain their carbon as CO_3^{2-}, HCO_3^- or CO_2. Some chemolithotrophs are aerobic using O_2 as an electron acceptor while others respire anaerobically using chemically reducible inorganic matter as an electron acceptor (Newman, 2001). An example of this type of metabolism is carried out by methanogens, which oxidize H_2 using CO_2 as an electron acceptor to form CH_4. Reactions carried out by chemolithotrophic microorganisms must derive sufficient energy from the oxidation/reduction reactions to fix carbon (that is, reduce CO_3^{2-}, HCO_3^- or CO_2 to organic carbon) and phosphorylate ADP.

In the aquifer below the vadose zone the populations and numbers of microorganisms vary significantly due to limitations to available oxygen. If the aquifer is shallow and is recharged through cracks and fissures, the water may be nutrient-rich and oxygenated resulting in an abundance of different microorganisms whose numbers can reach 10^6 per gram. Lower population numbers would be expected in aquifers where the supply of dissolved oxygen from surface recharge is limited. Deep aquifers are generally more depleted with respect to nutrients (unless contaminated) and oxygen causing the numbers and diversity of microorganisms to decline and often be limited to bacteria and archaebacteria. This finding has been supported, during the last 15–20 years, by carefully controlled drilling studies undertaken to evaluate the microbiology of deep, impermeable rock strata (Ghiorse, 1997; Kerr, 2002).

IIC.2 Microbial Controls on Subsurface Redox State

Since microorganisms chemically transform aquifer constituents such as dissolved oxygen, iron [aqueous and solid forms of Fe(III) and Fe(II)], and sulfur [aqueous species such as sulfate and dissolved sulfide], their metabolic reactions may exert significant influence on the redox geochemistry within the plume. As previously discussed, redox conditions within the aquifer may govern precipitation-dissolution reactions that control contaminant precipitation or coprecipitation, as well as the types and concentration of aquifer solids that may serve as adsorbents. From this perspective, some knowledge about the microbial populations as a function of space and time within the plume may be necessary to understand the existing redox status of the aquifer and make projections about how it may evolve. For heterotrophic microorganisms, the electrons or reducing equivalents (hydrogen or electron-transferring molecules) produced during degradation of organic compounds must be transferred to a terminal electron acceptor (TEA). Observations of microbial systems have led to the development of a classification system that groups microorganisms into three categories according to predominant TEAs:

- Aerobic bacteria — Bacteria which can only utilize molecular oxygen as a TEA. Without molecular oxygen, these bacteria are not capable of degradation.

- Facultative aerobes/anaerobes — Bacteria which can utilize molecular oxygen or when oxygen concentrations are low or nonexistent, may switch to nitrate, manganese oxides or iron oxides as electron acceptors.
- Anaerobes — Bacteria which cannot utilize oxygen as an electron acceptor and for which oxygen is toxic. Though members may utilize nitrate or other electron acceptors, it can be said that they generally utilize sulfate or carbon dioxide as electron acceptors.

In any environment in which microbial activity occurs, there is a progression from aerobic to anaerobic conditions (ultimately methanogenic) with an associated change in the redox status of the system. There is a definite sequence of electron acceptors used in this progression through distinctly different redox states. The rate, type of active microbial population, and level of activity under each of these environments are controlled by several factors. These include the concentration of the electron acceptors, substrates which can be utilized by the bacteria, and specific microbial populations leading to the progression of an aquifer from aerobic to methanogenic conditions (Salanitro, 1993). This results in a loss of organic carbon and various electron acceptors from the system as well as a progression in the types and physiological activity of the indigenous bacteria.

If microbial activity is high, the aquifer environment would be expected to progress rapidly through these conditions. The following scenario outlines a general sequence of events in which aerobic metabolism of preferential carbon sources would occur first. The carbon source may be from organic contaminant sources or other more readily degradable carbon which has entered the system previously or simultaneously with the contamination event.

- Oxygen-Reducing to Nitrate-Reducing Conditions – Once available oxygen is consumed, active aerobic populations begin to shift to nitrate respiration. Denitrification will continue until available nitrate is depleted, or usable carbon sources become limiting.
- Nitrate-Reducing to Manganese-Reducing Conditions – Once nitrate is depleted, populations which reduce manganese may dominate. Bacterial metabolism of substrates utilized by manganese-reducing populations will continue until the concentration of manganese oxide becomes limiting.
- Manganese-Reducing to Iron-Reducing Conditions – When manganese oxide becomes limiting, iron reduction becomes the predominant reaction mechanism. Available evidence suggests that iron reduction does not occur until all Mn(IV) oxides are depleted. In addition, bacterial Mn(IV) respiration appears to be restricted to areas where sulfate is nearly or completely absent.
- Iron-Reducing to Sulfate-Reducing Conditions – Iron reduction continues until substrate or carbon limitations allow sulfate-reducing bacteria to become active. Sulfate-reducing bacteria then dominate until usable carbon or sulfate limitations impede their activity.
- Sulfate-Reducing to Methanogenic Conditions – Once usable carbon or sulfate limitations occur, methanogenic bacteria are able to dominate.

Development of a general knowledge of the redox status of the aquifer throughout the plume is important relative to understanding the processes contaminant attenuation (or lack thereof) within the plume, as well as changes in the capacity for or stability of contaminant attenuation with the return to ambient conditions. There are several approaches to evaluating the redox state of the aquifer. One common approach is to monitor the oxidation-reduction potential in ground water using a platinum electrode with recalculation of the measured electrode potential as Eh. However, due to the lack of internal redox equilibrium in natural systems (Morris and Stumm, 1967) and limitations to electrode potential measurements in a complex matrix such as ground water, this measurement should be supplemented with other site-specific determinations. One supplemental approach to assessing redox status is the determination of concentrations of specific redox sensitive species such as oxygen, Fe(II), hydrogen sulfide, or methane as qualitative guides to the redox status of ground water (Lindberg and Runnells, 1984; USEPA, 2002). These measurements provide a means to generally characterize the ground water as oxic, suboxic, or anoxic and may provide more direct evidence of the occurrence of iron-reducing, sulfate-reducing or methanogenic conditions. Another approach that may be used to indicate the terminal electron acceptor process (TEAP) which dominates within the plume is measurement of the hydrogen (H_2) concentration in ground water (Lovely and Goodwin, 1988). Hydrogen concentration for the various TEAPs are shown in Table 2.4 (Chapelle et al., 1995).

Table 2.4 Range of hydrogen concentrations for a given terminal electron-accepting process that can be used for classification of the redox status within the contaminant plume.

Terminal Electron Accepting Process	Hydrogen (H_2) Concentration (nanomoles per liter)
Denitrification	<0.1
Iron (III) Reduction	0.2 to 0.8
Sulfate Reduction	1 to 4
Methanogenesis	5 to 20

The focus of this discussion has been on the influence of microbial activity on the redox status of ground water, which governs the types of aqueous and solid phase reactants that may be involved in contaminant attenuation. The following discussion elaborates on the influence of microbial reactions on the chemical speciation of inorganic contaminants.

IIC.3 Impacts on Contaminant Speciation and Attenuation

Microbe/metal interactions result in immobilization, mobilization, or transformation by extracellular precipitation reactions, intracellular accumulation, oxidation and reduction reactions, methylation and demethylation, and extracelluar binding and complexation. Many of these processes play an important role in achieving natural attenuation through immobilization or degradation. Many transformations of metals and metalloids are carried out by subsurface microorganisms for the purpose of obtaining energy for growth and reproduction; however, these transformations may not result in decreasing the mobility or toxicity of the metal. Some microbial transformations are carried out specifically to detoxify their environment, suggesting that microbes have an enormous capacity to sustain life. Therefore, the role of microbes in the subsurface is multifaceted. The principal mechanisms employed by microorganisms to transform metals and metalloids in the subsurface environment are:

- Oxidation and reduction reactions resulting from microbial respiratory activities (Lovely, 1993; Ahmann et al., 1994);
- Biosorption by cell walls, cell membranes and exopolymers and intracellular bioaccumulation (Beveridge, 1989); and
- Methylation and demethylation (Oremland et al., 1991; Bentley et al., 2002).

These microbial mechanisms are described with emphasis on reactions involved in natural attenuation of metals and radionuclides.

IIC.3.1 Contaminant Oxidation-reduction Reactions

Oxidation-reduction (redox) processes are chemical reactions that involve a transfer of electrons between reactants and products and consequently a change in the oxidation state of elements that can either be oxidized to higher valence states or reduced to lower valence states. Changes in the valance state of a particular element can result in the following:

- Change in speciation resulting in lower or higher toxicity
- Change in speciation resulting in lower element solubility (immobilization) or increased solubility (mobilization)
- Change in speciation that impacts adsorption/desorption behavior

The contaminants for which redox-mediated processes may lead to attenuation include elements that can occur in multiple oxidation states under environmentally relevant conditions. Thus, a transition metal such as Cr is redox-active since two stable oxidation states (VI and III) are readily observed in aqueous solution, whereas Ni is not redox-active as only one oxidation state (II) occurs in aqueous solutions at ambient conditions. (More detailed discussions on the redox activity of individual contaminants are provided in Volume 2.)

Oxidation-reduction (redox) reactions, which can be carried out by both heterotrophic and chemolithotrophic microorganisms, are either energy-generating or enzymatically-catalyzed without coupling to energy generation. Microbially catalyzed, energy generating redox reactions tend to be rapid and the metal transformations so extensive that the geological influence is often substantial. One example that results in the attenuation of metals is the reduction of soluble SO_4^{2-} by *Desulfovibrio* and *Desulfotomaculum* species involving oxidation of organic matter or H_2 for energy and use of sulfate as a terminal electron acceptor (Lovely, 1993). This redox reaction yields dissolved sulfide that can chemically react with a number of soluble, divalent metals producing insoluble metal sulfides. In some cases, the microbially-generated sulfide may chemically reduce an inorganic contaminant. For example, dissolved sulfide may result in reduction of arsenate to arsenite. Examples of enzymatically-catalyzed redox reactions that immobilize metals for attenuation in the subsurface are the reduction of mobile Cr(VI) to the less toxic and less mobile Cr(III) (Palmer and Wittbrodt, 1991) and reduction by some microorganisms of Se(VI) or Se(IV) to insoluble Se(0) (Ehrlich, 1995).

IIC.3.2 Biosorption and Intracellular Bioaccumulation

Biosorption, a form of contaminant *adsorption*, is the binding of inorganic ions to the outer surface of a microorganism by ion exchange, van der Waals attractions, or chemical reactions between the metal ion and cell wall, cell membrane, excreted metabolites, or exopolymers. Biosorption is not dependent on metabolism by the microbial cell. Intracellular bioaccumulation, or *absorption*, is the transport of metals across the cell wall and membrane and subsequent retention of the metals within the cell. Bioaccumlation is metabolism dependent because the transport process requires energy.

The outer surfaces of microorganisms are chemically complex with each group of organisms possessing differing cell wall, membrane, and expolymeric structures. These structures are composed of macromolecules having functional groups including carboxylates, amines, imidazole, phosphate, sulfydryl, sulfate, hydroxyl and others. Usually the microbes exhibit a net negative charge owing to the abundance of carboxylate and phosphate groups, however, positively charged amines and imidazole functional groups impart polyfunctional characteristics to the cell surface. Most inorganic contaminant binding occurs after initial complexation and neutralization of the chemically active site. This stoichiometric interaction between contaminant ions and active sites within the wall acts as a nucleation site for the deposition of additional ions from solution in a manner similar to surface precipitation onto aquifer minerals. The deposition product then grows in size within the intermolecular spaces of the wall fabric until it is physically constrained by the polymeric meshwork of the wall. Therefore, the amount of contaminants bound to the outer surfaces of organisms can be considerably greater than that accounted for by the number of charges available because binding occurs not only by ion exchange type reactions and covalent bonding to charged functional groups, but by precipitation and reduction reactions (Beveridge, 1989).

As with mineral surfaces in the aquifer solids, pH plays a critical role in the binding of inorganic contaminants. At low pH values cationic metal binding is diminished because negative charges on functional groups become protonated, reducing the negative charge density of the organism's surface. Although the quantitative role of extracellular binding in controlling the concentration of inorganic contaminants in the subsurface is not well defined, it does play a larger part in metal mobility than intracellular metal accumulation. The relative contribution of microbial binding processes to the overall immobilization of the contaminant within the plume is largely unknown. However, a simple comparison of the relative mass of microbes versus reactive minerals in aquifer solids would suggest that microbial binding plays a minor role.

IIC.3.3 Methylation and Demethylation

Microbial interactions with some inorganic contaminants considered in this document result in the transfer of methyl groups onto these elements by a process known as methylation. This process may result in either the increased toxicity or mobility of some inorganic contaminants. Biomethylation of metal(loid)s takes place when suitable organisms are present under anaerobic conditions with high concentration of available metal(loid)s and methyl donors. These conditions may exist in contaminated ground water (e.g., derived from landfill leachate). An example of this type of process is the methylation of inorganic selenium to dimethylselenide, a volatile product. Methylation of selenium decreases rather than increases its toxicity and probably represents a detoxification reaction that occurs readily in aerobic soils and sediments. Arsenate can also be methylated by some bacteria and filamentous fungi. Biosynthesis of organic compounds containing arsenic such as arsenocholine, arsenobetaine, and arsenosugars also occurs among various bacteria, algae, and many higher organisms (Andreae and Klumpp, 1979).

IIC.4 Implications for Natural Attenuation Assessment

Based on the previous discussion, it is apparent that the subsurface microbial community could influence inorganic contaminant transport. For many of the contaminants discussed in this document, microbial reactions will primarily exert an indirect influence on contaminant attenuation by governing the types, distribution, and concentrations of aqueous and solid phase reactants. However, microbial activity may constitute a more direct impact on contaminant speciation, including changes in the redox state of contaminants such as arsenic or selenium. From this perspective, it is recommended that the site characterization effort incorporate analysis of the extent to which microbial processes may govern ground-water chemistry within the plume. This is more critical at sites where the co-occurrence of readily degradable organic contaminants result in ground-water conditions significantly different than those observed in ambient ground water. For these situations, information on the mechanism, rate, capacity, and stability of contaminant attenuation may need to be evaluated within the context of the behavior of the organic component of the plume.

IID. References

Ahmann, D., A.L. Roberts, L.R. Krumholz, and F.M.M. Morel. Microbes grow by reducing arsenic. *Nature* 371: 750 (1994).

Andreae M.O. and D. Klumpp. Biosynthesis and release of organoarsenic compounds by marine algae. *Environmental Science and Technology* 13: 738-741 (1979).

Baumann, T., P. Fruhstorfer, T. Klein, and R. Niessner. Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water Research* 40: 2776-2786 (2006).

Bentley, R. and T.G. Chasteen. Microbial methylation of metalloids: arsenic, antimony, and bismuth. *Microbiology and Molecular Biology Reviews* 66: 250-271 (2002).

Beveridge, T.J. Role of cellular design in bacterial metal accumulation and mineralization. *Annual Reviews in Microbiology* 43: 147-171 (1989).

Buddemeier, R. W. and J.R. Hunt. Transport of colloidal contaminants in ground water: Radionuclide migration at the Nevada Test site. *Applied Geochemistry* 3: 535-548 (1988).

Catts, J. G. and D. Langmuir. Adsorption of Cu, Pb, Zn by delta-MnO_2: Applicability of the site binding-surface complexation model. *Applied Geochemistry* 1: 255-264 (1986).

Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. *Water Resources Research* 31: 359-371 (1995).

Dai, M., J.M. Kelley, and K.O. Buesseler. Sources and migration of plutonium in groundwater at the Savannah River Site. *Environmental Science and Technology* 36: 3690-3699 (2002).

Dixon, J.B. and D.G. Schulze (Eds.). *Soil Mineralogy with Environmental Applications.* Soil Science Society of America, Madison, WI (2002).

Drever, J.I. *The Geochemistry of Natural Waters.* Prentice-Hall, Englewood Cliffs, NJ (1982).

Dzombak, D.A. and F.M.M. Morel. *Surface Complexation Modeling; Hydrous Ferric Oxide.* John Wiley & Sons, New York, NY (1990).

Ehrlich, H.L. *Geomicrobiology*, 3rd edition. Marcel Dekker, New York, NY (1995).

Farley, K.J., D.A. Dzombak, and F.M.M. Morel. A surface precipitation model for the sorption of cations on metal oxides. *Journal of Colloid and Interface Science* 106: 226-242 (1985).

Ford, R.G. Rates of hydrous ferric oxide crystallization and the influence on coprecipitated arsenate. *Environmental Science and Technology* 36: 2459-2463 (2002).

Ford, R.G., A.C. Scheinost, and D.L. Sparks. Frontiers in metal sorption/precipitation mechanisms on soil mineral surfaces. *Advances in Agronomy* 74: 41-62 (2001).

Ford, R.G. Structural dynamics of metal partitioning to mineral surfaces. In *Natural Attenuation of Trace Element Availability in Soils.* R. Hamon, M. McLaughlin and D. Stevens (Eds.), SETAC Press, Pensacola, FL (2007).

Freeze, R.A. and J.A. Cherry. *Groundwater.* Prentice-Hall, Englewood Cliffs, NJ (1979).

Gelhar, L.W. *Stochastic Subsurface Hydrology.* Prentice-Hall, Englewood Cliffs, NJ (1993).

Gelhar, L.W., C. Welty, and K.R. Rehfeldt. A critical review of data on field-scale dispersion in aquifers. *Water Resources Research* 28: 1955-1974 (1992).

Ghiorse, W.C. Subterranean life. *Science* 275: 789-790 (1997).

Greenland, D.J. and C.J.B. Mott. Surfaces of soil particles. In *Chemistry of Soil Constituents.* D.J. Greenland and M.H.B. Hayes (Eds.), John Wiley, Chichester, UK (1978).

Gschwend, P.M. and M.D. Reynolds. Monodisperse ferrous phosphate colloids in an anoxic groundwater plume. *Journal of Contaminant Hydrology* 1: 309-327 (1987).

Holman, J.P. Reversible processes and cycles. In *Thermodynamics.* F.J. Cerra and J.W. Bradley (Eds.), McGraw-Hill, New York, NY, pp. 200-203 (1980).

Hsi, C.D. and D. Langmuir. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica et Cosmochimica Acta* 49: 1931-1941 (1985).

Israelachvili, J.N. Interactions involving polar molecules. In *Intermolecular and Surface Forces.* Academic Press Inc., San Diego, CA, pp. 48-82 (1994).

Keeley, J.F. *Ground Water Issue, Performance Evaluations of Pump-and-Treat Remediations,* EPA/540/4-89/005, U.S. Environmental Protection Agency, Ada, OK (1989).

Kerr, R.A. Deep life in the slow, slow lane. *Science* 296: 1056 (2002).

Langmuir, D. *Aqueous Environmental Geochemistry.* Prentice-Hall, Upper Saddle River, NJ (1997).

Lasaga, A.C. *Kinetic Theory in the Earth Sciences.* Princeton University Press, Princeton, NJ (1999).

Lindberg, R.D. and D.D. Runnells. Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science* 225: 925-927 (1984).

Lindsay, W.L. *Chemical Equilibria in Soils.* John Wiley & Sons, New York, NY (1979).

Lowers, H.A., G.N. Breit, A.L. Foster, J. Whitney, J. Yount, Md.N. Uddin, and Ad.A. Muneem. Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. *Geochimica et Cosmochimica Acta* 71: 2699-2717 (2007).

McBride, M.B. Chemisorption and precipitation reactions. In *Handbook of Soil Science.* M.E. Summer (Ed.), CRC Press, Boca Raton, FL (2002).

McBride, M.B. *Environmental Chemistry of Soils.* Oxford University Press, New York, NY (1994).

McCarthy, J.F. and J.M. Zachara. Subsurface transport of contaminants. *Environmental Science and Technology* 5: 496-502 (1989).

Morel, F.M.M. and J.G. Hering. *Principles and Applications of Aquatic Chemistry.* John Wiley & Sons, New York, NY (1993).

Morris, J.C. and W. Stumm. In *Equilibrium Concepts in Natural Waters Systems.* W. Stumm (Ed.), American Chemical Society, Washington DC (1967).

Newman, D.K. and J.F. Banfield. Geomicrobiology: how molecular-scale interactions underpin biogeochemical systems. *Science* 296: 1071-1077 (2002).

Newman, D.K. How bacteria respire minerals. *Science* 292: 1312-1313 (2001).

Nightingale, H.I. and W.C. Bianchi. Ground water turbidity resulting from artificial recharge. *Ground Water* 15: 146-152 (1977).

O'Melia, C.R. Aquasols: The behavior of small particles in aquatic systems. *Environmental Science and Technology* 14: 1052-1060 (1980).

Oremland, R.S., C.W. Culbertson, and M.R. Winfrey. Methylmercury decomposition in sediments and bacterial cultures: Involvement of methanogens and sulfate reducers in oxidative demethylation. *Applied and Environmental Microbiology* 57: 130-137 (1991).

Palmer, C.D. and P.R. Wittbrodt. Processes affecting the remediation of chromium-contaminated sites. *Environmental Health Perspectives* 92: 25-40 (1991).

Puls, R.W. and J.H. Eychaner. Sampling ground water for inorganics - pumping rate, filtration, and oxidation effects. In *Fourth National Outdoor Action Conference on Aquifer Restoration,* National Water Well Association, Dublin, OH (1990).

Ryan, J.N. and P.M. Gschwend. Colloid mobilization in two Atlantic coastal plain aquifers. *Water Resources Research* 26: 307-322 (1990).

Salanitro, J.P. The role of bioattenuation in the management of aromatic hydrocarbon plumes in aquifers. *Ground Water Monitoring and Remediation* 13: 150-161 (1993).

Sparks, D. *Environmental Soil Chemistry.* Academic Press, San Diego, CA (1995).

Sposito, G. Cation exchange in soils: An historical and theoretical perspective. In *Chemistry in the Soil Environment,* American Society of Agronomy, Madison, WI, pp. 13-30 (1981).

Sposito, G. *The Surface Chemistry of Soils.* Oxford University Press, New York, NY (1984).

Sposito, G. *The Chemistry of Soils.* Oxford University Press, New York, NY (1989).

Sposito, G. Distinguishing adsorption from surface precipitation. In *Geochemical Processes at Mineral Surfaces.* J.A. Davis and K.F. Hayes (Eds.), American Chemical Society Symposium Series 323, pp. 217-228 (1986).

Steefel, C.I. and P. van Cappellen. A new kinetic approach to modeling water-rock interaction: The role of nucleation, precursors, and Ostwald ripening. *Geochimica et Cosmochimica Acta* 54: 2657-2677 (1990).

Stumm, W. and J.J. Morgan. *Aquatic Chemistry.* John Wiley & Sons, New York, NY (1981).

Stumm, W. *Chemistry of the Solid-Water Interface.* John Wiley & Sons, New York, NY (1992).

Sverjensky, D.A. Standard states for the activities of mineral surface sites and species. *Geochimica et Cosmochimica Acta* 67: 17-28 (2003).

Thompson, A., O.A. Chadwick, S. Boman, and J. Chorover. Colloid mobilization during soil iron redox oscillations. *Environmental Science and Technology* 40: 5743 -5749 (2006).

USEPA. *Seminar Publication Site Characterization for Subsurface Remediation,* EPA/625/4-91/026, U.S. Environmental Protection Agency, Cincinnati, OH (1991).

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

Westall, J. Reactions at the oxide-solution interface: Chemical and electrostaic models. In *Geochemical Processes and Mineral Surfaces.* J.A. Davis and K.F. Hayes (Eds.), American Chemical Society Symposium Series 323, pp. 54-78 (1986).

Yao, K., M.T. Habibian, and C.R. O'Melia. Water and waste water filtration: concepts and applications. *Environmental Science and Technology* 5: 1105-1112 (1971).

Section III

Site Characterization to Support Evaluation of MNA

Richard T. Wilkin, Steven Acree, Steve Mangion, Patrick V. Brady, James E. Amonette, Paul M. Bertsch, Douglas B. Kent, Robert W. Puls, Ann Azadpour-Keeley, Robert G. Ford

In determining whether MNA is applicable to a site, characterization data are collected to define site hydrogeology and the reaction(s) that result in contaminant attenuation. Characterization of attenuation reactions will involve identification of the reactants that control contaminant immobilization or degradation. The reactants may be of aqueous and/or solids forms, with solid reactants potentially consisting of aquifer solids or microbes. Once the specific reaction mechanism is identified, site characterization will then proceed to determination of the capacity of groundwater conditions to sustain the attenuation reaction and assessment of the stability of immobilized contaminants to resist remobilization due to changes in ground-water chemistry. The types of samples collected from within the plume boundary will include ground water and aquifer solids. Analyses of these samples will include those more commonly employed to understand the overall geochemical context of subsurface chemistry, as well as more specialized analyses used to identify the chemical speciation of the contaminant in dissolved or solid form. Simple observations of the distribution of the contaminant between solid and liquid forms will be insufficient to identify the specific reaction process. A mechanistic understanding of the reaction is needed in order to assess the overall performance characteristics of the attenuation process. This section will provide an overview of the analytical techniques that are used to provide evidence for processes and chemical speciation in the subsurface.

IIIA Site Hydrogeology

Hydrogeology is the foundation of the conceptual model for natural attenuation (National Research Council, 2000). Three-dimensional characterization of the ground-water flow field and the changes that occur through time are crucial to understanding the transport and, ultimately, the fate of contaminants. Discussions of hydrogeologic site characterization in this document draw freely from USEPA (2003) and are largely limited to evaluations performed in saturated porous-media settings, such as unconsolidated aquifer materials. Although similar concepts are sometimes applicable in other geologic settings, such as fractured rock formations, ground water often moves primarily through discrete pathways at these sites. In such highly anisotropic settings, the direction of ground-water flow and contaminant transport often cannot be determined within a sufficient degree of certainty to support assessments of natural attenuation rates or processes. Assessment of contaminant transport and fate in these and other highly heterogeneous settings is an area of continuing research and is beyond the scope of this discussion. In similar fashion, hydrogeologic characterization of vadose zone materials is not specifically addressed in this section. Flow conditions are often more complex in the vadose zone than in similar saturated media. However, characterization of the hydrogeologic properties of the vadose zone, as well as the saturated zone, will be necessary at some sites. A general discussion of vadose zone characterization for contaminant transport assessments is found in USEPA (1991; 1993a; 1993b).

IIIA.1 Characterization Objectives

Much of the spatial variability in observed contaminant concentrations is the result of geologic heterogeneity. Differences in the geologic properties of aquifer materials from the micro-scale (e.g., grain-size distribution) to the field scale (e.g., stratigraphy) result in differences in hydraulic conductivity and the directions and rates of ground-water flow. Three-dimensional hydraulic gradients that occur due to the site-specific characteristics of ground-water recharge and discharge are also dominant controls on flow. Together, the differences in the hydraulic conductivity of different aquifer materials, hydraulic gradients, and the changes in gradients that often occur in response to natural or anthropogenic changes in ground-water discharge and recharge control the directions and rates of ground-water flow.

Detailed hydrogeologic characterization is essential for evaluating natural attenuation processes and rates, as well as for specification of the locations and frequencies for performance monitoring. The first step in characterizing contaminant transport, and, therefore the processes that may result in attenuation, is the determination of the path or paths of ground-water transport along which the contaminant will migrate. At a minimum, the hydrogeologic database should be sufficient to:

- Define geologic and hydrologic controls on the groundwater flow field (e.g., transmissive units, preferential pathways, and barriers to flow);
- Quantify flow rates and directions and their spatial and temporal variations;
- Support characterization of contaminant sources, the distribution of contaminants of concern, and the effects of dominant natural attenuation processes; and
- Identify possible receptors.

The scale and intensity of this characterization is determined by site-specific conditions (e.g., variability in geology and hydrology and the acceptable level of uncertainty in the outcome of the evaluations).

IIIA.2 Geologic Characterization

IIIA.2.1 Saturated Porous Media

The key geologic factors that control ground-water flow at sites where secondary porosity features such as fractures, including faults, joints, and partings along bedding planes, are not present include site stratigraphy and lithologic characteristics. Stratigraphy is the science concerned with the form, composition, thickness, areal extent, sequence, and correlation of both consolidated and unconsolidated geologic materials. It defines the framework of the ground-water flow field and constrains the pathways for contaminant migration (USEPA, 1991). Lithology is the description of the physical and mineralogic characteristics of geologic materials. Physical characteristics that control flow include grain-size distribution, grain shape, and packing. As discussed in other sections, mineral composition and coatings affect inorganic constituent distribution through a variety of chemical reactions including cation exchange, substitution, precipitation, dissolution, acid-base reactions, complexation and redox reactions (USEPA, 1991). Grain-size distribution, grain shape, and packing (i.e., arrangement) of grains influence the hydraulic conductivity, total porosity, and effective porosity of the geologic materials.

At many sites, evaluation of sedimentary depositional environments is an especially useful framework for the understanding of site stratigraphy and the distribution of lithologic controls on ground-water flow. Sedimentary facies (i.e., sedimentary bodies that are internally similar in characteristics) determine the three-dimensional geometries, connectivity, and heterogeneity of aquifer units and barriers to flow (Galloway and Sharp, 1998) in many porous-media settings. Ground water can move preferentially through coarser-grained materials, resulting in varying degrees of heterogeneity in flow patterns and contaminant transport. Interconnected facies of relatively coarse-grained materials may provide preferential pathways for contaminant migration. An example of a naturally occurring preferential pathway would be a deposit of interconnected sands of high hydraulic conductivity bounded by deposits of finer-grained materials. In similar fashion, anthropogenic features such as buried utility corridors and heterogeneous fill materials may also result in the formation of preferential pathways for ground-water flow or impediments to flow. However, even within a given preferential pathway, ground water may move in sinuous paths due, in part, to small-scale differences in hydraulic conductivity of the materials or to temporally variable, three-dimensional hydraulic gradients.

Interconnected transmissive materials may be separate and distinct pathways for contaminant movement. For example, the degree of hydrologic connection between different sedimentary facies depicted in Figure 3.1 is small. Monitoring points in different facies may appear to be similar and may be hydraulically down gradient of one another without significant ground-water flow and contaminant transport from one unit to the next. This is explicitly illustrated in Figure 3.1 where two wells are screened at similar depth below the water table along the pathway of ground-water transport. The two screens are placed within two different facies that likely possess different magnitudes of hydraulic conductivity (i.e., Well 1 screened in a higher conductivity material in the “medium to coarse-grained sand” vs. Well 2 screened in a lower conductivity in the “fine-grained silty sand”). The difference in hydraulic conductivity between these two facies may prevent a direct line of transport from Well 1 to Well 2. In such cases, apparent contaminant attenuation between monitoring points (i.e., due to lower concentration observed in Well 2) may be an artifact of sample location and not representative of actual conditions. Inferences about natural attenuation based on apparent decreases in contaminant concentration in the down gradient direction are likely to be incorrect in these situations unless ground-water flow paths are determined and monitored. This level of characterization is often difficult to accomplish using small numbers of monitoring points.

Three-dimensional characterization will be needed to evaluate and predict the effects of natural attenuation processes (e.g., advection, dispersion, diffusion, and sorption processes) on contaminants at many sites. Data required to construct the site geologic framework include stratigraphic and lithologic data obtained from geologic cores and supplemented with information from surface and, particularly, borehole geophysical methods. Innovative characterization technologies, such as the cone penetrometer and geologic sampling using direct-push methods, offer the potential for cost-effectively evaluating the geologic controls on ground-water flow and their variability in greater detail than previously possible without obtaining continuous cores during traditional drilling. Regardless of the chosen technology, the choice of sampling locations needed as a basis for evaluations of natural attenuation processes depends on factors such as the site-specific geology, contaminant characteristics, degree of physical, chemical, and biological heterogeneity, and the locations of points of compliance and or critical down gradient exposure points.

IIIA.2.2 Saturated Fractured Media

In rock or consolidated materials, features such as fractures often control ground-water flow. The primary factors affecting flow through fractured media are the density and orientations of fractures, the effective aperture width of the fractures, and properties of the rock matrix (Schmelling and Ross, 1989). An adequate characterization of a fractured rock system would generally include information on fracture orientation (i.e., strike and dip), aperture widths, fracture locations, and interconnection; hydraulic head throughout the contaminated volume; the distribution of rock porosity and permeability; sources of ground water and contaminants; contaminant distribution; and chemical interactions with the rock matrix. Chemical weathering of the rock and the subsequent mineralogic changes that occur along fractures can also be especially important controls on the fate and transport of inorganic contaminants.

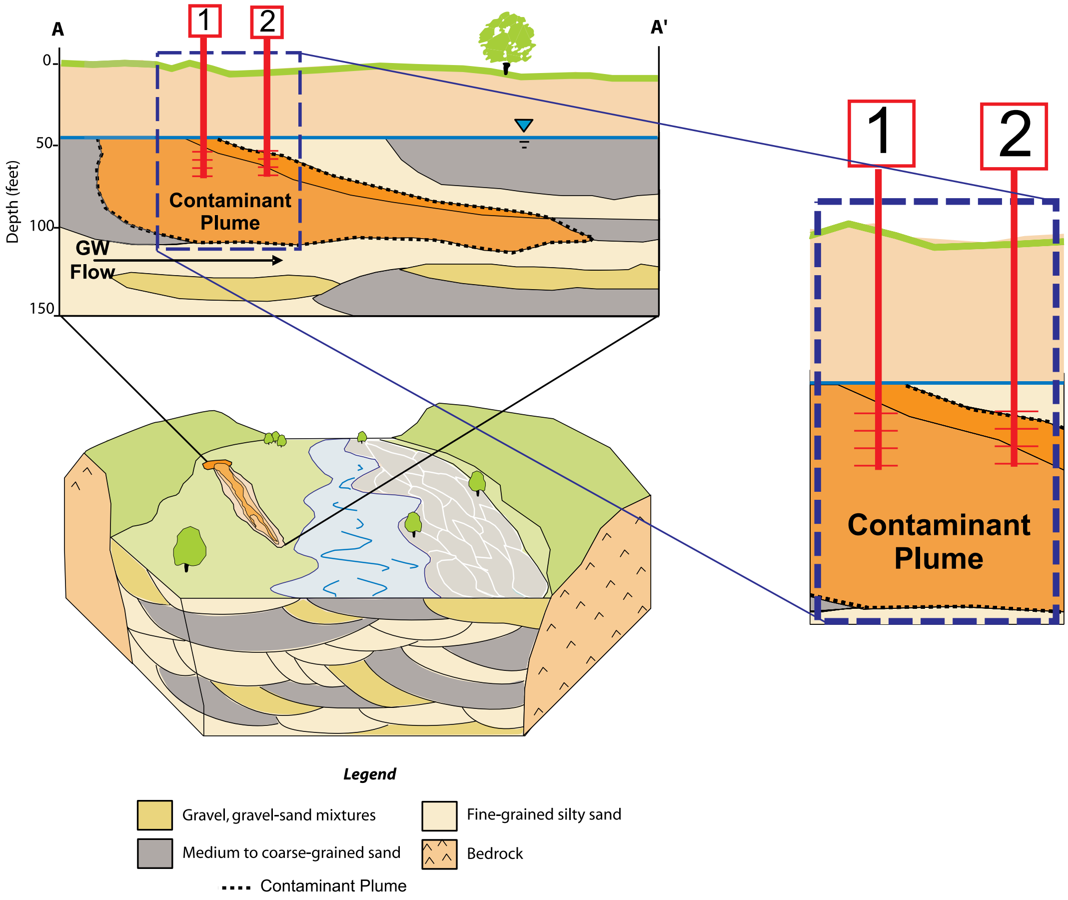


Figure 3.1 *Geologic block diagram and cross section depicting a stream environment. In this setting, numerous facies of channel materials are surrounded by finer-grained materials of lower hydraulic conductivity (modified from USEPA, 2003). Two monitoring wells, labeled [1] and [2], are shown in red. A magnified portion of the aquifer cross-section is shown to the right to clarify that the well screens are placed within two different facies possessing differing hydraulic conductivites.*

Many important features, such as fracture patterns, can often be determined by standard surficial geologic mapping techniques. Much additional data concerning subsurface conditions can also be obtained using downhole and surface geophysical methods. However, sufficient characterization to support natural attenuation process evaluations with the level of certainty needed to satisfy data quality objectives will be neither technically nor economically feasible at the scale of many sites.

IIIA.3 Hydrologic Characterization

Knowledge of the geologic framework provides much information needed to define the features that control groundwater flow. However, data regarding the hydraulic properties (e.g., hydraulic conductivities and effective porosities) of the aquifer materials and their distribution are needed to allow quantitative estimates of such parameters as ground-water flow rates, contaminant fluxes, and contaminant attenuation rates. Much of the necessary data regarding hydraulic properties will generally be acquired through hydraulic tests performed in the field (e.g., pumping tests, slug tests, packer tests, and tracer tests). Additional information regarding geologic and hydrologic site characterization concepts and techniques may be obtained from a variety of sources (e.g., Butler, 1998; Kruseman and de Ridder, 1989; USEPA, 1991; USEPA, 1993a; USEPA, 1998).

Hydrologic characterization of the ground-water flow system also requires an understanding of natural and anthropogenic sources for recharge, the characteristics of discharge, and the hydraulic gradients that are the result. Recharge sources include precipitation, surface-water bodies, irrigation, and losses from potable water distribution systems. Important locations of ground-water discharge include water production wells, springs, wetlands, and surface-water bodies. The locations and rates of groundwater recharge and discharge are important factors in determining site-specific hydraulic gradients and, therefore, the directions and rates of flow. Hydraulic gradients may be three dimensional in nature with strong vertical as well as horizontal components in many cases. This often results in a dynamic, three-dimensional flow system.

Temporal variations in either natural or anthropogenic recharge or discharge may result in fluctuations in both the horizontal and vertical components of hydraulic gradients, the directions/rates of contaminant migration, contaminant loading to ground water, and, potentially, redox conditions. These fluctuations may lead to changes in the geometry of the plume that should be considered during evaluations of natural attenuation and monitoring plan development. For example, seasonal changes in precipitation may result in non-uniform changes in water table elevations due to differences in recharge related to topography, different soil types, or land uses. This may result in seasonal changes in hydraulic gradients or discharge locations. Rapid and sustained changes in ground-water flow velocity are common in flood plains, particularly near large rivers that have major changes in the river stage. In some situations, changes in contaminant loading to ground water may also occur due to increased recharge through contaminated vadose zone materials or elevation of the water table into these materials. Longer-term patterns associated with sequences of unusually wet or dry years may also influence ground-water velocity over correspondingly longer time periods.

Anthropogenic influences on site hydrology, such as changes in ground-water withdrawal or irrigation rates and patterns, may have similar effects on plume behavior but occur on frequencies other than those corresponding to precipitation patterns. Irrigation or municipal water supply wells that pump intermittently can affect ground-water flow patterns in a complex manner that may be difficult to assess. In addition, land use changes that alter patterns of recharge, discharge, or withdrawal may be important sources of variability in the ground-water flow field that should be routinely considered during the life of an MNA remedy. The illustration in Figure 3.2 provides an example where the off-site installation and activation of an irrigation well can result in movement of the ground-water plume in

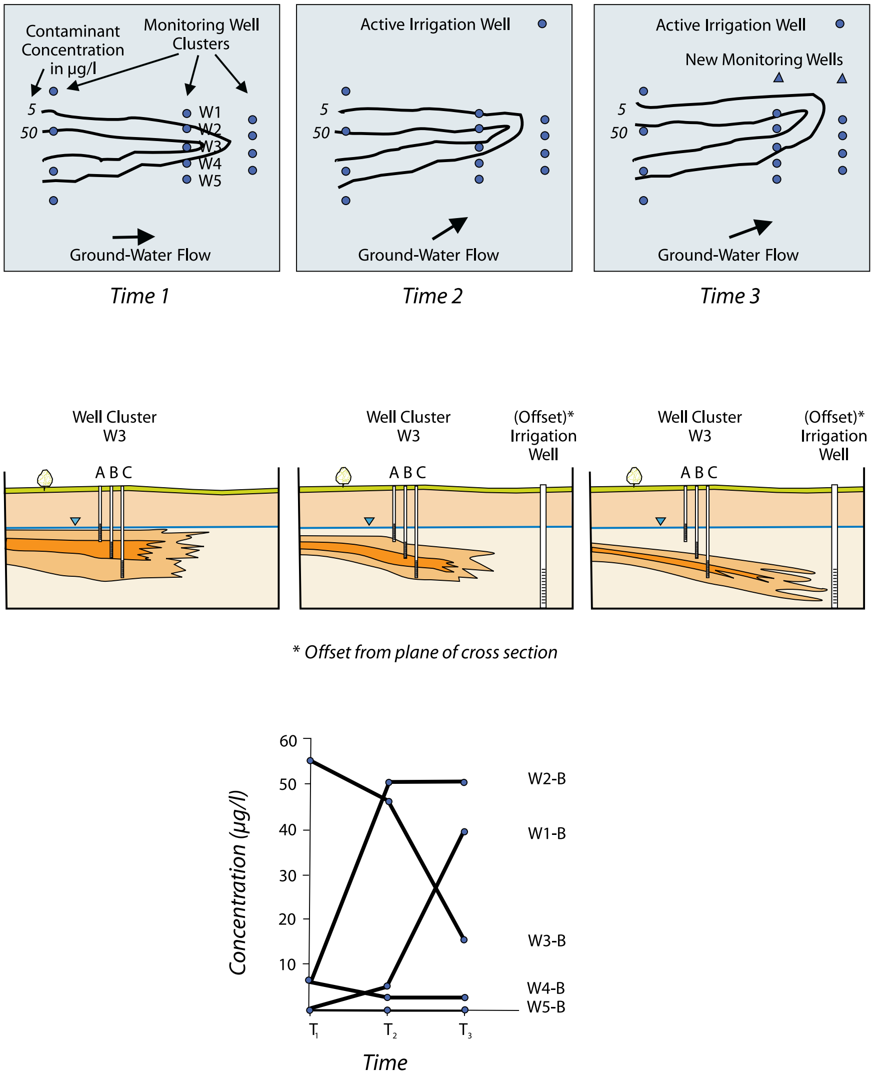


Figure 3.2 *Potential effects of changes in ground-water flow direction on temporal trends in contaminant concentrations (USEPA, 2003).*

response to this new ground-water withdrawal from the aquifer. In this situation, a decrease in contaminant concentration at a well screen originally placed within a portion of the plume with highest concentrations could be mistaken for evidence of an attenuation process. This misinterpretation in contaminant concentration trend can be prevented through periodic re-examination of the hydraulic gradient distribution within the monitored portion of the aquifer. In addition, these observations also provide guidance on how to adjust the location of monitoring points within the aquifer to insure that the entire plume is being monitored.

Elevations of surface-water bodies and ground-water elevation data periodically obtained from a network of wells and piezometers screened at appropriate depths within the contaminated aquifer units and surrounding units are essential elements of hydrologic analyses. Additional data for assessing ground-water flow include land use information such as the locations, rates, and schedules of irrigation; local precipitation data; and pumping rates and schedules for nearby wells. These data and the resulting estimates of hydraulic gradients are used in conjunction with interpretations of the hydraulic properties of subsurface materials and locations of contaminant sources to evaluate potential changes in contaminant loading, transport and attenuation rates, and transport directions with time. The evaluations should be three-dimensional in nature, including horizontal and vertical components of hydraulic gradients that result in three-dimensional contaminant transport.

In many cases, frequent (e.g., weekly or monthly) monitoring of ground-water and surface-water elevations may be warranted, particularly during early phases of monitoring, to improve the characterization of ground-water flow patterns. In some cases, monitoring of these parameters on a very frequent basis using automated recording equipment may be needed to determine the effects of variability in recharge and discharge rates or locations. Once the effects are determined, the information would be used in the specification of appropriate long-term monitoring frequencies. These data may also indicate changes in hydraulic gradients that warrant more frequent monitoring of chemical parameters. Based on the results of such assessments, monitoring frequencies may be adjusted to adequately capture the fundamental features of the observed trends. In general, several years of monitoring data are often necessary for estimation of the site variability in the ground-water flow field.

IIIA.4 Ground-Water/Surface-Water Interactions

Ground-water/surface-water interactions are of particular importance at sites where surface-water bodies are present. The hydrologic, as well as geochemical conditions, in areas where ground water discharges to or is recharged by surface water often differ markedly from those in the main body of the plume and may require intensive monitoring to determine the effect on remedial goals (Winter, 2000). Locations where ground water discharges to surface water may vary both temporally and spatially due to changing hydrologic conditions (Winter et al., 1998; USEPA, 2005a). Tools to characterize the hydraulic relationships between ground water and surface water include piezometers, devices for the direct measurement of ground-water flux and velocity, geophysical methods, and certain geochemical techniques. These tools may be used to define areas of plume discharge into the surface-water body, quantify rates of discharge, and to aid in the selection of monitoring point locations for determining the impact of the discharging water on the sediments and surface-water quality. Multilevel monitoring is generally required to characterize the interactions of ground water and surface water features. For situations where the contaminant plume intersects the transition zone between ground water and surface water, information on the distribution of ground-water discharge/recharge can be used in the selection of monitoring points to characterize chemical characteristics of the transition zone. Characterization of the transition zone can be employed to assess and demonstrate that contaminant concentrations in discharging ground water or accumulated in surface water sediments do not negatively impact human or ecological receptors. Additional discussions of methods for hydrologic characterization of ground-water/surface-water interactions and monitoring of the potential for contaminated ground-water discharge to surface water may be found in various sources, including USEPA (2000a).

IIIA.5 Hydrogeologic Data Interpretation

The data obtained during hydrogeologic characterization are used in conjunction with information on contaminant sources, distribution, and behavior; redox conditions; and possible receptors to develop a conceptual model describing site conditions (Figure 3.3). A three-dimensional conceptual site model incorporating temporal changes is generally necessary to provide a framework for interpreting the site data, judging the significance of changes in site conditions, and predicting the range of future behavior of the source and plume. Understanding plume formation and behavior is the basis for evaluating whether an MNA remedy may be able to achieve site remedial goals within given time frames. Conceptual site models are expressed tangibly in text, maps (e.g., chemical isoconcentration maps and potentiometric surface maps), cross sections (e.g., hydrogeologic and chemical distributions), plots of temporal trends, and other graphical formats, and should be formulated in terms of mathematical calculations describing the plume and site. The conceptual model is a dynamic tool that is continually challenged, evaluated, and refined as new data are obtained. The data and analyses necessary for formulation of an adequate three-dimensional conceptual model for describing the effects of natural attenuation processes depend on site-specific conditions.

The development of quantitative models (i.e., mathematical models) based on the conceptual site model is often an important part of site characterization and remedy selection for MNA. These quantitative models may be as simple as equations for estimation of ground-water flow rates (e.g., Darcy's law), or as complex as numerical models of ground-water flow and contaminant fate and transport. Such calculations are used to help understand site processes, locate monitoring points, estimate attenuation rates, and evaluate possible effects of different conditions on plume behavior. Quantitative models require particular types of data, and the data collection effort should be designed considering the requirements of the chosen model(s) and site-specific characterization objectives.

The conceptual site model for natural attenuation is the site-specific qualitative and quantitative description of the transport and fate of contaminants with respect to receptors and the geologic, hydrologic, biologic, and geochemical factors that control contaminant distribution (USEPA, 2003). The model expresses the understanding of the structure, processes, and factors that affect plume development and behavior. It is built on assumptions and hypotheses that have been tested using site-specific data.

IIIA.5.1 Attenuation Rate Estimates

The spatial and temporal distribution of the contaminant within the ground-water plume will depend on source location, the spatial distribution and velocity of water flow (or diffusion where advective flux is slow), and the abundance and biotic/abiotic reactivity of aqueous and solid phase biogeochemical components along the paths of water flow. The extent to which biogeochemical processes will cause contaminant attenuation during transport will depend on the relative rates of both fluid transport and chemical reactions (Morgan and Stone, 1985). For example, contamination will likely be negligible for systems in which the timescale for water flow within a hypothetical reaction volume is much shorter than the timeframe for significant reaction to take place. Conversely, significant attenuation may observed for contaminants in systems where reactions occur rapidly relative to the timescale for fluid transport. The latter situation is commonly assumed to apply to ground-water systems, but this needs to be confirmed during site characterization. This is particularly important for near-surface systems that may experience large variability in water flux and fluid velocities (e.g., Conant Jr., 2004).

Attenuation rate constant calculations can be an important tool for evaluating the feasibility of natural attenuation at a contaminated site, e.g., as part of the Tier II screening analysis. Specific applications identified in U.S. EPA guidelines (USEPA, 1999) include use in characterization of plume trends, as well as estimation of the time required for achieving remediation goals. As illustrated by Newell et al. (2002) different types of attenuation rate data may be obtained for a given site and careful consideration should be given to the appropriate use of the first-order rate constants derived from these data.

The illustrations in Figure 3.4 provide two examples of attenuation rate constant data that may be collected within the plume. The overall extent of plume attenuation can be estimated by examining contaminant concentrations at a series of wells within the ground-water flow system (Panel A). In this instance, the influence of dispersion on contaminant concentrations as a function of distance must be determined through comparison with a conservative dissolved tracer. The duration of a plume at a given location can be estimated through analysis of contaminant concentration trends with time (Panel B). This can be used to estimate the time required to reach ground-water remediation goals. In both cases, the overall determination of whether the ground-water plume is expanding, showing relatively little change, or shrinking (in three dimensions) will depend on the analysis of multiple well transects (concentration vs. distance) or well points (concentration vs. time) in order to provide appropriate spatial coverage. Since the directions and rates of ground-water flow can vary in time, the determination of concentration-based rate constants may be subject to errors of a magnitude determined to be unacceptable for site characterization. In order to reduce this level of potential error, one may determine mass-based rate constants provided details on the spatial and temporal variability of hydraulic flux is also well characterized. Newell et al. (2002) should be consulted for further details on the application and limitations of the various approaches for estimation of rate constants.

IIIA.5.2 Contaminant Flux

While contaminant concentration is a determining factor for human or ecological risk, this metric does not provide a measure of contaminant mass and distribution within the system of interest. Determination of a contaminant mass balance is critical for determining changes in contaminant mass or speciation during subsurface transport. For organic contaminants, a mass balance calculation aids determination of whether contaminant degradation or sorption is occurring. For inorganic contaminants, a mass balance is required to assess changes in chemical speciation and mobility. The mass balance is inclusive of liquid and solid matrices (e.g., aquifer sediments) within the boundaries of the conceptual model. The distribution of contaminant mass is important with respect to defining remedial objectives and assessing remedial performance.

Contaminant flux (M) is defined as the product of contaminant concentration (C) in the mobile phase (water and mobile colloids) and the volumetric flow of the mobile phase (Q):

$$M = C * Q$$

Contaminant flux can be calculated for point locations or cross-sectional areas perpendicular to water flux depending on the level of heterogeneity in water flow or contaminant concentration distribution (Einarson and Mackay, 2001; Buscheck et al., 2004). For inorganic contaminants, this general equation represents the flux of all contaminant species at a given point in time. Since a mobile inorganic contaminant can change chemical form, it may be useful or necessary to further define contaminant flux for individual contaminant species relevant to site-specific conditions.

$$M_i = C_i * Q$$

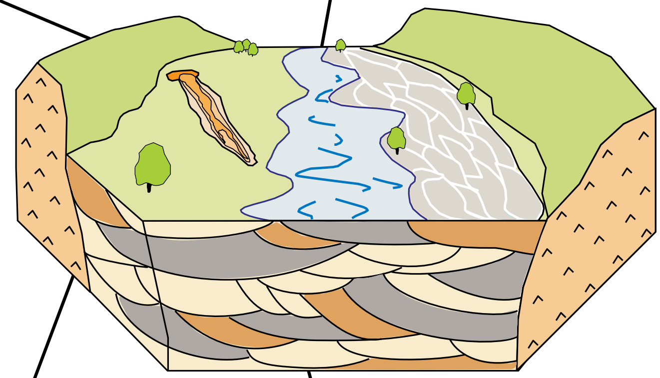
Contaminant transport occurs along water flow paths in the subsurface. Therefore, the first step to determining contaminant flux is developing an understanding of system hydrology. With the establishment of a water budget for the site (i.e., water flux distribution), then a mass budget can be developed to establish contaminant flux across relevant system boundaries.

Contaminant Source and Source Control Information

- Location, nature, and history of contaminant releases or sources
- Locations and characterizations of sources for ground-water contamination [*e.g.*, nonaqueous phase liquid (NAPL)]
- Locations and descriptions of source control and other ongoing and proposed remedial actions

Receptor Information

- Aquifer classification, current usage information, and reasonably anticipated future usage
- Locations and production data for water-supply wells
- Locations and information on human and ecological receptors under current and reasonably anticipated future conditions
- Areas susceptible to impact by vapor-phase contaminants (*e.g.*, indoor air)
- Information on local historical and cultural uses of land, water, and other resources used to identify receptor populations
- Descriptions of institutional controls currently in place



Geologic and Hydrologic Information

- Regional and site geologic and hydrologic settings, including controls on ground-water flow
- Analyses of depositional environments and geologic features that may serve as zones of preferential flow or barriers to flow, including geometry and physical properties of geologic facies (*e.g.*, texture, porosity, bulk density) and their variability
- Stratigraphy, including thickness and lateral continuity of geologic units, and bedding features
- Anthropogenic features (*e.g.*, buried corridors and heterogeneous fill materials) that control ground-water flow, and may serve as migration pathways or barriers
- Depth to ground water and temporal variation
- Characteristics of surface water bodies (*e.g.*, locations, depths, and flow rates), their interactions with ground water, and temporal variations
- Ground-water recharge and discharge locations, rates and temporal variability
- Hydraulic gradients, including horizontal and vertical components, and their variations in response to fluctuations in site hydrology (*e.g.*, seasonal or longer term precipitation patterns and changes in patterns of ground-water withdrawal or irrigation)
- Hydraulic properties (*e.g.*, hydraulic conductivities, storage properties, and effective porosities) and their variability and anisotropy within geologic units
- Quantitative description of the ground-water flow field
- Chemical properties of the subsurface matrix including mineralogy and organic matter

Contaminant Distribution, Transport and Fate

- Distribution of each contaminant phase (*i.e.*, gaseous, aqueous, sorbed, NAPL) and estimates of mass
- Mobility of contaminants in each phase
- Temporal trends in contaminant mass and concentrations
- Sorption information, including retardation factors, sorption mechanisms, and controls
- Contaminant attenuation processes and rate estimates
- Assessment of facilitated transport mechanisms (*e.g.*, complexation or colloidal transport)
- Geochemical characteristics that affect or are indicative of contaminant transport and fate, and mineralogy, if needed
- Potential for mobilization of secondary contaminants (*e.g.*, arsenic)
- Effects of other proposed or ongoing remedial activities on contaminant transport, fate and natural attenuation processes

Figure 3.3 *Elements of a conceptual site model for monitored natural attenuation of inorganic contaminants (modified from USEPA, 2003).*

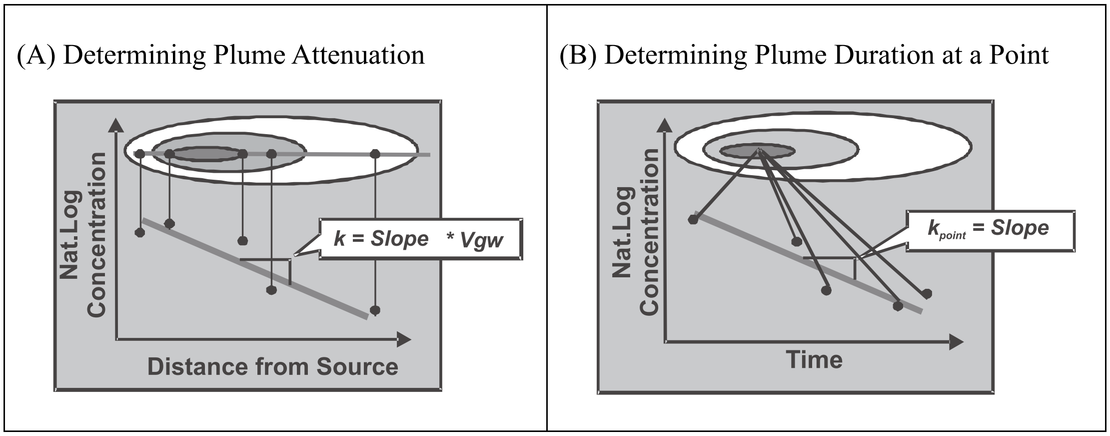


Figure 3.4 *Illustration of two approaches for determining attenuation rate constants within a contaminant plume. Critical assumptions underlie the applicability of these two analysis approaches: 1) analysis depicted in Panel A presumes that a plume centerline exists and that five monitoring wells are sufficient to define it, and 2) analysis depicted in Panel B presumes that the plume is stable. Both assumptions are to be verified through acquisition of supporting spatial and temporal data in order to reduce the uncertainty in rate estimates.*

IIIA.5.3 Source Term Characteristics

In addition to the geologic factors that influence ground-water transport, the chemical and physical characteristics of the source term can play a significant role in determining the physical dimensions of the ground water plume. The dimensions of the mobile plume may be impacted by characteristics of the contaminant source such as the total mass and rate of release of contaminant into the saturated zone within the aquifer. Active treatment of the source zone may also impact plume characteristics, particularly in cases where engineered remedies within the source zone introduce chemical reactants, stimulate microbial processes, or influence ground-water flow. Finally, the chemical characteristics of the contaminant source materials may impact the contaminant transport either directly through chemical reactions that influence aqueous speciation (e.g., Pb complexation by EDTA to form solution species) or indirectly by influencing ground-water chemistry (e.g., via biodegradation of organic co-contaminants such as fuel hydrocarbons or chlorinated solvents). In some instances, microbial reactions that are stimulated by the presence of organic contaminants may result in conditions beneficial to inorganic contaminant attenuation within the plume, e.g., generation of sulfate-reducing conditions that result in precipitation of metal sulfides. While this process may be beneficial to inorganic contaminant immobilization, the site investigation needs to include consideration of the long-term stability of the immobilized contaminant for a site at which the aquifer is generally oxic outside of the plume boundaries. This discussion serves to highlight the importance of factoring in evaluation of contaminant source characteristics and the management of the source area relative to down gradient plume behavior.

IIIB. Contaminant Quantification, Distribution and Speciation

Determination of the attenuation mechanism, assessment of aquifer capacity to attenuate contaminant mass, and the evaluation of the long-term stability of immobilized contaminants will necessitate analytical measurements conducted on aqueous and solid samples collected from within the plume. The types of measurements will include determination of total element concentrations as well as determination of aqueous and solid phase speciation of the contaminant and reactants involved in the attenuation reaction. The measurements will likely be applied to samples collected over a range of locations and times in order to adequately characterize the spatial and temporal variability of aquifer conditions within the plume. The following discussion will provide an overview of the types of measurements that may be required to evaluate the adequacy of site-specific attenuation reactions. The discussion will first address aqueous phase measurements followed by solid phase measurement techniques.

IIIB.1 Aqueous Characterization Approaches

Characterization of ground water will include assessment of the overall chemical conditions as well as the chemical speciation of the contaminant. Determination of the overall chemical conditions within the plume (e.g., redox status discussed in Section IIIC) sets the context for evaluating reactions that lead to contaminant attenuation. Chemical measurements to assess redox status of ground water can be achieved through a combination of field- and laboratory-based methods. Evaluation of the types and distribution of ions in ground water can adequately be addressed via laboratory measurements on properly preserved samples.

These data are typically required to assess what type(s) of sorption reactions control contaminant immobilization. Likewise, determination of contaminant degradation products is needed to verify attenuation is occurring. An underlying assumption for all analysis types is that the approaches to sample collection and preservation are adequate to maintain the intact chemical characteristics of the ground-water sample. Insuring the adequacy of sample collection protocols can be realized, in part, through adherence to recommendations for well installation and low-flow well sampling procedures (USEPA, 1994; USEPA, 1996). It is also recommended that the design of the well monitoring network consider temporal as well as spatial variability that may influence chemical measurements. For example, variations in ground-water levels may result in variations in ground-water redox chemistry. These considerations are explored more holistically in USEPA (2003), which should be consulted both from the perspective of designing the initial ground-water characterization plan as well as the long-term performance monitoring plan.

In general, a variety of water samples should be collected at the same time to allow analysis for metals, common anions, alkalinity, total dissolved carbon, dissolved oxygen, and pH. In some systems, assessment of oxidation-reduction potential (ORP) using a Pt electrode may be desirable for qualitative assessment of variability between screened intervals within the plume. For metals and anions, the use of ultra-clean sample bottles is essential to avoid artifacts, and these can be checked through the inclusion of trip blank samples consisting of deionized water or tap water in the same types of containers.

For preservation, samples for metal analysis are usually acidified immediately upon collection to pH 2 using either HNO_3 or HCl to avoid precipitation of oxide phases. Samples for anion analysis are not treated with acid, as this may swamp the anion of interest during the ion chromatography analysis. Subsamples of the same sample taken for anion analysis can be used for alkalinity determinations, as this quantity is robust. Measurements of dissolved oxygen and pH are best taken in the field using a closed flow cell instrumented with electrodes for in-line measurement. For most samples (especially total dissolved carbon), chilling to 4 °C as soon as possible after collection is useful, although changes of temperature for dissolved gas measurements are not recommended. Methods used for determination of total concentrations of metals in aqueous samples are usually the same as used for destructive analysis of solids with elimination of the digestion step. Oxidation-state determinations can be made on the basis of reactions with chromophores [e.g., s-diphenyl carbazide for Cr(VI), phenanthroline or ferrozine for Fe(II)] and determination of absorbance in the UV-Vis region of the spectrum. Field kits and ion-selective electrodes are available for many of these determinations as well as for pH and dissolved oxygen. Common anions are usually determined in the laboratory using ion chromatography or capillary electrophoresis.

Colorimetry involves specific complexation of the atom of interest in solution by a strongly absorbing compound having a high absorptivity at an accessible wavelength (i.e., a chromophore) and subsequent measurement of the absorptivity of the solution. Atomic absorption, emission, and fluorescence rely on the same electronic transitions involving valence-shell electrons of unbound atoms. With absorption, the amount of light lost in exciting electrons into unbound states is measured, whereas with emission and fluorescence, the amount of light emitted when these electrons return to the ground state is measured. Emission and fluorescence differ in the manner by which the electrons are excited—emission involves thermal excitation of the sample by injection into a flame (flame photometry) or a plasma (ICP-AES), whereas fluorescence uses photon excitation. The sensitivity of colorimetry, AAS, AES, and AFS are roughly comparable (ppm to ppb), although ICP-AES has the advantage of being able to analyze multiple elements more easily with fewer matrix interferences and across a wider concentration range than the other techniques. With ICP-MS, the masses of individual atoms are measured using a mass spectrometer, the intake of which is coupled to a plasma where the atoms are thermally ionized. This technique has many advantages including a wide dynamic range, ability to analyze all elements heavier than He, few matrix or spectral interferences, and the ability to measure isotopic ratios. Specific recommendations on contaminant speciation measurements and supporting ground-water chemistry data are provided within individual non-radionuclide contaminant chapters included in Volume 2 of this document.

IIIB.1.1 Filtration

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 the 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 associated contaminants) that could pass through 0.45 µm filter membranes. The use of filter membranes with pore sizes of 0.1 µm or less will generally provide a better assessment of the dissolved vs. particulate load of ground water.

Analytical methods have typically used 0.45 µm filters to differentiate between dissolved and particulate phases. If the intent of such determinations is an evaluation of truly dissolved concentrations, which would be important for geochemical modeling purposes, the inclusion of colloidal material less than 0.45 µm will result in incorrect values. Conversely, if the purpose of sampling is to estimate ‘mobile’ contaminant species in solution, significant underestimations of mobility may result, due to colloidal facilitated transport by particles, which are filtered out by 0.45 µm filtration. Kim et al. (1984) found the majority of the concentrations of rare earth elements to be associated with colloidal species that had passed a 0.45 µm filter. Wagemann and Brunskill

(1975) found more than a two-fold difference in total iron and aluminum values between 0.05 and 0.45 µm filters of the same type. Some aluminum compounds were observed to pass through a 0.45 µm filter, but were retained on a 0.10 µm filter (Hem and Roberson, 1967). DeVitre et al. (1987) found approximately 35% of the particulate bound manganese in the 0.015 to 0.10 µm size fraction in anoxic lake waters. Kennedy and Zellweger (1974) found errors of an order of magnitude or more in the determination of dissolved concentrations of aluminum, iron, manganese and titanium using 0.45 µm filtration as an operational definition for "dissolved". Sources of error were attributed to filter passage of fine-grained clay particles. De Mora and Harrison (1983) provided an excellent review on the subject of physical separation techniques for trace metal speciation.

During sample collection in anoxic or suboxic systems, iron oxidation and precipitation may occur prior to filtration and result in the removal from solution of previously dissolved species due to instantaneous sorption by the precipitate (Puls and Eychaner, 1990). Filter loading and clogging of pores with fine particles may also occur, introducing filtration errors due to reductions in effective pore size (Danielsson, 1982). Sheldon and Sutcliffe (1969) found that virtually all filters remove particles smaller than the stated pore size. In experiments with seawater and latex particles, using light scattering techniques, Johnson and Wangersky (1985) demonstrated that a high proportion of materials dispersed at sizes smaller than the filter pore size will interact with the filter surface. These interactions are dependent upon size, particle concentration, colloid surface chemistry, electrolyte concentration and composition, nature and concentration of adsorbents, chemical properties of the filter surface, and the frequency of collisions of dispersed particles with the filter surfaces.

Contaminants may exist as dissolved species, precipitated solids, polymeric species or be adsorbed to inorganic or organic particles of colloidal dimensions. Based on the above discussions, the filtration of ground water samples for metal analyses using 0.45 µm filters may not provide accurate data either for geochemical modeling or for contaminant migration estimates. Some mobile species are likely to be removed by 0.45 µm filtration prior to chemical analysis, while other particulate-associated metals will pass through the filters and be incorrectly considered 'dissolved'. A principle objective in sampling to test a geochemical speciation model is to obtain estimates of the free ion activities of the major, minor, and trace elements of interest. Since there are relatively few easily performed analytical procedures for making these estimates, an alternative is to test the analytically determined dissolved concentrations with model predictions, including both free and complexed species.

Collection of ground-water samples and measurement of their chemical properties will be necessary irregardless of whether degradation or attenuation is the primary attenuation mechanism. Characterization of aquifer solids may be necessary to support evaluation of degradation processes, but primarily when knowledge of specific microbial processes or identification of abiotic solid phase reductants is needed to constrain attenuation rate and capacity evaluations. In contrast, for contaminants in which immobilization is the primary (or only) viable attenuation mechanism, collection and characterization of aquifer solids is a specific requirement.

IIIB.2 Solid Phase Characterization Approaches

Determination of aquifer solids mineralogy and solid phase contaminant speciation is critical to identification of the contaminant immobilization process. Contaminant speciation is inclusive of oxidation state of the immobilized contaminant as well as the solid phase component(s) with which it is associated. Determination of contaminant solid phase speciation can be approached in two ways, structurally and operationally. Structural determination uses instrumental procedures (spectroscopy, microscopy) to identify and quantify the discrete phases present. This information, together with accumulated knowledge of their thermodynamic properties and the rates at which they precipitate/adsorb and dissolve/desorb, is employed to assess the capacity of the aquifer to sustain contaminant attenuation and evaluate the long-term stability of immobilized contaminants. The challenges associated with the structural approach include 1) difficulty in identifying specific phases at concentrations near or below instrumental detection limits, 2) need for good sampling statistics (e.g., a large number of micron-sized measurements are needed to ensure that the site is adequately represented), 3) inadequacy of available thermodynamic and kinetic data to evaluate reaction mechanisms, and 4) cost of instrumentation and model applications that may be employed during evaluation of aqueous and solid phase chemical data.

The operational approach, on the other hand, classifies contaminant form solely in terms of reactivity. Contaminated materials are contacted with solutions that simulate, in a short period of time, subsurface conditions expected over much longer time intervals. The amount of contaminant released by the material as a result of this contact is measured. In some instances, the rate of release is also quantified either by in-situ measurements or successive extractions. Examples of the operational approach include chemical extractions using a variety of solutions and procedures, and bioavailability studies that measure uptake by organisms directly. Sequential chemical extractions, in which contaminated materials are treated with successively harsher solutions, have found wide use in site characterization and several standard methods are available for specific situations (Tessier et al., 1979; Yanase et al., 1991). While highly relevant, bioavailability studies are rarely conducted because of the high cost and long time periods required. Operational determination of contaminant form avoids many of the problems associated with the structural approach, but still requires the development of substantial and expensive databases that correlate the amounts and rates of contaminant release during laboratory contact studies with actual contaminant reactivity under field conditions.

IIIB.2.1 Sampling and Fractionation

Collection of samples is the first step in determination of contaminant distribution within the source area and down gradient plume. The most important consideration is that the samples collected give a fair representation of the size and extent of the contamination. Enough samples must be collected to provide statistical certainty to any set of results. As soils and sediments are heterogeneous, minimum sample sizes of about 50 g are needed at each sampling point. These are mixed thoroughly before taking 1- to 10-g subsamples for analysis. In some instances, mixing of samples from different sampling points to provide composite samples can be done to decrease analytical costs, but this practice also tends to decrease the precision with which the geographical extent of the contamination can be determined. To avoid the possibility of bias, and to retain the ability to interpolate results, sampling points should be laid out on a three-dimensional grid that takes into account any pre-existing knowledge of the underlying stratigraphy. Samples may be collected in several rounds, starting with a coarse grid to identify the overall extent of the contamination and possible "hot" spots. Successive sampling rounds using finer grid sizes on subsets of the original coarse grid can be used to provide further data about regions of interest.

Aquifer samples can be collected using a variety of methods. In all cases, however, the goal will be to collect materials to allow for lithologic logging, to provide representative samples for laboratory investigations and for submission to analytical laboratories. The samples must meet the appropriate data quality objectives as identified in the project-specific Quality Assurance Plan (QAP). In all cases, aquifer materials should be collected with local, State, and Federal requirements in mind.

The procedures to follow for collection of soil and sediment samples will depend on the degree to which environmental availability is to be assessed. Aquifer materials can be collected, for example, using hollow-stem auger or hydraulic percussion methods. These are generally well-tested methods applicable to a wide variety of environments. With these methods various types of sample liners may be used, such as plastic or brass sleeves. The sleeves can be cut and capped to preserve materials and facilitate their transport. If oxidation-reduction processes are believed to be an important component of attenuation mechanism(s), special attention must be given to preserving the redox status of materials after they are retrieved from the subsurface. For example, if anoxic materials are collected they must be frozen after collection or stored in evacuated or inert-gas-purged containers in order to preserve primary mineralogy (USEPA, 2002; USEPA, 2006).

For total analyses, little care need be taken and the samples, once collected, can be air-dried and stored before analysis. The availability of many metals, however, depends greatly on their oxidation state, and this may change with time in storage due to microbial activity or exposure to air. Drying of samples can also affect the availability of some elements, e.g., due to irreversible (or slowly reversible) changes in the structure of illitic and vermiculitic clay minerals during drying. A realistic assessment of current availability, therefore, will attempt to make the measurement as soon after collection as possible using samples that have been stored under conditions that maintain their redox and moisture status at the levels seen in the field (USEPA, 2006). The best procedures for preserving samples thus involve, at a minimum, storage of field-moist samples at 4 °C in air-tight plastic bags from which the air has been squeezed. In instances where oxidation state is critical, injection of N_2(g) or Ar(g) into the bore hole, and collection of cores in thick plastic cylinders that are immediately capped and transferred into anoxic chambers for further processing or storage is advised. Lowering the temperature to 4 °C slows microbial activity substantially. Freezing the samples may result in lysing of microbial cells and can create a different organic mixture in the soils than was present at the time of sampling.

In preparation for actual analysis, some particle-size fractionation may be needed for easy sample handling and enhanced sensitivity. As a result of surface-area considerations, the most reactive fraction of soils and sediments is that having particle sizes less than about 50 μm (i.e., silt and clay). Gravel (particles > 2 mm) and cobbles can generally be removed by sieving with little or no impact on the analytical results. The sand fraction (50-2000 μm) is generally left intact, as its removal by wet-sieving creates more problems than it solves. Careful records need to be kept of the mass and volume of the fractions removed so that analytical results on the remaining fractions can be scaled to field conditions. Fractionation on the basis of properties other than particle size can be done to concentrate specific minerals, and this may prove beneficial in some instances (Laird and Dowdy, 1994).

IIIB.2.2 Total Amount

Determination of the total quantity of a metal contaminant present is generally performed on "bulk" sample sizes of at most a few grams. In instances where the total amount of contamination is very low and detection limits are encountered, analysis by electron or X-ray microscopic techniques can be performed in which specific particles containing the contaminant are identified. With the microscopic approach, sample sizes of μg to mg are common, and scaling to field concentrations is difficult.

The bulk analysis techniques are distinguished on the basis of whether they are sample destructive or nondestructive. The sample-destructive techniques require digestion of the sample using strong acid or base to destroy the original compounds present and release the elements in a soluble state. Once in the soluble state, the concentration of the contaminant is determined by spectroscopic means after nebulization or injection into a flame or plasma connected to a suitable detector. The most common detection techniques include colorimetry, atomic absorption spectrometry (AAS), atomic emission spectroscopy (AES) using either flame (photometry) or an inductively coupled plasma (ICP-AES), atomic fluorescence spectroscopy (AFS), and inductively coupled plasma mass spectrometry (ICP-MS).

Colorimetry involves specific complexation of the atom of interest in solution by a strongly absorbing compound having a high absorptivity at an accessible wavelength (i.e., a chromophore) and subsequent measurement of the absorptivity of the solution. Atomic absorption, emission, and fluorescence rely on the same electronic transitions involving valence-shell electrons of unbound atoms. With absorption, the amount of light lost in exciting electrons into unbound states is measured, whereas with emission and fluorescence, the amount of light emitted when these electrons return to the ground state is measured. Emission and fluorescence differ in the manner by which the electrons are excited—emission involves thermal excitation of the sample by injection into a flame (flame photometry) or a plasma (ICP-AES), whereas fluorescence uses photon excitation. The sensitivity of colorimetry, AAS, AES, and AFS are roughly comparable, although ICP-AES has the advantage of being able to analyze multiple elements more easily with fewer matrix interferences and across a wider concentration range than the other techniques. With ICP-MS, the masses of individual atoms are measured using a mass spectrometer, the intake of which is coupled to a plasma where the atoms are thermally ionized. This technique has many advantages including a wide dynamic range (pptr to ppm), ability to analyze all elements heavier than He, few matrix or spectral interferences, and the ability to measure isotopic ratios.

The nondestructive analysis techniques generally rely on inner-shell electronic transitions or nuclear transitions for elemental identification and thus are less reliant on decomposition of the sample into individual atoms. Nevertheless, a homogeneous sample consisting of particle sizes of <2 µm and presenting a flat surface is needed for best results. Thus, although the sample is not completely destroyed in preparation, it is altered by grinding to achieve the particle size needed. The most common of these techniques is X-ray fluorescence (XRF), which can use high-energy photons from an X-ray tube or radioactive source to excite electrons in the atoms of interest. The light emitted by these atoms upon return to the ground state is then detected using an X-ray detector such as a gas-filled proportional counter, scintillation detector, or solid-state semiconductor detector. X-ray emission spectroscopy is similar to XRF except that it uses high-energy particles (electrons, protons, or alpha particles) to excite the atoms rather than photons. In general, detection limits are in the ppm range for solids although X-ray emission spectroscopy is more sensitive for lighter elements (z<30) and X-ray fluorescence is more sensitive for heavier elements (z>45) (Amonette and Sanders, 1994).

Microscopic methods of elemental analysis are generally more expensive than the bulk techniques, but can prove of great use in identification of specific contaminant phases and their associations with minerals. Electron microscopy images particles through scattering of an electron beam. At the same time, the electron beam is stimulating the emission of X-rays by the sample and detection of these (as in X-ray fluorescence) allows simultaneous multielemental analysis of the material being imaged. Scanning electron microscopy (SEM) can be used with samples of any thickness, whereas transmission electron microscopy (TEM) requires preparation of samples on the order of 30-150 nm thick often in the form of thin sections. Conventional SEM and TEM require high vacuum for the analysis, due to the short pathlength of electrons in air, but new developments of the environmental SEM allows analysis of samples at pressures approaching ambient thus allowing observation of wet specimens for short periods of time. With the development of synchrotron X-ray sources, a microscopic technique based on X-ray fluorescence is available for high-value specimens. X-ray microscopy (XRM) has spatial resolution near 1 µm, and because of the very high photon fluxes available can achieve detection limits in the ppb range, better than any other X-ray technique. The XRM technique can be coupled with X-ray absorption spectrometry (XAS) to determine oxidation states and local structural information. Although primarily a research tool at the moment, XRM may prove quite useful for phase identification of critical samples when other techniques fail.

IIIB.2.3 Structurally Defined Form

One approach to the determination of environmental availability relies on identification of the discrete contaminant-bearing phases that are present and combining this information with phase-relevant thermodynamic or kinetic data using a geochemical model. Identification and quantification of the discrete phases present is gained through a combination of elemental, structural, and in some instances, solubility analysis. Techniques for structural analysis measure the arrangement of atoms both local to the contaminant and in extended structures. The combination of structural and elemental information uniquely determines a thermodynamic phase with specific properties.

The primary technique for structural analysis is X-ray diffraction (XRD), which relies on measuring the coherent scattering of a collimated beam of X-rays by the sample as a function of angle to the beam. The technique requires some degree of repetitive structural unit having dimensions on the order of the wavelength of the X-rays. Scattering from parallel planes of atoms separated by regular spacings yields an interference or diffraction pattern. The spacings at which constructive interference occurs (d) yield high intensity in the diffraction pattern and can be calculated from the angle of incidence (θ) and the wavelength of the X-ray (λ) using the Bragg equation, $d = n\lambda/2\sin\theta$, where n is an integer. The set of d-spacings and relative intensities measured for a compound are unique and can be compared with those for thousands of other compounds stored in a large database. In soils and sediments, however, mixtures of compounds occur and overlapping patterns for different compounds can make identification difficult in many instances. Also, XRD is sensitive down to about 1-5% by weight, and thus is not well-suited for identification of trace phases typical of contaminants in soils and sediments. To some extent, these drawbacks can be overcome by fractionating the sample to eliminate interfering compounds and to concentrate the contaminant-bearing phases. Diffraction also occurs with electron beams, as these have wave properties (albeit with shorter wavelengths than X-rays). Electron diffraction is used in TEM analysis to identify phases at the same time they are being imaged and their elemental compositions determined by X-ray emission. Diffraction techniques do not work well for poorly ordered phases, as these phases yield very broad peaks that have little value for identification purposes.

Vibrational spectroscopic techniques can be used in some instances to identify poorly ordered phases, as these methods detect molecular vibrations that depend on bond energies and atomic masses rather than long-range atomic order. The two major types of vibrational spectroscopy are infrared absorption and Raman scattering. Infrared absorption spectroscopy requires a long-wavelength (ca. 1-100 μm) source of light and measures the fraction of this light that is absorbed by the sample. Water absorbs strongly in much of this region, and so samples are best analyzed when dry, unless internal reflectance techniques are used. The long wavelengths used, however, are well suited for interferometry in which the incident beam is split in two and recombined after delaying one beam by a known path length. The resulting interference spectrum, collected as a function of path length difference, is then converting using a Fourier transform to yield an absorption spectrum in terms of wavelength. Because the entire spectrum is collected at all times, rather than scanning through each wavelength individually, the Fourier-transform approach (i.e., FTIR) is the most efficient means of collecting an infrared absorption spectrum.

Raman scattering spectroscopy measures the loss or gain in energy of monochromatic light as a result of interactions with molecular bonds. In theory, incident light of any wavelength can be used to measure these changes, and so some of the limitations of infrared absorption spectroscopy are avoided, such as the need to study dry samples. However, Raman scattering yields a weak signal, and fluorescence from the sample may interfere when incident light in the visible region is used. The recent development of Fourier-transform Raman spectroscopy using laser light in the near infrared region (ca 1 μm wavelength) has provided enough incident light intensity with minimal fluorescence to make Raman practical for many samples.

Vibrational spectroscopic techniques, while sensitive to local bond strengths, are rarely as definitive as XRD because the same types of bonds are found in most inorganic compounds (e.g., oxide, hydroxyl, sulfate, carbonate, etc.) and the differences among compounds are often subtle. This approach, however, can be used to positively identify solid solutions of poorly ordered materials, such as $(Fe,Cr)(OH)_3$ (Amonette and Rai,1990), based on shifts in bond energies due to substitution. Vibrational techniques also find use for identifying orientation and bonding of sorbed contaminants that exist in ground water as oxyanions (e.g., arsenic; Eggleston et al., 1998).

Under certain circumstances, solubility can be used to determine or at least confirm the environmentally relevant phase controlling the availability of an inorganic contaminant. These circumstances require collection of equilibrium solubility data across a range of pH (or some other primary solubility-controlling variable), in which the concentrations of the contaminant as well as other key species involved in formation of aqueous complexes with the contaminant are measured. Based on these data, and known thermodynamic solubilities of the putative contaminant phase, a solubility diagram can be constructed and compared with that for known phases. It is critical that equilibrium be attained or thermodynamic calculations will not be valid. Thus systems that approach equilibrium slowly may not be suitable. Rai et al. (1984) reviewed this approach and its applicability to twenty-one environmentally relevant elements.

IIIB.2.4 Operationally Defined Form

A more direct approach to assessing environmental availability of a contaminant, involves determining the conditions under which it can be dissolved and therefore mobilized into the ground water. This empirical approach presupposes nothing about the chemical form of the contaminant and thus has little predictive value in the event that ground water conditions change. Nevertheless, it offers much in the way of addressing economically the degree to which a total concentration of a contaminant poses an environmental risk.

The primary technique used is that of sequential selective extractions, with each successive extracting solution offering a harsher solution environment than the one that preceded it. The general assumption is that the earlier in the sequence that the contaminant is released, the higher is its environmental availability. Sequential extraction approaches are discussed in more detail in Sections IIIB.2.4.1 and IIIB.2.4.2.

The sequential (selective) extraction approach can be improved by incorporating measurements of the rate of release during each step in the procedure. This can be done by successive extractions for shorter time periods using the same reagent, by measurement of small aliquots taken from the extraction solutions at different times during the extractions, or by a continuous-flow extraction using a specially designed flow cell similar to that of Wollast and Chou (1985) used in mineral weathering studies. Despite the apparent need, the kinetic approach has not been widely applied to estimation of environmental availability of contaminants, although it has been suggested for use in assessing the availability of U in soils (Amonette et al., 1994b).

IIIB.2.4.1 Sequential Extractions

Sequential extraction methods will perhaps be the most practicable approaches for demonstrating contaminant partitioning in the solid phase and for providing information for substantiating proposed attenuation mechanisms. These methods can be particularly useful because they provide quantitative information on the capacity of a given material to attenuate inorganic contaminants. They are also advantageous because large numbers of samples can be analyzed and compared, unlike methods that involve spectroscopy and microscopy. However, as a cautionary note, sequential extraction methods are not without limitations. It must be acknowledged that results of sequential extraction tests are operationally defined and users of these tests must be aware of potential artifacts, as will be pointed out in the following discussion.

Sequential extraction procedures consist of subjecting a given quantity of soil or aquifer sample to a series of increasingly aggressive reagents under specified conditions. An underlying assumption is that the release of components in earlier extractions implies a higher potential for environmental mobility than components released later in the extraction sequence. A conceptual model of the sequential extraction approach is that solid materials consist of specific mineral fractions that can be extracted selectively by using appropriate reagents and experimental conditions. As mineral fractions are selectively dissolved, any element that they contain will release into solution and in this way the "speciation" of particulate trace metals can be determined. If it is determined that the majority of a contaminant of concern is present, for example, in the operationally-defined carbonate fraction, then geochemical modeling efforts might be appropriately focused on the factors that govern long-term stability of carbonate minerals.

Perhaps the most often followed or modified chemical extraction procedure is that of Tessier et al. (1979). Other approaches are outlined, for example, in Dragun (1988) and Yong et al. (1993). In the Tessier et al. (1979) method, five distinct extraction procedures are used to recover metals from the following sediment/soil fractions: 1) exchangeable sites; 2) carbonate minerals; 3) metal oxyhydroxides; 4) organic matter; and, 5) the residual fraction (Table 3.1). Metals associated with loosely bound sites (weak electrostatic attraction) are released by extraction in concentrated salt solutions. Divalent metal chloride salts prepared at a concentration of 1 molar are often used in this first step (e.g., $CaCl_2$ or $MgCl_2$). After extraction for a set period of time and mixing rate, the supernatant solution is analyzed using spectroscopic methods and the concentration of an element in solution is related back to a mass fraction of that element associated with operationally defined exchangeable sites. Metals associated with carbonate minerals are removed in a second step by wet chemical extraction in a sodium acetate-acetic acid buffer solution. This buffer (pH 5) is effective in dissolving calcite, an abundant carbonate mineral found in natural systems. Iron and manganese oxides are removed with hot hydroxylamine hydrochloride solution. Organic compounds, such as humic acids and fulvic acids, are targeted with acidic, oxidizing reagents (hydrogen peroxide plus nitric acid; note that other published extraction methodologies employ basic conditions to "selectively" remove organic matter, for example, 3 M KOH). The residual fraction is typically determined from a concentrated nitric acid digestion or total analysis (by complete digestion or by X-ray fluorescence spectroscopy) after subtracting out the fraction of metal extracted in steps 1 through 4. The residual fraction is considered to represent the fraction of metals present in tightly bound matrices, for example, in aluminosilicate matrices that are not effectively dissolved with any of the reagents used in steps 1-4.

This extraction scheme has been adapted for testing and validation against natural matrix standards by the Radioactivity Group of the National Institute of Standards (NIST) Ionizing Radiation Division (http://physics.nist.gov/Divisions/Div846/Gp4/environ.html). This work represents an effort to support metrology improvements in the radiochemistry community through research and development of low-level radionuclide Standard Reference Materials (SRMs) and

Table 3.1 Sequential extraction procedure of Tessier et al. (1979).

Step	Target Fraction	Chemicals/Conditions
Step 1: Exchangeable	Ionically bound metals and metalloids	1 M magnesium chloride (pH = 7.0) 1 hour, room temperature
Step 2: Carbonates	Metals/metalloids with carbonate minerals (e.g., calcite, dolomite)	1 M sodium acetate plus acetic acid (pH = 5.0) 4 hours, room temperature
Step 3: Fe and Mn oxides/ hydroxides	Metals/metalloids with iron and manganese hydroxides	0.04 M hydroxylamine hydrochloride in 25% (v/v) acetic acid (pH ~ 2) 6 hours, 96°C
Step 4: Organic matter	Metals/metalloids bound to natural organic matter (e.g., humic and fulvic acids)	0.02 M nitric acid, 18% hydrogen peroxide (pH = 2) 2 hours, 85 °C
Step 5: Residual	Aluminosilicate minerals, pyrite	16 N nitric acid 2 hours, 140 °C

Notes: Initial sample weight is generally 1 gram. This initial mass is used to report all metals fractions in terms of metal weight per gram of dry sediment. Samples are generally dried (aerobically or anaerobically) to a constant mass, gently ground and homogenized in an agate mortar. Samples should be constantly agitated during each extraction step. Extractions are conveniently carried out using polypropylene or Teflon centrifuge tubes. Initial and final pH values should be measured and recorded. Supernatant solutions are collected and analyzed by atomic absorption spectroscopy, inductively coupled plasma emission spectroscopy, or other suitable methods. Between steps, samples are centrifuged (typically 5000 to 10000 rpm, 30 minutes) and rinsed with deionized water (5-10 mL).

measurement quality assurance. The Radioactivity Group has undertaken a systematic study to test the relative selectivity of a Tessier-based extraction scheme for the speciation of a suite of radionuclides and stable elements (Schultz et al. 1998a; 1998b; 1998c; 1999). These tests have been conducted with a suite of natural matrix standards (soils and sediments) developed by NIST for the purpose of validating radiochemical methods. While the adoption of this extraction scheme may not be suitable for all sample matrices (see discussion below), the development of a uniform reference database relative to the performance for a given extraction scheme provides a valuable starting point for adapting an extraction scheme(s) better suited for site-specific conditions. The availability of certified SRMs for testing extraction schemes is critical for assessing data quality across analytical laboratories that may be utilized to support site characterization.

In sulfate–reducing systems, the iron sulfides mackinawite (FeS) and pyrite (FeS_2) may be potential hosts to a variety of metals. Huerta-Diaz and Morse (1990) presented a sequential extraction method for the determination of metal partitioning in iron sulfides. Their method involves the sequential leaching of samples using 1 M HCl to recover a "reactive" fraction (FeS; equivalent to acid volatile fraction discussed below), 10 M HF to recover the silicate fraction, and finally concentrated HNO_3 to recover the pyrite fraction. Moore et al. (1988) investigated the partitioning of metals in reducing sulfidic systems using sequential extraction techniques. They chose to use a three-step procedure: 1) 0.25 M hydroxylamine hydrochloride in 25% acetic acid to remove metals bound to oxyhydroxides of Fe and Mn and carbonates; 2) 0.1 M sodium pyrophosphate at pH 10 to recover the organic fraction; and 3) the sulfide fraction was recovered using potassium chlorate plus hydrochloric acid. These fractions were compared with total metal concentrations determined by digestion of samples in HF plus perchloric acid.

Numerous reagents and extraction schemes have been developed for iron minerals in soils and sediments (e.g., Mehra and Jackson, 1960; Chao and Zhou, 1983; Walker, 1983; Canfield, 1989; Ryan and Gschwend, 1991; Kostka and Luther, 1994). Because of the importance of iron minerals for sequestering metals and metalloids in the environment, it is worthwhile to summarize the most commonly used wet chemical techniques for iron, and the oxide and sulfide minerals dissolved using these various reagents (Table 3.2). Slight variations in technique can have profound influences on the outcome of chemical extractions, for example, whether 1 M or 4 M hydrochloric acid is used (e.g., Chao and Zhou, 1983). Consequently, in all cases where sequential extraction methods are employed it will be necessary to clearly document the types of reagents used, extraction times, temperature, and laboratory procedures. Validation of laboratory procedures by spiking

Table 3.2 Summary of reagents used to selectively dissolve iron oxides and sulfides.

Extractant	Composition	pH	Time (h)	Fe minerals Extracted
Ascorbate[1]	0.17 M sodium citrate; 0.6 M sodium bicarbonate; 0.023 M ascorbic acid	8	24	ferrihydrite
HCl[1-3]	0.5–6 M hydrochloric acid	<2	1	ferrihydrite mackinawite
Hydroxylamine hydrochloride[1-4]	0.04 M hydroxylamine hydrochloride in 25% (v/v) acetic acid, 96 °C	<2	6	ferrihydrite mackinawite
Oxalate[5]	0.2 M ammonium oxalate/ 0.2 M oxalic acid	2.5	48	ferrihydrite lepidocrocite magnetite (partial) mackinawite
Dithionite[1,2,6,7]	0.11 M sodium bicarbonate/0.27 M sodium citrate, add 0.5 grams sodium dithionite at 80 °C, repeat dithionite addition	5-7	4	ferrihydrite goethite (partial) hematite (partial) magnetite (partial)
Ti-citrate[8]	0.05 M Ti(III) citrate EDTA-bicarbonate	7	2	ferrihydrite goethite hematite (partial)
Chromous chloride[9,10]	1 M Cr(II) chloride in 0.5 M hydrochloric acid; reagent prepared using a Jones reductor	<2	1	pyrite mackinawite elemental sulfur

Notes: see references for experimental details; [1]Kostka and Luther (1994); [2]Canfield (1989); [3]Chao and Zhou (1983); [4]Tessier et al. (1979); [5]Schwertmann (1964); [6]Mehra and Jackson (1960); [7]Walker (1983); Ryan and Gschwend (1991); [9]Zhabina and Volkov (1978); [10]Tack et al. (1997).

extraction experiments with known quantities of minerals and assessment of recovery will be needed in most cases to evaluate and verify assumptions related to sequential extraction approaches (see, for example, Chao and Zhou, 1983; Kostka and Luther, 1994; Keon et al., 2001). In this way, the results of sequential extraction experiments can depart from purely operational definitions and approach the point where such results can be confidently applied to assess mineral-contaminant associations.

Over the past 10 years, the European environmental research community has developed a three-step sequential extraction scheme, the so-called BCR method (formerly the Community Bureau of Reference, now referred to as The Standards, Measurements and Testing Programme of the European Commission; see Rauret et al., 1999). The extraction scheme has been evaluated using standard reference materials (CRB 601, sediment; CRM 483, sewage sludge amended soil) by multiple laboratories (Ure et al., 1993; Quevauviller et al., 1997; Rauret et al., 1999). In step 1 of the BCR scheme, metals present in ionic forms, bound to carbonates, and in exchangeable forms are separated (Table 3.3). In step 2, metals bound to amorphous iron and manganese oxides are leached, while in step 3 metals bound to organic matter and sulfides are selectively dissolved (Table 3.3). The use of prescribed procedures and standard reference materials to verify performance is an important development and a potential advantage of the BCR extraction approach.

Assessments of environmental risk may be more suitably focused on the water soluble and exchangeable soil fractions, i.e., the most labile metal/metalloid forms released in the first step of the sequential extraction schemes described above. While total metals contents and pseudo metals contents (sum of all extractable forms) are valuable in defining the extent of metal buildup in contaminated soils and sediments, these fractions may be less useful for assessing environmental and ecological impacts (Gupta et al., 1996). Use of single-step extraction tests with salt solutions of $CaCl_2$ and $NaNO_3$ for the determination of the most readily bioavailable metal fraction is discussed, for example, by Maiz et al. (1997) and Gupta et al. (1996). Although single-step procedures may be useful in developing models of ecological risk, these procedures will generally not be adequate in developing the necessary understanding of attenuation mechanisms and long-term contaminant behavior needed to adopt monitored natural attenuation as a site remedy.

Table 3.3 BCR extraction scheme applied to 1 gram of sample.

Step	Reagents/Conditions	Target Fraction
Step 1	40 mL of 0.11 M acetic acid; 16 h at room temperature	Ionic, exchangeable, carbonates
Step 2	40 mL of 0.50 M hydroxylamine hydrochloride plus 0.05 M nitric acid, 16 h at room temperature	Amorphous iron and manganese oxides
Step 3	10 mL 8.8 M hydrogen peroxide at room temperature for 1 h plus 1 h at 85 °C, reduce solution volume to near dryness; 50 mL 1 M ammonium acetate adjusted to pH 2 with nitric acid; 16 h at room temperature	Organic matter, sulfides

Notes: see Rauret et al. (1999) for detailed experimental procedures.

In most cases, assessment and monitoring of natural attenuation processes for inorganic contaminants will require some type of sequential extraction procedure in Tier II. Tier II and Tier III sequential extraction efforts might be carried out to: i) further refine the conceptual model of natural attenuation; ii) increase the spatial resolution of metal partitioning data at a site; and, iii) validate extraction procedures by spiking extraction experiments with known quantities of reference minerals to assess method performance and test assumptions regarding solid phase partitioning. The selection of a sequential extraction procedure must take into consideration site-specific factors, such as physical soil/aquifer characteristics, redox conditions, and contaminant type. Examples of sequential extraction approaches on a contaminant-specific basis are presented in the element-specific chapters in Volume 2 of this document. It is possible that several procedures might be tried before an optimal method is selected at any site. Samples for sequential extraction tests should be collected near the source region and at points moving down gradient through the contaminant plume and at points past the down gradient and lateral plume fronts. Vertical resolution should cover the area most impacted by the contaminant plume but vertical sampling should also encompass subjacent and superjacent regions of the aquifer. These spatial data will be needed in order to develop a model of contaminant uptake along the flowpath. Sequential extraction procedures should be carried out prior to any active remediation and they may be a useful component of annual site monitoring activities.

IIIB.2.4.2 Sequential Extraction Considerations

Many examples of selective extraction recipes can be found in the literature. The choice of procedure will necessarily involve consideration of project objectives and site-specific details. Moreover, the pros and cons of using sequential extraction methods for determining metals speciation in the solid phase have been extensively discussed and debated in the literature (e.g., Kheboian and Bauer, 1987; Belzile et al., 1989; Nirel et al., 1990; Tessier and Campbell, 1991). Sequential extractions clearly provide a very practical methodology for getting at critical information about where metals reside in a sample that can be linked to bioavailability and geochemistry of contaminant metals. Further, a considerable amount of work has gone into verifying the selective extraction methods for specific elements of interest (e.g., Gruebel et al., 1988). On the other hand, a number of complicating factors can strongly direct the outcome of sequential extraction procedures and the interpretation of results with regard to potential metal mobility. The two most identifiable experimental problems with sequential extraction procedures are the non-selectivity of extractants and potential trace element redistribution among phases during extraction (e.g., Rendell et al., 1980; Rapin et al., 1986). For example, metals that are released during extraction can potentially re-adsorb to other surfaces present in the sample at the time of extraction, or the extracting solution itself can impact geochemical conditions that favor metal removal by re-adsorption or precipitation. As noted previously in Section IIIB.3.1, extraction results are operationally defined and they are influenced by factors such as choice of reagents, extraction time, and solid to solution ratios.

An example of an extraction artifact relating to arsenic is described in Wilkin and Ford (2002). Extraction of samples with dilute hydrochloric acid is commonly adopted to assess metal and metalloid partitioning to the acid-volatile sulfide (AVS) fraction of soils and sediments. This extraction test is also used to estimate potential metal toxicity of aquatic sediments (DiToro et al., 1990; Allen et al., 1993; USEPA, 2000b). The method takes advantage of the comparatively high solubility of metal monosulfides like FeS, PbS, CdS, and ZnS at low pH. However, insoluble metal sulfides of Cu and Hg are not effectively dissolved in hydrochloric acid (e.g., Mikac et al., 2000). Furthermore, arsenic chemistry in sulfidic systems contrasts with that of divalent metals in that the solubility of arsenic sulfides like orpiment (As_2S_3) increases with pH; solubility minima for orpiment are found at low pH. This means that at the low pH conditions typical of HCl extractions, precipitation of arsenic sulfide is favored. Two potential artifacts complicate the use of low pH extractions for As solid-phase partitioning in sediments containing acid-volatile sulfides. If orpiment is present in sediment, it will not be efficiently dissolved with hydrochloric acid. A more serious problem, however, relates to interpretations of arsenic extraction data. During acid-extraction, arsenic may be released from labile sediment components, i.e., loosely bound or sorbed sites. If AVS is present, arsenic sulfide is expected to precipitate at low pH and thereby significantly impact arsenic partitioning by transferring arsenic from a labile and potentially bioavailable fraction to what would be considered, using conventional interpretations, a refractory, bio-unavailable fraction (i.e., a fraction insoluble in hydrochloric acid).

A second example of element redistribution during chemical extraction procedures relating to lead is described in Gerth (1990) and Ford et al. (1999). In these studies metal partitioning to iron hydroxide was evaluated using a 2 h extraction with ammonium oxalate. The procedure takes advantage of the rapid dissolution of ferrihydrite in ammonium oxalate relative to other more stable transformation products of ferrihydrite, such as goethite. However, an insoluble Pb-oxalate phase was identified as an end-product of the chemical extraction. The formation of this insoluble phase was clearly a consequence of the choice of reagents used in the extraction procedure. Again without knowledge of this artifact, interpretation of extraction results would have likely guided the conclusion that lead was immobile and non-bioavailable, which in fact may or may not be the case. The magnitude of extraction non-selectivity and/or extraction artifacts can be assessed through the addition of specific mineral components targeted by the individual extraction steps. These internal reference materials can be synthesized in a manner that includes the contaminant in a sorbed form. Synthesis methods for many of the solid phase components targeted by the various proposed extraction protocols are included in the cited references. The inclusion of this form of quality control into the overall extraction methodology will increase the level of confidence in these analytical data.

IIIB.2.5 Attenuation Capacity

The capacity of geological materials to attenuate contaminants has been a subject of extensive research. The static or batch adsorption method has often been used to assess the capacity of soils and aquifer materials to remove metal components from the aqueous phase. The ease of carrying out batch-adsorption tests clearly factors into the popularity of this testing strategy. In this method, aqueous solutions are mixed with a given mass of solid material for a set period of time. The aqueous solution is next separated from the solid adsorbent material, typically by filtration, and chemically analyzed to determine changes in solute concentrations. The concentration of a dissolved component before reaction with the adsorbent minus the concentration after reaction is used to calculate the mass of the component that has been removed by adsorption (or some other removal process). The approach is simple yet numerous experimental parameters impact the results of a given batch-adsorption test (USEPA, 1992; USEPA, 1999; Jenne, 1998).

For inorganic species of concern, critical experimental parameters include contact time, solution pH, method of mixing, solid:solution ratio, and the concentration of other dissolved components in the solution (e.g., Barrow and Shaw, 1979; Roy et al., 1986). Solution composition is of critical importance since dissolved constituents in the background matrix of the ground water can influence contaminant partitioning either through competition for sorption sites or modification of the surface charge of the aquifer matrix. In addition, due to chemical interactions between the aquifer matrix and the solution in which it is suspended, it is important that solution matrix employed closely mimics the in-situ conditions from which the aquifer matrix was collected. For example, exposure of reduced sediments to a solution matrix containing molecular oxygen will likely cause significant changes in the mineralogical composition of the aquifer matrix during the time period of the batch test (USEPA, 2006). The results from a test performed in this manner provide no meaningful data relative to the assessment of in-situ sorption properties.

The methods used to prepare samples for use in laboratory-based studies, including batch-adsorption tests, can have a profound influence on test results. For example, oven-drying samples, although useful for homogenizing materials and for obtaining accurate dry weights, in most cases affects the chemical properties of sediments and may influence the results of batch-adsorption procedures. This affect will vary from material to material but may be the consequence of surface area changes that come about after drying, mineral transformations that occur at elevated temperatures or result from oxidation reactions. Consequently, oven-drying is generally not an advisable practice to accelerate material drying. Air-drying is more preferable although this method may take a longer period of time (several days). Air-drying can be considered to be a partial drying procedure to bring the moisture content of a material to near equilibrium with the atmosphere under which drying is taking place. The duration of air-drying should be kept to the minimum time possible and the progress should be tracked with methods such as weighing. Anaerobic soils provide a special case. Drying of such materials must be carried out in a anaerobic chamber or glove box. Drying of anaerobic materials can be accelerated by using a stream of dry, high-purity (oxygen-free) inert gas.

Batch-adsorption tests should be carried out under constant-temperature conditions (e.g., ±3 °C) and should attempt to mimic site chemical conditions. The influence of pH on batch-adsorption tests is extremely important and the effect of pH will vary depending on the nature of the adsorbent and the solute of interest. Measurements of the equilibrium pH of the soil-water suspension should be given along with adsorption results. For anaerobic systems, batch tests and pH measurements should be carried out in a glove box so that air-sensitive soil components do not oxidize and influence contaminant sorption (USEPA, 2006). Methods for ensuring proper mixing of solid and solution mixtures and selection of appropriate solid: solution ratios are discussed for example in USEPA (1992).

Results of batch-adsorption tests are conveniently analyzed using linear regression tools and adsorption isotherm equations that relate the amount of solute adsorbed to the equilibrium concentration of the solute. Two of the more frequently used adsorption models employ the Langmuir Equation (Section IIIB.3.2) and the Freundlich Equation (Section IIIB.3.3). The choice of one of these adsorption models or other possible adsorption equations will typically stem from the simplicity of the equation and from statistical reasoning using the regression coefficient. These equations can be used to quantitatively describe adsorption data and be "plugged" into reaction transport models used to develop site models (see Section ID).

Dynamic, continuous flow column experiments are a more detailed and desirable method for obtaining metal uptake and desorption potential. In column experiments, aquifer materials are packed into a column apparatus, typically a glass chromatography column equipped with Teflon end-plate assemblies. Columns typically contain sampling ports at the influent and effluent ends and preferably along the length of the column. The sampling ports are designed to allow for water sampling along the center axis of the column. Representative solutions are then pumped through the column using for example a high-performance liquid chromatography pump at a flow rate selected to approximate an average seepage velocity expected in the field. Effluent solutions and sampling ports along the column are then monitored with respect to contaminant concentrations, geochemical parameters (e.g., pH, redox potential), and volume of solution eluted from the column. These data allow for the construction of contaminant breakthrough curves based on the reduced contaminant concentrations ($C_{\text{effluent}}/C_{\text{input}}$) and sample pore volume. The results of column tests can be augmented by the application of mineralogical characterization techniques to allow for the identification of reaction products that can lead to insight regarding uptake mechanisms and provide an improved basis for predicting long-term trends.

The results of static-batch and dynamic-column tests ultimately will be fed into a mathematical model (i.e., a surface complexation model, or Freundlich adsorption isotherm) to develop a quantitative description of contaminant sorption to and desorption from aquifer materials. Examples of this methodology are presented for example in Dunnivant et al. (1992) and Kent et al. (1995), studies that explore the transport of cadmium and chromium/selenium, respectively, in aquifer systems.

In context of using laboratory- or field-derived data as input to computer modeling codes, Bethke and Brady (2000) have recently pointed out potential problems with the "K_d" or single parameter distribution coefficient approach. When sorption is suspected as being the dominant attenuation mechanism, these authors argue that the simple distribution coefficient will in many cases not adequately describe contaminant movement through aquifer systems, especially for the ionic species typical of inorganic contaminants of concern in this document. The distribution coefficient simply gives the ratio of a metal ion's sorbed concentration (mol/g sediment) to its dissolved concentration (mol/cm^3). Alternatively, Freundlich or Langmuir adsorption isotherms or surface complexation models are available to more accurately model field observations. The advantage of the isotherm approach is that adsorption trends can be tied specifically to materials collected from a specific site, yet the method is empirical and it must be acknowledged that extrapolation of results can not be made outside of measured ranges. The surface complexation model does indeed provide a more realistic description of ion adsorption from fundamental principles, yet available databases for surface complexation constants are limited. Almost all applications of surface complexation modeling efforts use hydrous ferric oxide as the dominant sorbing material, this may not be appropriate for all sites.

IIIB.3 Model Representations to Interpret Contaminant Sorption Observations

While thermodynamic equilibrium-based geochemical models are useful for providing boundary conditions for estimating the extent of contaminant partitioning to aquifer solid phases, the kinetics and reversibility of the sorption process are factors that warrant consideration on a site-specific basis if monitored natural attenuation is proposed as a remedial strategy for inorganic contaminants. Another important consideration is that a purely thermodynamic treatment of partitioning is a purely macroscopic description and therefore, is not dependent on an atomic or a molecular scale model which may be employed to represent sorption reactions occurring within the aquifer (Sposito, 1981).

There are two general approaches to modeling contaminant sorption behavior, namely empirical and mechanistic models. Empirical models provide a mathematical description of observed experimental data without necessarily invoking a theoretical basis or microscopic model for the observed relationship. Mechanistic models seek to describe a system based on thermodynamic principles. In theory, the mechanistic approach is desirable because it is more robust and widely applicable in that the effects of changes in ionic strength and pH within a system are fully integrated into the models. On the other hand, mechanistic models require a rather complete chemical and physical description of the system to be modeled and thus are still less commonly used than the empirical models. In general, mathematical descriptions of contaminant sorption to solid surfaces capture the electrostatic and/or chemical forces (or some combination thereof) that result in a net attraction of dissolved contaminants to the solid surface. Empirical models are derived to describe sorption trends irrespective of the specific mechanisms, e.g., electrostatic/chemical forces, involved in the partitioning process. In contrast, mechanistic models attempt to describe the relationship between properties of the solid surface and the net attraction/repulsion of the dissolved contaminant.

IIIB.3.1 Distribution Coefficient/Partition Coefficient, K_d

The partition coefficient, K_d, is the simplest model for predicting sorption in soil systems. It is defined as the ratio of the quantity of adsorbate sorbed per unit mass of solid to the quantity of adsorbate in solution at equilibrium:

$$K_d = q/C$$

where q = concentration of adsorbate on the solid at equilibrium (µg/g) and C = total dissolved concentration remaining in solution (µg/ml).

This approach assumes that the system is reversible and that sorption is independent of the adsorbate concentration in the aqueous phase. Like all the empirical models the constant K_d value does not account for changing physical and chemical conditions in the soil. An extension of the constant K_d is the parametric K_d model where the dependence of K_d of a particular contaminant on various physical and chemical properties of the system is determined by stepwise linear regression analysis and polynomial expressions are developed that express K_d as a function of the relevant soil and aqueous conditions. The parametric K_d approach is preferable in that it allows for the K_d value to vary dependant on prevalent conditions, however, it arguably involves as complete an analytical characterization of the system as the mechanistic models while still remaining an empirical approach.

The basic tenant of the constant K_d approach, i.e., that partitioning is a linear function of concentration, has been shown to be invalid in many instances. Adsorption isotherm models have been used by soil scientists to model situations were adsorption deviates from linearity. The two most commonly used models are the Langmuir and Freundlich adsorption isotherm models.

IIIB.3.2 The Langmuir Model

The Langmuir model was originally developed to describe the adsorption of gas molecules on a homogenous solid surface. The assumptions underlying the model are that every adsorption site is equivalent, and that the ability of a site to bind the adsorbate is independent of whether neighboring sites are occupied. The Langmuir equation is expressed as:

$$q = \frac{bKC}{1+KC}$$

Where q is the concentration of adsorbate on the solid and C is the concentration in solution, b is the maximum number of available sites for adsorption (assumes monolayer coverage) and *K* is a constant related to binding strength. The Langmuir equation can be rearranged to a linear form:

Let $K_d = q/C$

then $K_d = bK - Kq$

and a plot of K_d versus q should be linear with a slope of –K and intercept of b.

Sposito (1984) reports that it is not uncommon for the relationship between K_d and q to be convex to the q axis rather than linear. This type of isotherm has been fit with a two site Langmuir isotherm:

$$q = \frac{b_1K_1C}{1+K_1C} + \frac{b_2K_2C}{1+K_2C}$$

The adherence of an adsorption isotherm to a two site Langmuir model has been interpreted as evidence for two discrete binding sites on the solid phase, however, no mechanistic interpretation can really be inferred from the goodness of fit of sorption data to these isotherms.

IIIB.3.3 The Freundlich Isotherm

The Freundlich isotherm has the form:

$$q = AC_i^{\beta}$$

Where A and β are adjustable parameters and β can have a value between 0 and 1. Hence a plot of log q vs. log C should be a straight line with an intercept of log A and slope of β. Note that when β = 1, then the Freundlich equation reduces to the linear K_d.

Sorption isotherms have been widely used to describe and predict adsorption of a contaminant in soil and sediment systems, however, as stated previously they are purely empirically derived relationships and the validity of the calculated parameters can only be expected to hold within the bounds of the experimental data used to create the initial isotherm. They also provide no mechanistic interpretation of the reactions governing the solubility of a contaminant in a system; they are insensitive to the mode of sorption (i.e. precipitation or adsorption). In view of these facts mechanistic models of the soil sediment system have been developed. The mechanistic approach uses thermodynamic relationships to model aqueous speciation and electric double layer theory to model changes in surface charge as a function of pH, electrolyte concentration and valence. Mechanistic models are potentially much more robust than adsorption isotherm approaches and, once the model has been established, potentially much more powerful in their predictive capabilities with respect to changing physical and chemical conditions within the system.

IIIB.3.4 Mechanistic Models for Predicting Sorption - Surface Complexation

A variety of mechanistic approaches have been applied to provide a molecular description of adsorption in soil-water systems. A number of approaches are based on a mathematical description of the distribution of ions in the vicinity of a charged surface, and the surface charge and potential in the interfacial region. These mathematical models, termed surface complexation models (SCMs), capture the influence of electrostatic forces between the solid surface and charged ions within solution as well as the influence of chemical interactions between these two entities that leads to the formation of coordinative bonds. The various models that are commonly employed to describe surface complexation reactions differ in their description of the distribution of charge at the solid-water interface and how ions are distributed in the aqueous layer that bathes the solid surface. Details of the various models are available from several sources and should be consulted by those unfamiliar with the implementation of surface complexation modeling to describe contaminant solid-solution speciation (e.g., Sposito, 1984; Davis and Kent, 1990; Stumm, 1992; Goldberg, 1995). A brief synopsis of the various models is provided in Table 3.4. In general, two different types of surface complexes are proposed in the various models: 1) inner-sphere surface complexes in which the contaminant forms a bond with a surface functional group, and 2) outer-sphere surface complexes where the contaminant partitions to the surface via electrostatic attraction (similar to the process of ion exchange).

Table 3.4 Synopsis of the various surface complexation models (SCMs) commonly employed to describe solute partitioning to solid surfaces.

Surface Complexation Model	Description of Solute Partitioning to Solid Surface	Influence of Surface Charge
Constant Capacitance Model (CCM)	Inner-sphere complexes	Exponential electrostatic term that modifies value of surface complexation constant
Diffuse Layer Model (DLM)	Inner-sphere complexes	Exponential electrostatic term that modifies value of surface complexation constant
Triple Layer Model (TLM)	Inner- and outer-sphere complexes	Two exponential electrostatic terms that modify values of inner-sphere and outer-sphere surface complexation constants
Nonelectrostatic Model (NEM)	Inner-sphere complexes	None

A key difference between SCMs and empirical models is the employment of thermodynamic concepts to model chemical reactions occurring at the solid surface. By proposing specific chemical reactions for the partitioning of solution ions to the solid surface it becomes feasible to account for the influence of the bulk solution composition such as pH, which can exert an influence on both surface charge as well as solute speciation. In addition, the bulk water composition can influence contaminant sorption via the presence of ions in solution that compete for available surface sites. Examples of surface complexation reactions that may be postulated within an SCM are as follows:

$$=\mathrm{SH} + \mathrm{Zn}^{2+} \leftrightarrow =\mathrm{S\text{-}Zn}^{+} + \mathrm{H}^{+}$$

(=SH represents functional group on FeS)

$$=\mathrm{SH} + \mathrm{Mg}^{2+} \leftrightarrow =\mathrm{S\text{-}Mg}^{+} + \mathrm{H}^{+}$$

$$=\mathrm{SH} + \mathrm{OH}^{-} \leftrightarrow =\mathrm{S}^{-} + \mathrm{H_2O}$$

$$=\mathrm{FeOH} + \mathrm{Pb}^{2+} \leftrightarrow =\mathrm{FeOPb}^{+} + \mathrm{H}^{+}$$

(=FeOH represents functional group on FeOOH)

$$=\mathrm{FeOH} + \mathrm{Ca}^{2+} \leftrightarrow =\mathrm{FeOPb}^{+} + \mathrm{H}^{+}$$

$$=\mathrm{FeOH} + \mathrm{H}^{+} \leftrightarrow =\mathrm{FeOH_2}^{+}$$

A mass action equation can then be written for each of these reactions (similar to solution complexation reactions) and solved to calculate *conditional* surface complexation constants. For SCMs that account for the influence of electrostatic interactions, the conditional surface complexation constant is typically modified via multiplication by an exponential electrostatic factor in order to calculate an *instrinsic* surface complexation constant.

The reactions describing ion partitioning to a solid surface provide the physicochemical context for assessing changes in sorption that may accompany changes in ground-water chemistry. Several observations are evident from the example reactions shown above:

1) pH can influence the speciation of surface functional groups as well as the surface charge,
2) ion sorption can influence surface charge, and
3) major ions in solution (e.g., Mg^{2+} and Ca^{2+}) can compete with the contaminants of concern (e.g., Zn^{2+} and Pb^{2+}) for available sorption sites.

Thus, an SCM provides one with the ability to project how changes in solution chemistry can impact contaminant uptake; a significant limitation of empirical partitioning relationships. While this flexibility provides a powerful tool for examining the evolution of a contaminant plume, current implementations of most SCMs is limited by the heterogeneous nature of solid surfaces within an aquifer (types of sorption sites) and the ability to predict surface charging behavior. Recent efforts have been employed to develop nonelectrostatic surface complexation constants for site-specific descriptions of subsurface contaminant transport (e.g., Kohler et al., 2004). This approach will most likely be successful for contaminants that predominantly form strong chemical bonds with available solid surfaces.

IIIB.3.5 Mineral Solubility

Characterization of the solid phase will, in most cases, be an integral component of monitored natural attenuation assessment and application. Some insight regarding the mineralogical composition of aquifer systems can be obtained by analyzing solution compositions. Investigations of mineral solubility in aquifer systems usually concentrate on the question: does a mineral control the concentration of a particular element, and, if so, what is the identity of the mineral? In order to answer these questions, geochemical models are frequently employed to calculate ion activities and mineral saturation indices. In aquifer systems, some chemical reactions are sufficiently fast that equilibrium relationships are immediately attained. For example, protonation/deprotonation reactions of acids and bases and ion pairing reactions are fast chemical reactions. Other reactions, in particular those reactions involving solids, can proceed so slowly that equilibrium is not attained even after decadal time periods. Yet, equilibrium is a practical reference point and equilibrium relationships are useful for predicting reactions that are likely or unlikely to occur.

Mineral solubility is influenced by the ionic strength of solution. Unless conditional equilibrium constants are employed, solution activity models are a necessary component of geochemical modeling efforts. Activity models account for the non-ideal behavior of solute ions in aqueous solutions. Non-ideal behavior is a consequence of electrostatic interactions between water molecules and charged solute ions. Methods for computing individual ion activity coefficients are presented in numerous textbooks (e.g., Stumm and Morgan, 1981; Nordstrom and Munoz, 1986). For most ground water studies of low ionic strength waters, the extended Debye-Hückel equation or the Davies equation will provide reasonable activity models. In these equations, activity coefficients are estimated based on input values for solution ionic strength and temperature. For concentrated waters that are high in total dissolved solids, virial methods such as the Pitzer model are available for estimating ion activity coefficients (Langmuir, 1997).

The unit of concentration for dissolved species most frequently used for aqueous solutions is molality, m_i (mol/kg). Analytical concentrations are often expressed in mass based units, e.g., ppm (parts per million). A useful conversion is:

$$\text{Conc. in ppm} = \text{Conc. in mol/kg} \times \text{formula weight in g/mol} \times 1000$$

The effective concentration or activity of a dissolved species, a_i, is given by:

$$a_i = (\gamma_i\, m_i)/(\gamma_i^0\, m_i^0)$$

Where γ_i is the ion-specific activity coefficient and $(\gamma_i^0\, m_i^0)$ refers to the standard state, which for aqueous solutions is typically chosen as an ideal, 1 molal solution, i.e., both γ_i^0 and m_i^0 are equal to 1.

In order to evaluate whether a ground water is oversaturated, undersaturated, or at equilibrium with a particular phase, geochemical speciation models are of practical use. As an example, consider the solubility expression for cadmium sulfide (greenockite):

$$CdS(s) + H^+ = Cd^{2+} + HS^-$$

The mass-action expression that applies to the equilibrium is:

$$K_r = \frac{a_{Cd^{2+}}\, a_{HS^-}}{a_{CdS}\, a_{H^+}} = 10^{-14.4}$$

Ground water may or may not be at saturation with respect to greenockite, depending on whether the phase is indeed present, available surface area, residence time of water, and kinetic factors that may impede dissolution and/or precipitation. If the water is at equilibrium, then the ion activity product, Q, should be the same as the equilibrium constant, i.e.,

$$Q = \frac{a_{Cd^{2+}}\, a_{HS^-}}{a_{H^+}} = K_r = 10^{-14.4}$$

where the activity of CdS is taken to be unity. Calculation of the saturation index (SI) for a water can then be used to determine if the solution is undersaturated, at equilibrium, or oversaturated with respect to precipitation (see Section IIB.2.1, Table 2.3).

It is important to point out that solubility products for precipitates, such as cadmium sulfide, depend on whether the solid is freshly precipitated (typically disordered) or crystalline (well ordered). At 25 °C, Daskalakis and Helz (1992) report a solubility product of $10^{-14.36}$ for crystalline cadmium sulfide (greenockite). Wang and Tessier (1999) give a value of a freshly prepared CdS precipitate of $10^{-14.15}$. Hence, freshly precipitated cadmium sulfide is metastable with respect to greenockite since:

$$\mathrm{CdS(disordered)} = \mathrm{CdS(greenockite)} \qquad K_r = 10^{0.21}$$

and

$$\Delta G_r^0 = -\alpha RT \log K = -1.20 \text{ kJ/mol}$$

If it is possible to calculate activities of free ions from a given water analysis, then it is a relatively simple matter to calculate the degree saturation of a large number of possible mineral phases, keeping in mind that temperature and ionic strength are needed to correct the ion activity product.

In the example above, pH and the molal concentrations and ion activity coefficients for Cd^{2+} and HS^- are needed in order to compute the ion activity product. If complexes of cadmium are present, then $m_{Cd}{}^{2+}$ is not the same as the total concentration of dissolved cadmium. If we consider only mononuclear bisulfide complexes,

$$m_{Cd,\,total} = m_{Cd^{2+}} + m_{CdHS^+} + m_{Cd(HS)_2^0} + m_{Cd(HS)_3^-}$$

Depending on the solution composition, cadmium complexes with chloride, bicarbonate, hydroxide, or sulfate may be important in addition to bisulfide complexes. Similarly, m_{HS^-} is not the same as the total concentration or analytical concentration of dissolved sulfide. Both protonated and deprotonated forms of sulfide and complexed forms of sulfide may be present. Speciation calculations, therefore, are critically dependent on the completeness and quality of thermodynamic constants in the thermodynamic database used for geochemical modeling (see Section ID).

In cases where mineral solubility is controlled in part by redox conditions, calculation of the saturation index is not straightforward. For example, when an aqueous solution has attained saturation with respect to a mineral such as the iron oxide magnetite (Fe_3O_4), then the reaction

$$Fe_3O_4 + 8H^+ = Fe^{2+} + 2Fe^{3+} + 4H_2O$$

is at reversible equilibrium when

$$\frac{a_{Fe^{2+}} a_{Fe^{3+}}^2 a_{H_2O}^4}{a_{H^+}^8} = 10^{4.2} = K_r$$

Magnetite solubility depends therefore on pH and redox. It follows that to calculate the saturation index for magnetite, activities of both the ferrous and ferric ions are needed input variables. Accurate measurement of ferric iron concentration at circumneutral pH is a notoriously difficult task. There are several ways to approach this problem:

- Measure separately both Fe(II) and Fe(III) in a water sample and estimate activity coefficients in order to calculate the activities of Fe^{2+} and Fe^{3+}
- Use Eh as a master redox variable to fix Fe(II):Fe(III) ratios
- Measure Fe(II), calculate Fe(III) by assuming control by the solubility of Fe_2O_3, FeOOH, or $Fe(OH)_3$
- Use some other measured redox pair to fix Fe(II)/Fe(III)

There are methods available to determine separately the concentration of ferrous iron and ferric iron (e.g., To et al., 1999); however, these methods are most effective for use in low pH waters, such as aquatic systems impacted by mine wastes. At near-neutral pH, the concentration of Fe(III) is typically very low so that analytical detection limits constrain the use of direct measurements.

The second method is to use the measured Eh of a water to estimate the Fe(II)/Fe(III) ratio in solution. Applying the Nernst equation to the iron(II/III) couple, we have

$$E = E^0 - \frac{RT}{nF} \ln \Pi a_i^{\nu_i} = 0.770 - 0.0592 \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

Using this approach, Fe(II)/Fe(III) can be calculated from a potential measurement using a platinum electrode. Nordstrom et al. (1979) conclude that this approach is most effective at pH <6 and at total iron concentrations exceeding 10^{-6} molal. A third method is to assume that the solubility of a ferric-bearing mineral controls the activity of Fe^{3+}. For example, consider the solubility expression of hydrous ferric oxide:

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O \qquad K_r = 10^{-36.6}$$

(Langmuir, 1996)

So that,

$$\log a_{Fe^{3+}} = \log K - 3 \log a_{H_2O} - 3pH \cong -36.6 - 3pH$$

In this example, the activity of Fe^{3+} can be estimated based on a measurement of pH. In the last example, a separate redox pair, e.g., As(III)/As(V), can be used to fix the Fe(II)/Fe(III) ratio in solution by applying the Nernst equation. The correctness of any one of these approaches relies on how closely the assumptions are obeyed for a given system.

IIIB.3.5.1 Coprecipitation Reactions

The concept of a solid solution implies an isomorphic substitution, for example, regular substitution of Mn for Ca in a carbonate mineral. Minerals formed in the environment often contain substitutional impurities and coprecipitation is likely to be a primary natural attenuation mechanism. Thermodynamic models of solid solutions indicate that the solubility of a component becomes greatly reduced as that component becomes a constituent in a solid phase. In other words, solid solutions in binary systems, for example, are less soluble (more stable) than pure end-member compositions. A considerable effort has gone into understanding the thermodynamic and kinetic factors that control the formation of solid solutions from aqueous solutions (e.g., Lippmann, 1977; Busenberg and Plummer, 1989; Glynn et al., 1990; Glynn and Reardon, 1990).

Laboratory and field studies indicate that cadmium is effectively removed by calcerous materials (e.g., Dudley et al., 1988; Davis et al., 1987). The solid solution $(Ca,Cd)CO_3$ is complete and the endmember solubility products differ by three orders of magnitude at room temperature:

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \qquad \log K_{CaCO_3} = -8.3$$

and

$$CdCO_3 = Cd^{2+} + CO_3^{2-} \qquad \log K_{CdCO_3} = -11.3$$

Combining these solubility expressions we obtain an exchange reaction:

$$CaCO_3 + Cd^{2+} = CdCO_3 + Ca^{2+}$$

The equilibrium constant for this type of reaction is often referred to as a distribution constant, *D*, and is given by the quotient of the solubility products of $CaCO_3$ and $CdCO_3$:

$$D = \frac{a_{CdCO_3}}{a_{CaCO_3}} \bullet \left(\frac{a_{Cd^{2+}}}{a_{Ca^{2+}}} \right)^{-1} = \frac{K_{CaCO_3}}{K_{CdCO_3}} = 10^3$$

The activity ratio of the solids by definition can be replaced by the ratio of the mole fractions multiplied by activity coefficients:

$$D = \left(\frac{X_{CdCO_3}}{X_{CaCO_3}} \right) \bullet \left(\frac{\gamma_{CdCO_3}}{\gamma_{CaCO_3}} \right) \bullet \left(\frac{a_{Ca^{2+}}}{a_{Cd^{2+}}} \right)$$

Therefore, the amount of substitution of Cd into calcium carbonate is a function of the solubility product ratio of $CaCO_3$ to $CdCO_3$, the solution activity ratio of Cd^{2+} to Ca^{2+}, and a term that represents activity coefficients of the solid solution components:

$$\left(\frac{X_{CdCO_3}}{X_{CaCO_3}} \right) = \frac{K_{CdCO_3}}{K_{CdCO_3}} \bullet \left(\frac{a_{Cd^{2+}}}{a_{Ca^{2+}}} \right) \bullet \left(\frac{\gamma_{CdCO_3}}{\gamma_{CdCO_3}} \right)$$

In general practice the first two terms, solubility product ratio and the solution activity ratio, are straightforward to obtain. Activity coefficients in the solid phase in most cases differ markedly from 1. In principle, the activity term can be determined experimentally by measuring the mole fraction ratio over a range of solution activity ratios at constant temperature.

An analysis of solution concentration data alone will generally not be adequate to confirm any precipitation or coprecipitation mechanism of attenuation. Multiple lines of evidence, including solution and solid-phase data, which supports a specific natural attenuation mechanism will in most cases be necessary to pursue monitored natural attenuation as a partial or sole cleanup remedy.

IIIB.3.5.2 Thermodynamic Data

Site characterization and remedial investigations that involve contaminant transport in the environment are usually accomplished, in part, with geochemical modeling. Consequently, thermodynamic properties are essential components to geochemical modeling efforts. Normally, the thermodynamic constants used in modeling exercises are taken from published compilations of such properties (e.g., Wagman et al., 1982). In some cases these compilations contain minimal documentation as to the source or quality of compiled data. In other cases, compilations contain outdated information. Users of thermodynamic databases can easily be misled into believing that modern databases are up to date in terms of data quality and completeness.

As an example to illustrate problems noted above, a specific example of orpiment (As_2S_3(s)) is discussed. Eary (1992) listed a number of values of the Gibbs free energy of formation, ΔG_f^0, of orpiment, each from a separate literature source. The values tabulated by Eary (1992) range from –168.8 kJ/mol to –90.7 kJ/mol. This wide range in Gibbs free energy values equates to equilibrium constants describing orpiment dissolution and precipitation that can span almost 7 orders of magnitude. For example, consider the solubility expression for orpiment to form arsenite in solution:

$$0.5As_2S_3 + 3H_2O = As(OH)_3^0 + 1.5HS^- + H^+$$

An equilibrium constant for this reaction can be computed from the ΔG_f^0 values for orpiment given above and fixed values of ΔG_f^0 for H_2O(l), $As(OH)_3^0$, and HS^- of –639.8 kJ/mol, -237.18 kJ/mol, and 12.05 kJ/mol, respectively. The more negative ΔG_f^0 value for orpiment gives a log *K* value for the above reaction of –30.5, while the greater value gives a log *K* value of –23.7. The pH dependent trend of orpiment solubility resulting from these differing log *K* values is shown in Figure 3.5. The solubility diagram is constructed at ΣH_2S concentration of $10^{-5.5}$ *m*, so that thioarsenite species have a negligible contribution to orpiment solubility (Wilkin et al., 2003). It is clear that depending on the log *K* value employed in reaction modeling, solutions will have vastly different saturation indices and one would reach different conclusions about possible attenuation mechanisms for arsenic.

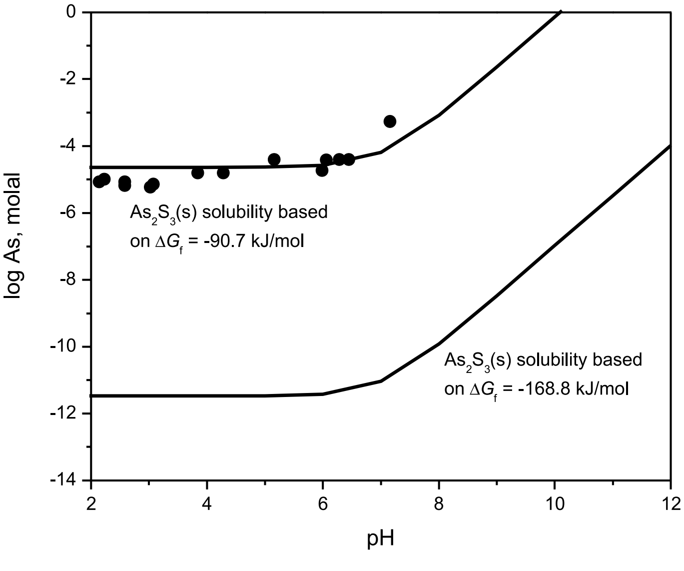


Figure 3.5 *pH-dependent solubility trend of orpiment predicted using two different Gibbs free energy of formation values (see text). The model curves correspond to a constant ΣH_2S concentration of $10^{-5.5}$ m. The data points are measured solubility data taken from Webster (1990). The experimental data are consistent with a ΔG_f^0 for orpiment of approximately –90 kJ/mol, yet most thermodynamic compilations adopt a value of –168.8 kJ/mol. Application of the lower value will vastly over predict the stability of orpiment.*

Which value of ΔG_f^0 for orpiment is more appropriate? The most recent solubility and calorimetric studies seem to support a ΔG_f^0 formation value close to –90 kJ/mol for crystalline orpiment (Webster, 1990; Eary, 1992; Johnson et al., 1980). The key point is that users of geochemical models should be familiar with the sources of thermodynamic data used and attempt to evaluate whether constants in thermodynamic compilations are in reasonable agreement with recent experimental evidence or whether there may be discrepancies that could impact how model results are interpreted.

IIIC. Characterization of System Redox and Underlying Microbial Processes

Oxidation-reduction processes affect the chemical composition of ground water and impact the aqueous and solid phase chemical speciation of inorganic contaminants. Thus, characterizing the redox status of ground water systems will likely play an important role in understanding controls on contaminant attenuation. As stated previously in Section IIC, the subsurface microbiology within a plume will, in part, influence the predominant redox characteristics of the system. Microbial processes may influence the redox chemistry of important components within the aquifer, such as iron and sulfur, participating as reactants within attenuation reactions that result in contaminant immobilization or degradation. Thus, it is recommended that site characterization include both assessment of the prevailing subsurface redox chemistry impacting contaminant transport, as well as more explicit analysis of specific microbial processes for sites at which the plume conditions support microbial activity that differs from ambient conditions. For example, a more detailed microbial community analysis may be warranted in order to improve the reliability of assessing attenuation capacity for sites where contaminant source characteristics govern aquifer geochemistry within the down gradient plume. The following discussion provides approaches and tools available to characterize the overall redox status of site ground water, as well as the specific microbial communities that support the observed redox chemistry within the plume.

IIIC.1 Process Identification

Identification of a redox-mediated attenuation process starts with knowledge of the aqueous and solid-phase species present. Although analysis of the contaminant concentration in ground water at various distances from the source can indicate attenuation, inclusion of data for pH, E_H, major solutes, and redox-sensitive species such as Fe^{2+}, O_2, and H_2S is needed to demonstrate that redox processes may be involved.

Further evidence for redox-mediated processes may be derived from determination of the mineral species present. The absence of Fe and Mn oxides and the presence of Fe sulfides, for example, suggest that the aquifer is predominantly reducing, whereas the inverse of this situation suggests an oxidizing aquifer. A variety of techniques can be used for mineral identification and is detailed elsewhere in this document (Section IIIB.2). A major consideration related to mineralogical characterization relates to the preservation of original mineralogy in aquifer materials by preventing contact with oxygen during sample collection and removal of pore water. For example, iron-bearing minerals may exist in a reduced state within the saturated zone. Yet such minerals that are stable in reducing environments are subject to significant alteration upon exposure to oxygen. Solid phase structural and chemical transformations are commonly mediated or facilitated by the pore water. Thus, removal of pore water may act to retard or impede transformation. In order to preserve redox characteristics of samples collected in the field, cores materials should be immediately capped and frozen. Sample freezing can be accomplished either by submersing in liquid nitrogen or placement in a portable freezer located in the field. Following transport to a laboratory setting, frozen materials should be thawed under an oxygen-free or inert atmosphere, e.g., within an anaerobic glove box. Extended periods of storage should be avoided, since sample mineralogy will alter with time during approach to a new equilibrium state. Procedures for the collection and processing of aquifer solids to minimize alterations to mineralogy are outlined in several EPA documents (USEPA, 2002; USEPA, 2005b; USEPA, 2006).

In some situations, intense local microbial activity may be entirely responsible for the redox status of the aquifer. The nature of the active microbial population (e.g., iron-reducing, sulfate-reducing, or sulfur-oxidizing bacteria) can often be inferred from geochemical data. Thus, trends in the concentration of organic substrates (soluble organic C) and their metabolites (e.g., H_2, H_2S, CH_4, CO_2, NO_2^-, HS^-, Fe^{2+}) can indicate whether and which microorganisms are active in a particular subsurface region. In some instances, direct and specific determination of microbial population by culturing or genetic analysis (e.g., messenger ribonucleic acid profiles) of aquifer solids extracts may be warranted.

Although the best support for a particular redox process comes from direct examination of reactants and products at the site, a strong case for the process can be made with laboratory tests using core materials taken from the site. These tests involve batch or column studies in which the geochemical inputs and conditions are comparable to those at the actual site, and evidence for the process is obtained from analysis of the solution phase (supernate or effluent) during the test and of the solid phases at its conclusion. Attenuation obviously must be demonstrated through the solution-phase data, and direct identification of the attenuated form of the contaminant provided from the solid-phase data. As described below, this same general approach with suitable modifications can be used to determine capacity, kinetics, and stability.

IIIC.1.1 Redox Measurements

Measurement of redox parameters in ground water is inherently challenging due to the fact that a steep redox gradient is often present between the sampling location (subsurface) and the location where the particular measurement is made (surface). Consequently, special care must be taken to preserve the redox integrity of ground-water samples. In some cases water samples can be preserved by using inert gases or by acidification because oxidation rates generally decrease substantially with decreasing pH. In other cases where sample preservation is not possible or practical, it is recommended that analyses be carried out in the field at the time of sample collection (e.g., for dissolved oxygen and Eh). Summaries of methods used to determine redox status can be found in, for example, USEPA (2002), Baedecker and Cozzarelli (1992), and Walton-Day et al. (1990). Table 3.5 provides a list of parameters that can be used to assess the redox status of ground water systems.

Other laboratory approaches include selective dissolution of reactive fractions (see Section IIIB.2.4.1). For example, reactive Fe^{2+} (i.e., that which is sorbed as well as that present in sulfides carbonates, hydroxides, and green rusts) can be estimated by extraction with 0.5 M HCl followed by complexation with ferrozine (Roden and Zachara, 1996; Amonette et al., 2000). From the oxidizing side, Mn(III,IV) oxides and poorly ordered Fe(III) (hydr)oxides can be determined by extraction with hydroxylamine solutions (Chao, 1972; Chao and Zhou, 1983; Ross, 1985).

The direct reactions and laboratory tests, however, measure only the redox-buffering capacity at a single point in time. Microbial activity, through conversion of organic C, can create and replenish the reductive capacity of a site. Thus, more accurate measurements of reductive capacity may necessitate consideration of inputs of dissolved constituents from source areas or up gradient portions of the aquifer such as dissolved organic C, as well as terminal electron acceptors such as oxygen, nitrate, and sulfate, in order to assess ability of the microbial community to maintain or degrade the redox capacity of a site.

IIIC.2 Capacity

Once the operative redox-mediated attenuation process has been identified, an assessment of its capacity to attenuate the contaminant is needed. The primary soluble electron donor in most ground waters is dissolved organic carbon, although, under some circumstances, sulfide (H_2S, and HS^-)

Table 3.5 Ground-water redox parameters and measurement approaches.

Parameter	Measurement Approach
Oxidation-reduction potential (ORP)	Combination platinum electrode with Ag/AgCl reference electrode; KCl filling solution. Electrode performance is determined using reference solutions (e.g., Zobell's solution, hydroquinone).
Dissolved oxygen	Membrane-covered electrodes; colorimetric tests, modified Winkler titration. Electrode performance is determined using air-saturated water and sodium sulfite solutions.
Dissolved hydrogen	Sample collection in glass vessel and analysis by gas chromatography/reduced gas analyzer.
Iron speciation	Ferrous iron determined by colorimetric analysis (e.g., ferrozine, 1,10-phenanthroline). Ferric iron determined by adding reducing agent and measuring ferrous iron, and/or by determination of total iron and subtracting Fe(II). Measurement made in the field or preservation required.
Sulfur speciation	Sulfate and other sulfoxyanions (sulfite, thiosulfate) are typically determined by ion chromatography or capillary electrophoresis. Sulfide can be determined by colorimetric, gravimetric, coulometric, or voltametric methods. Measurement made in the field or preservation required.
Nitrogen speciation	Colorimetric, chromatographic, and potentiometric methods available for nitrate, nitrite, and ammonium. Preservation of sample is recommended.
Arsenic speciation	Anion exchange, chromatographic, and hydride generation methods are available for arsenite, arsenate, and several organic forms of arsenic. Preservation is recommended.
Chromium speciation	Colorimetric, exchange, and voltametric methods are available for determination of Cr(VI) and Cr(III).
Selenium speciation	Selenium oxyanions can be determined by ion chromatography or capillary electrophoresis. Preservation of sample is recommended.

and Fe^{2+} species can dominate. Important electron acceptors include oxygen, nitrate, nitrite, and sulfate. Thus, in addition to the contaminant, ground-water analyses should include measurements of these constituents. Equally important is a hydrological assessment of ground water flow rates, which, when combined with the concentration data, allows an estimate of the average influx of oxidants or reductants to the site. In addition, quantification of the accessible redox-buffering capacity of the aquifer solids may be important, since these solids may represent a significant fraction of the capacity of the aquifer. Methods for characterizing the oxidation capacity and reducing capacity of aquifer solids are listed in Table 3.6. These methods represent examples of approaches that have been tested and documented in the literature. For site-specific applications of these methods, some method development or modification may be required to obtain optimal results (USEPA, 2002).

Laboratory tests can be performed in which a known oxidant [e.g., $O_{2(aq)}$ or Cr(VI)] or reductant [e.g., $H_2S_{(aq)}$] is reacted with the aquifer solids under controlled environmentally relevant conditions (Fruchter et al., 1996; Istok et al., 1999). The quantity of this reagent consumed by reaction is then expressed in terms of the mass or volume of the aquifer solids. Rough estimates of maximum reductive capacity present in a soil can also be obtained from digestions using acidic Cr(VI) solutions. Thus, adaptations of Cr(VI) titration methods for organic C in soils (e.g., Nelson and Sommers, 1996) are suitable as they include the contributions of Fe(II) and sulfides to overall reductive capacity. Other laboratory approaches include selective dissolution of reactive fractions (see Section IIIB.2.4.1) with the assignment of a specific mass-based oxidation/reduction capacity to the phase quantified by extraction. For example, reactive Fe^{2+} (i.e., that which is sorbed as well as that present in sulfides carbonates, hydroxides, and green rusts) can be estimated by extraction with 0.5 M HCl followed by complexation with ferrozine (Roden and Zachara, 1996; Amonette et al., 2000). From the oxidizing side, Mn(III,IV) oxides and poorly ordered Fe(III) (hydr)oxides can be determined by extraction with hydroxylamine solutions (Chao, 1972; Chao and Zhou, 1983; Ross, 1985).

The direct reactions and laboratory tests, however, measure only the redox-buffering capacity at a single point in time. Microbial activity, through conversion of organic C, can create and replenish the reductive capacity of a site. Thus, more accurate measurements of reductive capacity

Table 3.6 Methods that may be employed for estimating the oxidation and reduction capacity for solid materials (from USEPA, 2002).

Method	Source	Comments
Cr(II) (oxidation capacity)	(Barcelona and Holm, 1991a) (Barcelona and Holm, 1991b) (Barcelona and Holm, 1992)	Most aggressive but oxygen-free atmosphere recommended; high estimate
Digestion with Ti(III)-EDTA (oxidation capacity)	(Ryan and Gschwend, 1991)	Developed for extraction of Fe oxides; applicability limited to iron oxide dominated sediments
Titration/digestion with dithionite solution (oxidation capacity)	(Loeppert and Inskeep, 1996) (Williams et al., 2000)	Valid for only specific remedial technology; targets Fe oxides
Chemical Oxygen Demand by digestion with acid dichromate (reduction capacity)	(USEPA, 1979) (Barcelona and Holm, 1991a) (Barcelona and Holm, 1991b) (Barcelona and Holm, 1992)	Precipitate coatings if pH not buffered; high estimate
Digestion in hydrogen peroxide solution (reduction capacity)	(Nelson and Sommers, 1996)	Developed for quantifying organic matter content
Dissolved oxygen consumption in air-saturated water (reduction capacity)	(Williams et al., 2000)	Dynamic column test with mathematical simulation; test design must minimize gas diffusion from external sources; time-consuming, but realistic

may necessitate consideration of inputs such as dissolved organic C, as well as terminal electron acceptors such as oxygen, nitrate, and sulfate, in order to assess ability of the microbial community to maintain or degrade the redox capacity of a site. For this analysis, it may be necessary to evaluate microbial response to dissolved constituent inputs through sampling of aquifer solids for the purpose of conducting microcosm studies to examine microbial activity and/or contaminant attenuation. Recommendations for the design and implementation of microcosm studies are provided in USEPA (1998). Evaluation of microcosm response to variations in electron donor/acceptor concentrations in solution, relative to contaminant attenuation, provides means for directly assessing the limits in these reactant concentrations under which attenuation remains viable. For situations in which contaminant degradation is the primary attenuation process, microcosm measurements will likely include determination of trends in contaminant loss as well as the increase of degradation products. For situations in which contaminant immobilization dominates, it is recommended that microcosm characterization include determination of the quantity and solid phase speciation of contaminant sorption. The degree to which microcosm studies replicate subsurface conditions within the plume may be assessed through comparison of similarities (or lack thereof) between measured aqueous and solid phase chemical parameters based on measurement of aquifer microcosm properties (e.g., water chemistry, mineralogy).

An additional line of evidence to support capacity assessments includes development of a reaction or reactive transport model that incorporates quantitative description of the processes that control contaminant attenuation. Requirements for model construction and parameter inputs have previously been specified in Section ID. The utility of this type of analysis is the ability to quickly assess a range of ground-water conditions that may influence the efficiency of modeled attenuation reactions. However, as previously noted, the degree of uncertainty in model predictions will be constrained by the accuracy of parameter inputs to represent aquifer conditions within the plume. Thus, verification of model performance is warranted to demonstrate the ability of the model to reproduce measured ground-water conditions prior conducted model tests of aquifer capacity to support attenuation.

IIIC.3 Stability

If a redox-mediated attenuation mechanism has been identified and a reasonable estimate of the capacity of the aquifer to attenuate the contaminant has been made, evaluation of the stability of immobilized contaminants is needed to assess the potential for contaminant remobilization due to anticipated changes in ground-water chemistry. This component of the site characterization effort may include direct measurements of contaminant stability via laboratory- or field-based evaluations, which could be supplemented with implementation of reaction or reactive-transport models that explicitly consider the solid-phase speciation of the contaminant. The ultimate goal of this effort is to gauge the response of the aquifer, from the perspective of contaminant remobilization, to changes in aquifer redox status that may be driven by future increases in the influx of dissolved components such as oxygen or the cessation of microbial processes that accompany decreased influx of degradable organic contaminants.

Contaminant stability may be estimated through laboratory tests constructed using aquifer solids collected from within the zone of contaminant attenuation. Controlled tests could be then be devised that evaluate contaminant response to changes in specific ground-water parameters that may result in release of the contaminant from aquifer solids. For sites in which the ground-water chemistry differs significantly within the plume compared to up gradient or ambient conditions, this may entail exposure of the aquifer solids to ambient ground-water samples. Alternative approaches may include systematic variation of one or more parameters identified as being critical to the stability of the form in which the contaminant is immobilized. For example, this may involve systematic variation in ground-water sample pH over a range that captures current conditions as well as anticipated conditions that may be reflected by the pH measured in background wells installed within the aquifer. Other parameters that might be assessed include those that reflect conditions that might develop as a result of potential land-use changes, including influxes of dissolved constituents that might compete for adsorption sites and/or may form soluble complexes with the contaminant. An alternative approach to assessing the stability of an immobilized contaminant may include the implementation of in-situ studies using single-well push-pull tests (Istok et al.,1997; Haggerty et al., 1998; Senko et al., 2002). These tests can similarly be devised to evaluate contaminant response to changes in ground-water chemistry through manipulation of specific parameters via mixing of synthetic solutions with ground water retrieved from the well and subsequently re-injected into the aquifer. The re-injected water is then allowed to react with the aquifer solids for short periods of time (days to weeks), and then several pore volumes are withdrawn and analyzed to assess the fate of the contaminant and/or analyze potential by-products that result during a re-mobilization reaction. Comparison of reagent concentrations with those of a non-reactive tracer injected with the reagent can be use to evaluate the degree of mixing between water sources with the reaction zone and to assess the overall rate of reaction.

As noted previously, modeling studies may provide a supplementary line of evidence to assess the sensitivity of the immobilized contaminant to changes in ground-water chemistry. This type of analysis provides an indirect means to gauge contaminant response, as well as a means to assess the impact of other ground-water characteristics that may not be practically assessed via direct measurements. However, as previously noted, the degree of uncertainty in model predictions will be constrained by the accuracy of reaction expressions and parameter inputs to represent aquifer conditions within the plume. Ultimately, these tests may require more explicit analysis of the microbial community that supports existing conditions or mediates future changes to redox conditions within the boundary of the plume. Approaches to identify and quantify active microbial communities within the subsurface are discussed below.

IIIC.4 Microbial Community Characterization

Microbiological evidence to support the natural attenuation of inorganic contaminants as a remedial alternative in ground water involves the characterization of microbial population size, diversity, composition, physiological and genetic/phylogenic traits. This section addresses techniques used for the characterization of subsurface microbial communities. In addition, some microbiological sampling practices for the assessment of ground water are discussed and emerging methodologies are identified.

IIIC.4.1 Standard and Emerging Techniques

Analyses focused on the composition and diversity of bacterial community structures cannot rely on traditional microbiological procedures alone. This is especially critical in subsurface ecological systems because the vast majority of the microbial communities that reside in that environment have not been cultivated using culture-dependent methods (Amann et al., 1995). Although the importance of emerging molecular approaches in subsurface microbiology will be stressed later in this section, a successful program will likely include a combination of culture-independent methods as well as traditional cultivation strategies. Often, molecular tools are applied to pure culture isolates harvested from defined media. In other words, traditional selective and enrichment techniques are used to develop specific microbial communities to be further characterized with molecular monitoring (i.e., genes coding for 16S rRNAs [16S rDNA] to identify potential gene expressions). Since standard microbiological techniques are readily available in most environmental laboratories, only a brief discussion of them is provided here (see also Table 3.7).

- Most probable-number (MPN) technique is a standard methodology used to estimate the number of specific physiological types of bacteria. Usually, a modified basal medium is amended with a carbon substrate and electron acceptors for total heterotrophic aerobes or anaerobes, denitrifying, iron-reducing, sulfate-reducing, and methanogenic bacteria (Fedorak et al., 1987; Lovley, 1991; Mahne and Tiedje, 1995; Chapelle et al., 2002; Tanner, 1989). A three-tube dilution series is often used to provide a 10-fold dilution. The same regiment is applied to semi-solid media to provide plate counts.
- Acridine orange direct count (AODC) is the most versatile technique for yielding a count of the total intact cells without differentiation for viability (Ghiorse and Balkwill, 1983). Differential staining for live vs. dead can be used via the Bac-light™ method (Loyd and Anthony, 1995).
- Phospholipid ester-linked fatty acids (PLFA) is a popular assay used to identifty "biomarkers" to provide a quantitative insight into three important attributes of microbial communities including viable biomass, community structure, and metabolic activity (Lehman et al., 1995). An estimation of non-viable populations can be accompanied through the measurement of diglyceride fatty acids (DGFA). Both assays are independent of the bias inherent in classical culturing techniques providing a more accurate estimation of in-situ microbial populations. The lipid biomarker analysis is, however, incapable of identifying every microbial species in an environmental sample because many species contain over-lapping PFLA.
- Community-level physiological profile (CLPP) can be carried out using Biolog-GN plates (Biolog, Inc., Hayward, CA). This "phenotypic fingerprinting" assay is useful for screening bacterial isolates and consortia to establish correlation between their activity and composition.
- rRNAa can be used for the determination of microbial biomass (Loyd and Anthony, 1995).

Table 3.7 Standard and emerging techniques for microbial community characterization.

Method	Type of Information
Most probable-number (MPN)	Enumeration, Cultural
Acridine orange direct counts (AODC)	Enumeration, Morphological Cultural
Phospholipid ester-linked fatty acids (PLFA)	Enumeration, Biochemical
Community-level physiological profile (CLPP)	Physiological

Microcosms are routinely prepared using subsurface cores and ground-water samples for the characterization of microbial communities. Recently, there has been an increased interest in the use microcosms to perform molecular community fingerprinting such as denaturing gradient gel electrophoresis due to the generation of a sufficient cell mass.

IIIC.4.2 Molecular Characterization

Within the last decade, a variety of culture-independent genetic analyses have been used to complement traditional culture-dependent methods (enrichment and isolation). Many of these molecular biological methods rely on 16S rDNA sequences, including in-situ hybridization (Amann et al., 1990; Amann et al., 1995), direct amplification of 16S rDNA, and additional analysis using community "DNA fingerprinting" such as temperature gradient gel electrophoresis (TGGE) (Felske et al., 1998), denaturing gradient gel electrophoresis (DGGE) (Muyzer et al. 1993), restriction fragment length polymorphism (RFLP) (Martinez-Murcis et al., 1995), single-strand conformation polymorphism (SSCP) (Lee et al., 1996), terminal RFLP (Clement et al., 1998), or 16S rDNA cloning-sequencing (Wise et al., 1997). To date, most of the results obtained by using molecular techniques have been provided by cloning-sequencing of 16S rDNA fragments. Although 16S rDNA cloning-sequencing is successful on the reconnaissance of microbial diversity by detecting infrequent sequences from various habitats, thereby avoiding limitations of traditional cultivation techniques, it is time-consuming and problematic for multiple sample analysis. Since the cloning approach cannot provide an immediate overview of the community structure, many environmental laboratories apply DGGE to detect population shifts. DGGE can be used for simultaneous analysis of multiple samples obtained at various time intervals to detect microbial community changes; an advantageous feature in studying microbial ecology and MNA.

These methods characterize differing aspects of the subsurface microbial community, which may be used alone or in combination to further delineate the impact of microbial processes on ground-water chemistry. DGGE provides a simple approach to obtaining profiles of microbial communities and identifying temporal and spatial variations which occur in response to various environmental conditions (Muyzer et al., 1993). It is also possible to infer the phylogeny of community members by DNA sequence analysis of re-amplified fragments, after they are excised from the gel, where bands corresponding to each microorganism can be separated through DGGE. Fluorescent in-situ hybridization (FISH) provides a powerful tool for directly studying organisms within the environment by providing information on cell morphology, phylogenic affiliation and the ability to quantify organisms (Amann et al.,1990; Amann et al., 1995). During the last few years numerous efforts have been made to increase the sensitivity of FISH, including multi-labeled polynucleotide probes (Pernthaler et al., 2002). The RFLP approach involves electrophoretic analysis where DNA is detected with probes after Southern blotting. RFLP is applied broadly since it has a good predictive power and can rapidly identify phylogenic relatedness of clusters of very closely related or even identical strains. It can screen large numbers of isolates to identify a much smaller subset of representative types to be resolved by 16S rRNA sequencing. Although RFLP generates a complex set of rDNA bands that can be used to group closely related strains, it does not provide the distance between strains that are not closely related, as does rRNA sequencing. In contrast, the T-RFLP approach uses restriction enzymes, coupled with PCR, in which only fragments containing a fluorescent tag are detected. The use of T-RFLP is advantageous as a rapid screening tool and does not require culturing or a genetic database.

IIIC.4.3 Sampling Considerations

Hydrogeologic conditions are of overriding significance in designing and conducting subsurface microbiological sampling programs because the selection of equipment and the location of sampling points are necessarily subject to site-specific conditions. With regard to the type of sample (core or water), core samples provide more information in defining the horizontal and vertical distribution of microbes even though they are intrinsically disruptive and prohibit repeated sampling at the same location. Ground-water samples, on the other hand, can be obtained from the same well repeatedly but may not quantitatively or qualitatively reflect conditions in the aquifer. Since there are uncertainties that mandate caution in the extrapolation of information obtained from either type of sample, a thorough characterization may require both water and core samples.

In studies addressing the origin and nature of subsurface microbes, an important consideration is the extent organisms cultured or manipulated in the laboratory represent the intrinsic microbial community. Therefore, microbiologists are challenged when collecting not only representative but also microbially uncontaminated samples. To minimize contamination, after a core is obtained using strict aseptic methods, care should be taken not to disturb or contaminate the sample. Processing should be performed as quickly as possible under anaerobic and aseptic conditions while in the field. Surface layers of the core should be scraped away using a sterile sampling devise and discarded so that only the center of the core is packaged in doubled sterile sample bags. The portion used for DNA/PLFA analyses must be rapidly frozen with liquid nitrogen and stored at –70 L°C. Another portion should be flushed with inert gases (N_2 or Ar), sealed in canning jars and placed inside cans containing oxygen-scavenging catalyst packets (Gas Pak; BBL Inc., Franklin Lakes, N.J.), and stored at 4 °C for microbial counts and cultural techniques for analysis within 24 hours. Frozen (-70 °C) genomic DNA can be extracted from core sample using an UltraClean soil DNA kit (MoBio. Solana, CA).

Ground-water samples will be unfiltered for microbial counts and cultural techniques and filtered for DNA/PLFA analysis. Community analysis involving “DNA fingerprinting” requires ultrafiltration of ground water (50 to 100 L) using inorganic (Anodisc™, Whatman) filters (0.2 µm pore size). The filter is placed in sterile bag and rapidly freeze dried with liquid nitrogen. Since PCR bias can be introduced, particularly during cell lysis and PCR amplification, a physical method such as bead mill homogenization should be used to effectively lyse all cell types, including those that are most recalcitrant to physical and enzymatic treatments (More et al., 1994).

IIIC.5 Implications for Natural Attenuation Assessment

Ultimately, the extent and degree of site characterization to define the redox status of the aquifer will represent a balance between technical information needs and the cost associated with the different proposed data collection or evaluation schemes. The primary objective of site characterization is to identify the mechanism leading to contaminant attenuation at a given site. Emphasis of this characterization effort should be given to direct measurements of ground water conditions and solid phase characteristics of the aquifer that result from these conditions. Measurements and/or tests conducted with subsurface samples retrieved within the zones where attenuation occurs will provide the most direct means to evaluate on-going reaction processes. This knowledge will guide approaches to assess the capacity of the aquifer to sustain contaminant attenuation within the plume and to evaluate the long-term stability of immobilized contaminants. Evaluations conducted on subsurface samples also have the benefit of implicitly incorporating characteristics/factors of ground water and aquifer solids that may be difficult to adequately parameterize within analytical models.

IIID. References

Allen, H.E., G. Fu, and B. Deng. Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environmental Toxicology and Chemistry* 12: 1441-1453 (1993).

Amann, R.I., L. Krumholz, and D.A. Stahl. Fluorescent-oligonucleotide probing of whole cells for determinative, phylogenetic, and environmental studies in microbiology. *Journal of Bacteriology* 172: 762-770 (1990).

Amann, R.I., W. Ludwig, and K.H. Schleifer. Phylogenic identification and in situ detection of individual microbial cells without cultivation. *Microbiology Review* 59: 143-169 (1995).

Amonette, J.A. and R.W. Sanders. Nondestructive techniques for bulk elemental analysis. In *Quantitative Methods in Soil Mineralogy.* J.E. Amonette and L.W. Zelazy (Eds.), Soil Science Society of America, Madison, WI (1994).

Amonette, J.A. Methods for determination of mineralogy and environmental availability. In *Soil Mineralogy with Environmental Applications.* J.B. Dixon and D.G. Schulze (Eds.), Soil Science Society of America, Madison, WI (2002).

Amonette, J.E. and D. Rai. Identification of noncrystalline $(Fe,Cr)(OH)_3$ by infrared spectroscopy. *Clays and Clay Minerals* 38: 129-136 (1990).

Amonette, J.E. Iron redox chemistry of clays and oxides: environmental applications. In *Electrochemical Properties of Clays,* CMS Workshop Lectures Volume 10 A. Fitch (Ed.), The Clay Minerals Society, Aurora, CO, pp. 89-146 (2004).

Amonette, J.E., G.R. Holdren, K.M. Krupka, and C.W. Lindenmeier. Assessing the environmental availability of uranium in soils and sediments. NUREG/CR-6232, PNL-9750. U.S. Nuclear Regulatory Commission, Washington DC (1994).

Amonette, J.E., D.J. Workman, D.W. Kennedy, J.S. Fruchter, and Y.A. Gorby. Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environmental Science and Technology* 34: 4606-4613 (2000).

Barcelona, M.J. and T.R. Holm. Oxidation-reduction capacities of aquifer solids. *Environmental Scientific Technology* 25: 1565-1572 (1991a).

Barcelona, M.J. and T.R. Holm. Oxidation-reduction capacities of aquifer solids. *Environmental Science and Technology* 25: 2540 (1991b).

Barcelona, M.J. and T.R. Holm. Oxidation-reduction capacities of aquifer solids. *Environmental Science and Technology* 26: 2538-2539 (1992).

Barrow, N.J. and T.C. Shaw. Effects of soil:solution ratio and vigour of shaking on the rate of phosphate adsorption by soil. *Journal of Soil Science* 30: 67-76 (1979).

Belzile, N., P. Lecomte, and A. Tessier. Testing readsorption of trace elements during partial chemical extractions of bottom sediments. *Environmental Science and Technology* 23: 1015-1020 (1989).

Bethke, C.M. and P.V. Brady. How the Kd approach undermines ground water cleanup. *Ground Water* 38: 435-443 (2000).

Bish, D.L. Quantitative X-ray diffraction analysis of soils. In *Quantitative Methods in Soil Mineralogy.* J.E. Amonette and L.W. Zelazy (Eds.), Soil Science Society of America, Madison, WI (1994).

Brady, P.V., M.V. Brady, and D.J. Borns. *Natural Attenuation: CERCLA, RBCA's, and the Future of Environmental Remediation*. Lewis Publishers, Boca Raton, FL (1997).

Buscheck, T.E., N. Nijhawan, and K. O'Reilly. Mass flux estimates to assist remediation decision-making. In *2003 Proceedings of the Seventh International In Situ and On-Site Bioremediation Symposium (Orlando, FL; June 2003).* V.S Magar, and M.E. Kelley (Eds.), Batelle Press, Columbus, OH (2004).

Busenberg, E. and L.N. Plummer. Thermodynamics of magnesian calcite solid-solutions at 25°C and 1 atm total pressure. *Geochimica et Cosmochimica Acta* 53: 1189-1208 (1989).

Butler, J.J. *Design, Performance, and Analysis of Slug Tests.* Lewis Publishers, Boca Raton, FL (1998).

Canfield, D.E. Reactive iron in marine sediments. *Geochimica et Cosmochimica Acta* 53: 619-632 (1989).

Chao, T.T. and L. Zhou. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. *Soil Science Society of America Journal* 47: 225-232 (1983).

Chao, T.T. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Science Society of America Proceedings* 36: 764-768 (1972).

Chapelle, F.H., K. O'Neill, P.M. Bradley, B.A. Methe, S.A. Ciufo, L.L. Knobel, and D.R. Lovley. A hydrogen-based subsurface microbial community dominated by methanogens. *Nature* 415: 312-314 (2002).

Clement, B.G., L.E. Kehl, K.L. DeBord, and C.L. Kitts. Terminal restriction fragment patterns (TRFPs), a rapid, PCR-based method for the comparison of complex bacterial communities. *Journal of Microbiological Methods* 31: 135-142 (1998).

Conant Jr., B. Delineating and quantifying ground water discharge zones using streambed temperatures. *Ground Water* 42: 243-257 (2004).

Danielsson, L.G. On the use of filters for distinguishing between dissolved and particulate fractions in natural waters. *Water Research* 16: 179-182 (1982).

Daskalakis, K.D. and G.R. Helz. Solubility of CdS(greenockite) in sulfidic waters at 25°C. *Environmental Science and Technology* 26: 2642-2648 (1992).

Davis, J.A. and D.B. Kent. Surface complexation modeling in aqueous geochemistry. In *Mineral-Water Interface Geochemistry.* M.F. Hochella Jr. and A.F. White (Eds.), Mineralogical Society of America, Washington DC (1990).

Davis, J.A., C.C. Fuller, and A.D. Cook. A model for trace metal sorption processes at the calcite surface: Adsorption of Cd^{2+} and subsequent solid-solution formation. *Geochimica et Cosmochimica Acta* 51: 1477-1490 (1987).

DeMora, S.J. and R.M. Harrison. The use of physical separation techniques in trace metal speciation studies. *Water Research* 7: 723-733 (1983).

DeVitre, R.R., F. Bujard, C. Bernard, and J. Buffle. A novel in situ cascade ultrafiltration unit specifically designed for field studies of anoxic waters. *International Journal of Environmental Analytical Chemistry* 31: 145-163 (1987).

Dragun, J. *The Soil Chemistry of Hazardous Materials.* Hazardous Materials Control Research Institute, Silver Spring, MD (1988).

Dudley, L.M., J.E. McLean, R.C. Sims, and J.J. Jurniak. Sorption of cadmium and copper from the water soluble fraction of an acid mine waste by two calcerous soils. *Soil Science* 145: 207-214 (1988).

Dunnivant, F.M., P.M. Jardine, D.L. Taylor, and J.F. McCarthy. Cotransport of cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer materials. *Environmental Science and Technology* 26: 360-368 (1992).

Eary, L.E. The solubility of amorphous As_2S_3 from 25 to 90°C. *Geochimica et Cosmochimica Acta* 56: 2267-2280 (1992).

Eggleston, C.M., S. Hug, W. Stumm, B. Sulzberger, and M. Afonso. Surface complexation of sulfate by hematite surfaces; FTIR and STM observations. *Geochimica et Cosmochimica Acta* 62: 585-593 (1997).

Einarson, M.D. and D.M. Mackay. Predicting impacts of groundwater contamination. *Environmental Science and Technology* 35: 66A-73A (2001). (Supporting Information available at http://pubs.acs.org/subscribe/journals/esthag/35/supmat/files/es66A.fil/Einarson_SI.pdf)

Fedorak, P.M., K.M. Semple, and D.W.S. Westlake. A statistical comparison of two culturing methods from enumerating sulfate-reducing bacteria. *Journal of Microbiological Methods* 7: 19-27 (1987).

Felske, A., A.D. Akkermans, and W.M. DeVos. Quantification of 16S rRNAs in complex bacterial community by multiple competitive reverse transcription-PCR in temperature gradient gel electrophoresis fingerprints. *Applied and Environmental Microbiology* 64: 4581-4587 (1998).

Ford, R.G., K.M. Kemner, and P.M. Bertsch. Influence of sorbate-sorbent interactions on the crystallization kinetics of nickel- and lead-ferrihydrite coprecipitates. *Geochimica et Cosmochimica Acta* 63: 39-48 (1999).

Fruchter, J.S., J.E. Amonette, C.R. Cole, Y.A. Gorby, M.D. Humphrey, J.D. Istok, F.A. Spane, J.E. Szecsody, S.S. Teel, V.R. Vermeuel, M.D. Williams, and S.B. Yabusaki. In situ redox manipulation field injection test report-Hanford 100-H Area. PNNL-11372/UC-602. Pacific Northwest National Laboratory, Richland, WA (1996).

Galloway, W.E. and J.M. Sharp, Jr. Characterizing aquifer heterogeneity within terrigenous clastic depositional systems. In *SEPM Concepts in Hydrogeology and Environmental Geology No. 1: Hydrogeologic Models of Sedimentary Aquifers.* G.S. Fraser and J.M. Davis (Eds.), Society for Sedimentary Geology, Tulsa, OK (1998).

Gerth, J. Unit-cell dimensions of pure and trace metal-associated goethites. *Geochmica et Cosmochimica Acta* 55: 455-460 (1990).

Ghiorse, W.C. and D.L. Balkwill. Enumeration and morphological characterization of bacteria indigenous to subsurface environments. *Developments in Industrial Microbiology* 24: 213-244 (1983).

Gihwala, D. and M. Peisach. Analysis using prompt gamma-ray emission. In *Elemental Analysis by Particle Accelerators.* Z.B. Alfassi and M. Peisach (Eds.), CRC Press, Boca Raton, FL (1992).

Gilkes, R.J. Transmission electron microscope analysis of soil materials. In *Quantitative Methods in Soil Mineralogy.* J.E. Amonette and L.W. Zelazy (Eds.), Soil Science Society of America, Madison, WI (1994).

Glynn, P.D. and E. Reardon. Solid-solution aqueous solution equilibria: Thermodynamic theory and representation. *American Journal of Science* 290: 164-201 (1990).

Glynn, P.D., E. Reardon, L.N. Plummer, and E. Busenberg. Reaction paths and equilibrium end-points in solid-solution aqueous-solution systems. *Geochimica et Cosmochimica Acta* 54: 267-282 (1990).

Goldberg, S. Adsorption models incorporated into chemical equilibrium models. In *Chemical Equilibrium and Reaction Models.* R.H. Loeppert, A.P. Schwab, and S.Goldberg (Eds.), Soil Science Society of America, Madison, WI (1995).

Goldberg, S. Use of surface complexation models in soil chemical systems. *Advances in Agronomy* 47: 233-329 (1992).

Gruebel, K.A., J.A. Davis, and J.O. Leckie. The feasibility of using sequential extraction techniques for arsenic and selenium in soils and sediments. *Soil Science Society of America Journal* 52: 390-397 (1988).

Gupta, S.K., M.K. Vollmer, and R. Krebs. The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. *Science of the Total Environment* 178: 11-20 (1996).

Haggerty, R., M.H. Schroth, and J.D. Istok. Simplified method of "push-pull" test data analysis for determining in situ reaction rate coefficients. *Ground Water* 36: 314-324 (1998).

Helmke, P.A. Neutron activation analysis. In *Methods of Soil Analysis.* A.L. Page et al. (Eds.), Agronomy Monograph 9, American Society of Agronomy and Soil Science Society of America, Madison, WI (1982).

Hem, J.D. and C.E. Roberson. Form and stability of aluminum hydroxide complexes in dilute solution. U.S. Geological Survey, Water Supply Paper 1967 (1967).

Huerta-Diaz, M. and J.W. Morse. A quantitative method for determination of trace metals concentrations in sedimentary pyrite. *Marine Chemistry* 29: 119-144 (1990).

Istok, J.D., J.E. Amonette, C.R. Cole, J.S. Fruchter, M.D. Humphrey, J.E. Szecsody, S.S. Teel, V.R. Vermeul, M.D. Williams, and S.B. Yabusaki. In situ redox manipulation by dithionite injection: Intermediate-scale laboratory experiments. *Ground Water* 37: 884-889 (1999).

Istok, J.D., M.D. Humphrey, M.H. Schroth, M.R. Hyman, and K.T. O'Reilly. Single-well, "push-pull" test for in situ determination of microbial activities. *Ground Water* 35: 619-631 (1997).

Jenne, E.A. Adsorption of metals by geomedia: Data analysis, modeling, controlling factors, and related issues. In *Adsorption of Metals by Geomedia.* E.A. Jenne (Ed.), Academic Press, San Diego, pp. 1-73 (1998).

Johnson, B.D. and P.J. Wangersky. Seawater filtration: Particle flow and impact considerations. *Limnology and Oceanography* 30: 966-971 (1985).

Johnson, G.K., G.N. Papatheodorou, and C.E. Johnson. The enthalpies of formation and high-temperature thermodynamic functions of As_4S_4 and As_2S_3. *Journal of Chemical Thermodynamics* 1980: 545-557 (1980).

Kalkwarf, D.R. Solubility classification of airborne products from uranium ores and tailings piles. NUREG/CR-0530, Pacific Northwest Laboratory, Richland, WA (1979).

Kalkwarf, D.R. Solubility classification of airborne uranium products collected at the perimeter of the Allied Chemical plant, Metropolis, Illinois. NUREG/CR-1316, Pacific Northwest Laboratory, Richland, WA (1980a).

Kalkwarf, D.R. Solubility classification of airborne uranium products from LWR-Fuel plants. NUREG/CR-1428, Pacific Northwest Laboratory, Richland, WA (1980b).

Kennedy, V.C. and G.W. Zellweger. Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water. *Water Resources Research* 10: 785-790 (1974).

Kent, D.B., J.A. Davis, L.C.D. Anderson, and B.A. Rea. Transport of chromium and selenium in a pristine sand and gravel aquifer: Role of adsorption processes. *Water Resources Research* 31: 1041-1050 (1995).

Keon, N.E., C.H. Swartz, D.J. Brabander, C. Harvey, and H.F. Hemond. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environmental Science and Technology* 35: 2778-2784 (2002).

Kheboian, C. and C.F. Bauer. Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. *Analytical Chemistry* 59: 1417-1423 (1987).

Kim, J.I., G. Buckau, F. Baumgartner, H.C. Moon, and D. Lux. Colloid generation and the actinide migration in Gorleben groundwaters. In *Scientific Basis for Nuclear Waste Management,* v. 7. G.L. McVay (Ed.), Elsevier, NY (1984).

Kohler, M., G.P. Curtis, D.E. Meece, and J.A. Davis. Methods for estimating adsorbed uranium(VI) and distribution coefficients of contaminated sediments. *Environmental Science and Technology* 38: 240-247 (2004).

Kostka, J.E. and G.W. Luther. Partitioning and speciation of solid phase iron in saltmarsh sediments. *Geochimica et Cosmochimica Acta* 58: 1701-1710 (1994).

Kruseman, G.P. and N.A. de Ridder. *Analysis and Evaluation of Pumping Test Data.* International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands (1989).

Laird, D.A. and R.H. Dowdy. Preconcentration techniques in soil mineralogical analyses. In *Quantitative Methods in Soil Mineralogy.* J.E. Amonette and L.W. Zelazy (Eds.), Soil Science Society of America, Madison, WI (1994).

Langmuir, D. *Aqueous Environmental Geochemistry.* Prentice-Hall, Upper Saddle River, NJ (1997).

Lee, D.H., Y.-G. Zo, and S.-J. Kim. Nonradioactive method to study genetic profiles of natural bacterial communities by PCR-single strand-conformation polymorphism. *Applied and Environmental Microbiology* 62: 3112-3120 (1996).

Lehman, R.M., F.S. Colwell, D.B. Ringelberg, and D.C. White. Combined microbial community-level analyses for quality assurance of terrestrial subsurface cores. Microbiological Methods 22: 263-281 (1995).

Lippmann, F. The solubility products of complex minerals, mixed crystals, and three-layer clay minerals. *Neues Jahrbuch für Mineralogie Abhandlung* 130: 243-263 (1977).

Loeppert, R.H. and W.P. Inskeep. Iron. In *Methods of Soil Analysis: Part 3 - Chemical Methods.* D.L. Sparks (Ed.), Soil Science Society of America, Madison, WI, pp. 639-664 (1996).

Lovley, D.R. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiology Review* 55: 259-287 (1991).

Loyd, D. and J.H. Anthony. Vigour, vitality and viability of microorganisms. FEMS *Microbiology Letters* 133: 1-7 (1995).

Mahne, I. and J.M. Tiedji. Criteria and methodology for identifying respiratory denitrifiers. A*pplied and Environmental Microbiology* 61: 1110-1115 (1995).

Maiz, I., M.V. Esnaola, and E. Millán. Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure. *Science of the Total Environment* 206: 107-115 (1997).

Martinez-Murcis, A.J., S.G. Acinas, and F. Rodriguez-Valeria. Evaluation of prokaryotic diversity by restrictase digestion of 16S rDNA directly amplified from hypersaline environments. *FEMS Microbial Ecology* 14: 219-232 (1995).

Mikac, N., S. Niessen, B. Ouddane, and J. Fischer. Effects of acid volatile sulfides on the use of hydrochloric acid for determining solid-phase associations of mercury in sediments. *Environmental Science and Technology* 34: 1871-1876 (2000).

Moore, J.N., W.H. Ficklin, and C. Johns. Partitioning of arsenic and metals in reducing sulfidic sediments. *Environmental Science and Technology* 22: 432-437 (1988).

More, M.I., J.B. Herrick, M.C. Silva, W.C. Ghiorse, and E.L. Madsen. Quantitative cell lysis of indigeous microorganisms and rapid extraction of microbial DNA from sediment. *Applied and Environmental Microbiology* 60: 1572-1580 (1994).

Morgan J.J. and A.T. Stone. Kinetics of chemical processes of importance in lacustrine environments. In *Chemical Processes in Lakes.* W. Stumm (Ed.), John Wiley & Sons, Inc., New York, NY, pp. 389-426 (1985).

Muyzer, G., E.C. DeWaal, and A.G. Uitterlinden. Profiling of complex microbial populations by denaturing gradient gel electrophoresis analysis of polymerase chain reaction-amplified genes coding for 16S rRNA. *Applied and Environmental Microbiology* 59: 695-700 (1993).

National Research Council. Natural Attenuation for Groundwater Remediation. Committee on Intrinsic Remediation, Water Science and Technology Board, Board on Radioactive Waste Management. National Academy Press, Washington DC (2000).

Nelson, D.W. and L.E. Sommers. Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis. Part 3: Chemical Methods.* D.L. Sparks (Ed.), Soil Science Society of America, Madison, WI (1996).

Nirel, P.M.V. and F.M.M. Morel. Pitfalls of sequential extractions. *Water Research* 24: 1055-1056 (1990).

Nordstrom, D.K. and J.L. Munoz. *Geochemical Thermodynamics.* Blackwell Scientific Publications, Palo Alto, CA (1986).

Nordstrom, D.K., E.A. Jenne, and J.W. Ball. Redox equilibria of iron in acid mine waters. In *American Chemical Society Symposium Series 93, Chapter 3.* E.A. Jenne (Ed.), American Chemical Society, Washington DC (1979).

Pernthaler, A., C.M. Preston, J. Pernthaler, F.E. DeLong, and R. Amann. A comparison of fluorescently labeled oligonucleotide and polynucleotide probes for the detection of pelagic marine bacteria and archaea. *Applied and Environmental Microbiology* 68: 661-667 (2002).

Puls, R.W. and J.H. Eychaner. Sampling ground water for inorganics - pumping rate, filtration, and oxidation effects. In *Fourth National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods,* National Water Well Association, Dublin, OH, pp. 313-327 (1990).

Quevauviller, Ph., G. Rauret, J.F. López-Sánchez, R. Rubio, A. Ure, and H. Muntau. Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. *Science of the Total Environment* 205: 223-234 (1997).

Rai, D. et al. Chromium reactions in geologic materials. EA-5741, Battelle Pacific Northwest Laboratories for Electric Power Research Institute, Palo Alto, California (1988).

Rai, D. et al. Chemical attenuation rates, coefficients, and constants in leachate migration, Volume 1: A critical review. EA-3356, Battelle Pacific Northwest Laboratories for Electric Power Research Institute, Palo Alto, California (1984).

Rai, D., R.J. Serne, and D.A Moore. Solubility of plutonium compounds and their behavior in soils. *Soil Science Society of America Journal* 44: 490-495 (1980).

Rapin, F., A. Tessier, P.G.C. Campbell, and R. Carignan. Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure. *Environmental Science and Technology* 20: 836-840 (1986).

Rauret, G., J.F. López-Sánchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, and Ph. Quevauviller. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring* 1: 57-61 (1999).

Rendell, P.S., G.E. Batley, and A.J. Cameron. Adsorption as a control of metal concentrations in sediment extracts. *Environmental Science and Technology* 14: 314-318 (1980).

Roden, E.E. and J.M. Zachara. Microbial reduction of crystalline iron(III) oxides: Influence of oxide surface area and potential for cell growth. *Environmental Science and Technology* 30: 1618-1628 (1996).

Ross, G.J., C. Wang, and P.A. Schuppli. Hydroxylamine and ammonium oxalate solutions as extractants for iron and aluminum from soils. *Soil Science Society of America Journal* 49: 783-785 (1985).

Roy, W.R., J.J. Hassett, and R.A. Griffin. Competitive interactions of phosphate and molybdate on arsenate adsorption. *Soil Science* 142: 203-210 (1986).

Ryan, J.N. and P.M. Gschwend. Extraction of iron oxides from sediments using reductive dissolution by titanium(III). *Clays and Clay Minerals* 39: 509-518 (1991).

Sass, B.M. and D. Rai. Solubility of amorphous chromium(III)-iron(III) hydroxide solid solutions. *Inorganic Chemistry* 26: 2228-2232 (1987).

Sawhney, B.L. and D.E. Stilwell. Dissolution and elemental analysis of minerals, soils, and environmental samples. In *Quantitative Methods in Soil Mineralogy.* J.E. Amonette and L.W. Zelazy (Eds.), Soil Science Society of America, Madison, WI (1994).

Schmelling, S.G. and R.R. Ross. Superfund Ground Water Issue, Contaminant Transport in Fractured Media: Models for Decision Makers, EPA/540/4-89/004. U.S. Environmental Protection Agency, Ada, OK (1989).

Schultz M.K., S. Biegalski, K.G.W. Inn, L. Yu, W.C. Burnett, J. Thomas, and G. Smith. Optimizing the removal of carbon phases in soils and sediments for sequential extractions by coulometry. *Journal of Environmental Monitoring* 1: 183-190 (1999).

Schultz M.K., W.C. Burnett, and K.G.W. Inn. Evaluation of a sequential extraction method for determining actinide fractionation in soils and sediments. *Journal of Environmental Radioactivity* 40: 155-174 (1998a).

Schultz M.K., W.C. Burnett, G. Smith amd K.G.W. Inn. Geochemical partitioning of actinides using sequential chemical extractions: Comparison to stable elements. *Journal of Radioanalytical and Nuclear Chemistry* 234: 251-256 (1998b).

Schultz M.K., W.C. Burnett, K.G.W. Inn, Z. Lin, G. Smith, S. Biegalski, and J.J. Filliben. Identification of radionuclide partitioning in soils and sediments: Determination of best settings for the exchangeable fraction of the NIST standard sequential extraction protocol. *Journal of Applied Radiation and Isotopes* 49: 1289-1293 (1998c).

Senko, J.M., J.D. Istok, J.M. Suflita, and L.R. Krumholz. In-situ evidence for uranium immobilization and remobilization. *Environmental Science and Technology* 36: 1491-1496 (2002).

Sheldon, R.W. and W.H. Sutcliffe. Retention of marine particles by screens and filters. *Limnology and Oceanography* 17: 494-498 (1969).

Sheppard, J.C., M.J. Campbell, and J.A. Kittrick. Retention of Neptunium, Americium, and Curium by diffusible soil particles. *Environmental Science and Technology* 13: 680-684 (1979).

Sparks, D. *Environmental Soil Chemistry.* Academic Press, San Diego, CA (1995).

Sposito, G. The Surface Chemistry of Soils. Oxford University Press, New York, NY (1984).

Stumm, W. and J.J. Morgan. *Aquatic Chemistry.* John Wiley & Sons, New York, NY (1981).

Tack, F.M., F. Lapauw, and M.G. Verloo. Determination and fractionation of sulphur in a contaminated dredged sediment. *Talanta* 44: 2185-2192 (1997).

Tanner, R.S. Monitoring sulfate-reducing bacteria: comparison of enumeration media. *Journal of Microbiological Methods* 10: 83-90 (1989).

Tessier, A. and P.G.C. Campbell. Comment on "Pitfalls of sequential extractions" by P.M.V. Nirel and F.M.M. Morel. *Water Research* 25: 115-117 (1991).

Tessier, A., P.G.C. Campbell, and M. Bison. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844-851 (1979).

To, T.B., D.K. Nordstrom, K.M. Cunningham, J.W. Ball, and R.B. McCleskey. New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. *Environmental Science and Technology* 33: 807-813 (1999).

Ure, A.M., Ph. Quevauviller, H. Munteau, and B. Griepink. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the commission of the European Communities. *International Journal of Environmental and Analytical Chemistry* 51: 135-151 (1993).

USEPA. Chemical Oxygen Demand. *Methods for Chemical Analysis of Water and Wastes,* EPA Method 410.4, EPA/600/4-79-020 (1979).

USEPA. Seminar Publication: Site Characterization for Subsurface Remediation, EPA/625/4-91/026, U.S. Environmental Protection Agency, Cincinnati, OH (1991).

USEPA. *Batch-type Procedures for Estimating Soil Adsorption of Chemicals.* Technical Resource Document, EPA/530/SW-87/006-F, Office of Solid Waste and Emergency Response, Washington DC (1992).

USEPA. *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide, Volume 1: Solids and Ground Water,* EPA/625/R-93/003a, U.S. Environmental Protection Agency, Washington DC 20460 (1993a).

USEPA. *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide, Volume 2: The Vadose Zone, Field Screening and Analytical Methods,* EPA/625/R-93/003, U.S. Environmental Protection Agency, Washington DC (1993b).

USEPA. *Ground Water Sampling -- A Workshop Summary,* EPA/600/R-94/205, Office of Research and Development, Ada, OK (1994). (http://www.epa.gov/ada/download/reports/gwwkshop.pdf)

USEPA. *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures,* EPA/540/S-95/504, Office of Research and Development, Washington DC (1996). (http://www.epa.gov/ada/download/issue/lwflw2a.pdf)

USEPA. *Site Characterization Library, Volume 1,* EPA/600/C-98/001, U.S. Environmental Protection Agency, Las Vegas, NV (1998).

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

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

USEPA. *Proceedings of the Ground-Water/Surface-Water Interactions Workshop,* EPA/542/R-00/007, U.S. Environmental Protection Agency, Washington DC (2000a).

USEPA. *An SAB Report: Review of an Integrated Approach to Metals Assessment in Surface Waters and Sediments,* EPA-SAB-EPEC-00-005, U.S. Environmental Protection Agency, Washington DC (2000b).

USEPA. *Workshop on Monitoring Oxidation-reduction Processes for Ground-water Restoration,* EPA/600/R-02/002, Office of Research and Development, Cincinnati, OH (2002). (http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf)

USEPA. *Performance Monitoring for Natural Attenuation Remedies in Ground Water,* OSWER 9355.4-25, U.S. Environmental Protection Agency, Washington DC (2003).

USEPA. *The Impact of Ground Water-Surface Water Interactions on Contaminant Transport with Application to an Arsenic Contaminated Site,* EPA/600/S-05/002, U. S. Environmental Protection Agency, Cincinnati, OH (2005a).

USEPA. *Field Study of the Fate of Arsenic, Lead, and Zinc at the Ground-Water/Surface-Water Interface,* EPA/600/R-05/161, Office of Research and Development, Cincinnati, OH (2005b). (http://www.epa.gov/ada/download/reports/600R05161/600R05161.pdf)

USEPA. *Mineralogical Preservation of Solid Samples Collected from Anoxic Subsurface Environments,* EPA/600/R-06/112, Office of Research and Development, Cincinnati, OH (2006). (http://www.epa.gov/ada/download/issue/600R06112.pdf)

Wagemann, R. and G.J. Brunskill. The effect of filter pore-size on analytical concentrations of some trace elements in filtrates of natural water. *International Journal of Environmental and Analytical Chemistry* 4: 75-84 (1975).

Wagman, D.D., W.H. Evans V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, and R.L. Nuttall. The NBS tables of chemical thermodynamic properties. *Journal of Physical Chemical Reference Data* 11, 1-392 (1982).

Walker, A.L. The effects of magnetite on oxalate- and dithionite-extractable iron. *Soil Science Society of America Journal* 47: 1022-1026 (1983).

Wang, F. and A. Tessier. Cadmium complexation with bisulfide. *Environmental Science and Technology* 33: 4270-4277 (1999).

Webster, J.G. The solubility of As_2S_3 and speciation of As in dilute and sulphide-bearing fluids at 25 and 90°C. *Geochimica et Cosmochimica Acta* 54: 1009-1017 (1990).

Westall, J. Reactions at the oxide-solution interface: Chemical and electrostaic models. In *Geochemical Processes and Mineral Surfaces.* J.A. Davis and K.F. Hayes (Eds.), American Chemical Society Symposium Series 323, American Chemical Society, Washington DC, pp. 54-78 (1986).

Wilkin, R.T. and R.G. Ford. Use of hydrochloric acid for determining solid-phase arsenic partitioning in sulfidic sediments. *Environmental Science and Technology* 36: 4921-4927 (2002).

Wilkin, R.T., D. Wallschläger, and R.G. Ford. Speciation of arsenic in sulfidic waters. *Geochemical Transactions* 4: 1-7 (2003).

Williams, M.D., V.R. Vermeul, J.E. Szecsody, and J.S. Fruchter. 100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater. PNNL-13349, Pacific Northwest National Laboratory, Richland, WA (2000).

Winter, T.C., J.W. Harvey, O.L. Franke, and W.M. Alley. Ground water and surface water: a single resource. U.S. Geological Survey Circular 1139 (1998).

Winter, T.C. Interaction of ground water and surface water. In Proceedings of the Ground-Water and Surface-Water Interactions Workshop, EPA/542/R-00/007, U.S. Environmental Protection Agency, Washington DC (2000).

Wise, M.G., J.V. McArthor, and L.J. Shimkets. Bacterial diversity of a Carolina bay as determined by 16S rRNA gene analysis: confirmation of novel taxa. *Applied and Environmental Microbiology* 63: 1505-1514 (1997).

Yanase, N., T. Nightingale, T. Payne, and P. Duerden. Uranium distribution in mineral phases of rock by sequential extraction procedure. *Radiochimica* Acta 52/53: 387-393 (1991).

Yong, R.N., R. Galvez-Cloutier, and Y. Phadungchewit. Selective sequential extraction analysis of heavy-metal retention in soil. *Canadian Geotechnical Journal* 30: 834-847 (1993).

Zhabina, N.N. and I.I. Volkov. A method of determination of various sulfur compounds in sea sediments and rocks. In *Environmental Biogeochemistry and Geomicrobiology, v. 3.* W. Krumbein (Ed.), Ann Arbor Science Publishers, Ann Arbor, MI, pp. 735-746 (1978).

United States
Environmental Protection
Agency

National Risk Management
Research Laboratory
Cincinnati, OH 45268

Official Business
Penalty for Private Use
$300

EPA/600/R-07/139
October 2007