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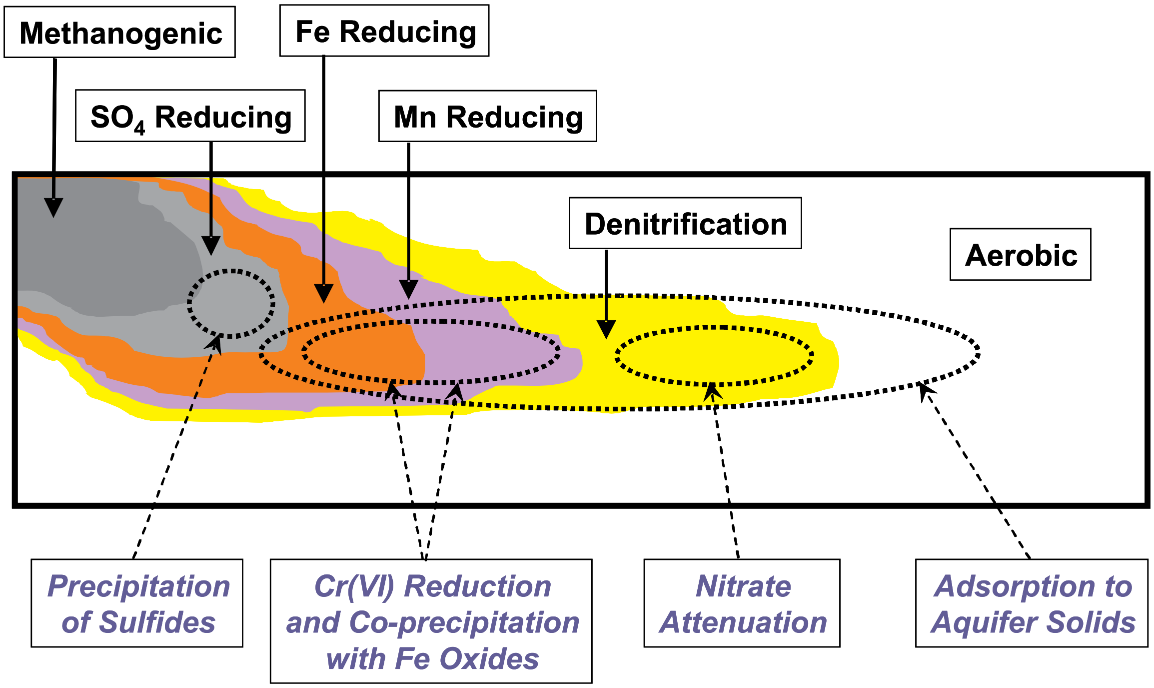
Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

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



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

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Notice

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

Foreword

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

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

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

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Executive Summary

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

The current document represents the second volume of a set of three volumes that address the technical basis and requirements for assessing the potential applicability of MNA as part of a ground-water remedy for plumes with non-radionuclide and/or radionuclide inorganic contaminants. Volume 2, titled “Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium,” consists of individual chapters that describe 1) the natural processes that may result in the attenuation of the listed contaminants and 2) data requirements to be met during site characterization. Emphasis is placed on characterization of immobilization and/or degradation processes that may control contaminant attenuation, as well as technical approaches to assess performance characteristics of the MNA remedy. A tiered analysis approach is presented to assist in organizing site characterization tasks in a manner designed to reduce uncertainty in remedy selection while distributing costs to address four primary issues:

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

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

This document is limited to evaluations performed in porous-media settings. Detailed discussion of performance monitoring system design in fractured rock, karst, and other such highly heterogeneous settings is beyond the scope of this document. Ground water and contaminants often move preferentially through discrete pathways (e.g., solution channels, fractures, and joints) in these settings. Existing techniques may be incapable of fully delineating the pathways along which contaminated ground water migrates. This greatly increases the uncertainty and costs of assessments of contaminant migration and fate and is another area of continuing research. As noted in OSWER Directive 9200.4-17P, “MNA will not generally be appropriate where site complexities preclude adequate monitoring.” The directive provides additional discussion regarding the types of sites where the use of MNA may be appropriate.

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

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

Cadmium

Richard T. Wilkin

Occurrence and Distribution

Cadmium is comparatively rare in the environment with an average abundance similar to other second- and third-row transition metals (e.g., silver and mercury). The median concentration of cadmium in soils and sediments ranges from about 0.04 to 1.8 mg kg^{-1} (Reimann and Caritat, 1998). Where cadmium concentrations are elevated, it is typically found in association with sulfide ores of zinc and sometimes with ores of copper and lead. The primary mineral associations of cadmium are with otavite ($CdCO_3$), greenockite (CdS), sphalerite (ZnS), smithsonite ($ZnCO_3$), and hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$). Soil weathering can lead to release of the Cd^{2+} ion, which is generally soluble and mobile in water.

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

Remedial Technologies

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

Regulatory Aspects

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

Geochemistry and Attenuation Processes

Aqueous Speciation

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

The fractional abundance of Cd-OH species in water as a function of pH is shown in Figure 1.1. The distribution diagram for cadmium hydroxy complexes indicates that Cd^{2+}, $Cd(OH)^{+}$, $Cd(OH)_2^0$ are the most significant species below pH 12. At low total concentrations of cadmium, hydrolysis of Cd^{2+} becomes significant above about pH 9. Complexation of cadmium with chloride and ammonia becomes important as aqueous concentrations of these ligands exceed 10^{-2} molal and 10^{-3} molal, respectively (e.g., Lindsay, 1979).

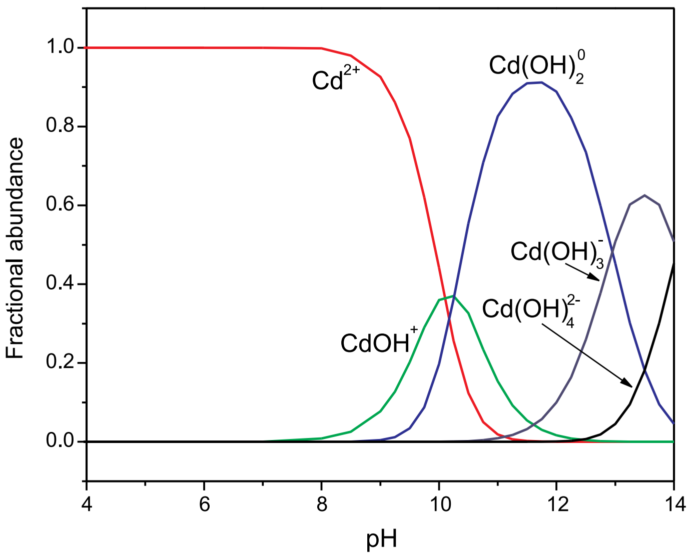

Figure 1.1 *Species distribution of Cd(II) in pure water as a function of pH at 25 °C.*

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

The identity of cadmium bisulfide complexes and their formation constants have been discussed by Daskalakis and Helz (1992) and Wang and Tessier (1999). Uncertainty persists regarding the stoichiometry of the most important cadmium complexes in sulfidic waters. This uncertainty mainly stems from the experimental approach that has been traditionally used to extract thermodynamic data, i.e., evaluation of CdS solubility over a range of total cadmium concentrations, total sulfide concentrations, and pH. Data presented in Wang and Tessier (1999) indicate that $Cd(HS)_2^0$ is the dominant species at $\Sigma S(-II)=10^{-5}$ molal and over the pH range from 6 to 8, typically encountered in natural sulfidic waters. At lower total sulfide concentrations, $CdHS^+$ and Cd^{2+} become increasingly important (Wang and Tessier, 1999).

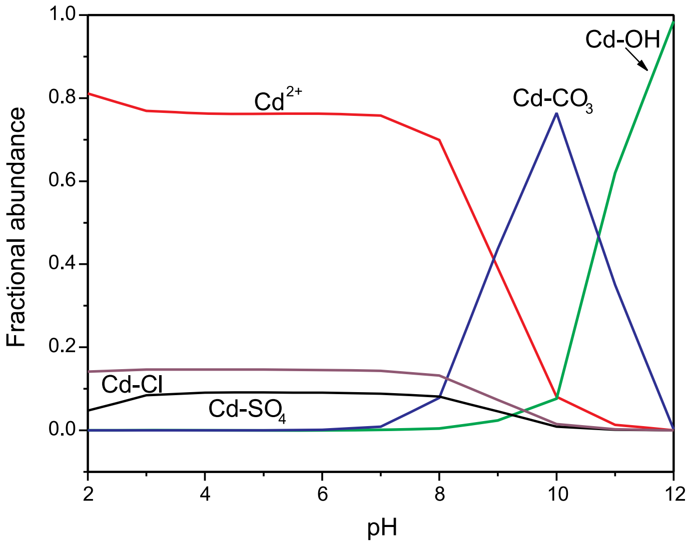

Figure 1.2 *Cadmium speciation as a function of pH in solution containing chloride (100 mg L^{-1}), sulfate (100 mg L^{-1}), and inorganic carbon (100 mg L^{-1}). Cadmium chloride complexes include $CdCl^+$ and $CdCl_2^0$. Cadmium sulfate complexes include $CdSO_4^0$ and $Cd(SO_4)_2^{2-}$. Cadmium complexes with inorganic carbon include $CdCO_3^0$, $CdHCO_3^+$, and $Cd(CO_3)_2^{2-}$. Cadmium hydroxy complexes include $CdOH^+$, $Cd(OH)_2^0$, and $Cd(OH)_3^-$. Total cadmium is equal to 1 mg L^{-1}.*

Solubility

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

$$CdCO_3 + H^+ = Cd^{2+} + HCO_3^- \qquad (\log K = -0.9)$$

and

$$CdS + H^+ = Cd^{2+} + HS^- \qquad (\log K = -14.4)$$

In natural deposits, cadmium often substitutes for zinc in the mineral structures of sphalerite (ZnS) and smithsonite ($ZnCO_3$). O'Day et al. (1998) suggest that as cadmium-substituted sphalerite weathers, cadmium is preferentially partitioned into the aqueous phase over zinc. Zinc was found to form various zinc hydroxides and/or zinc-iron oxyhydroxides depending on the total amount of iron in the system. Cadmium was not identified in the solid-phase products from weathering indicating its general tendency to be mobile in the aqueous phase (O'Day et al., 1998; Carroll et al., 1998).

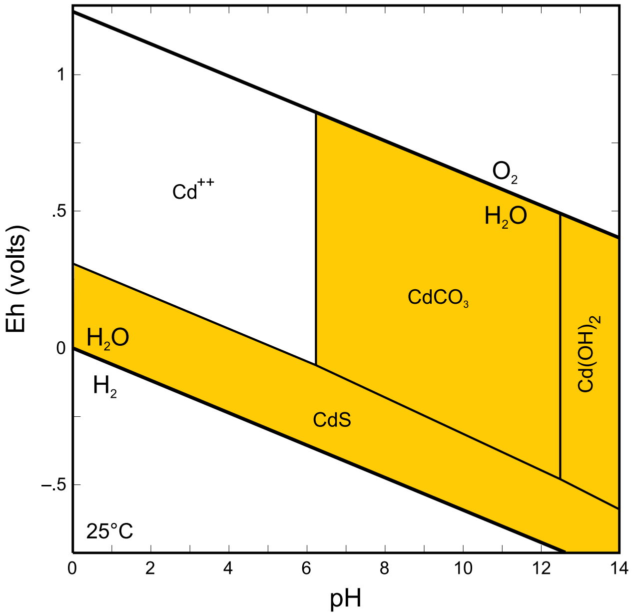

Figure 1.3 *Eh-pH diagram for cadmium (total Cd = 10^{-5} molal, total C = 10^{-3} molal, total S = 10^{-3} molal; all organic cadmium complexes are suppressed; activity coefficients for all species are set equal to 1).*

Cadmium carbonates - Cadmium is known to form solid-solutions with calcium carbonate (calcite). The Cd^{2+} and Ca^{2+} ions are nearly the same size with crystal radii of 1.09 and 1.14 angstroms, respectively, assuming octahedral coordination. The formation of Ca-Cd carbonate solid solutions is environmentally significant because solid solutions are generally more stable and less soluble than endmember compositions. Cadmium uptake from aqueous solution by calcite has been widely studied (e.g., McBride, 1980; Davis et al., 1987; Papadopoulos and Rowell, 1988; Zachara et al., 1991; Stipp et al., 1992, 1993; Tesoriero and Pankow, 1996; Chiarello et al., 1997; Martin-Garin et al., 2003). Cadmium uptake is thought to consist of two processes. The first process is rapid sorption and the second process is incorporation into the crystal lattice and formation of an otavite-calcite solid-solution. The latter process has been confirmed through determination of cadmium solid phase speciation during reaction with calcite (Bailey et al., 2005). Cadmium partitioning to carbonaceous materials has been applied by Wang and Reardon (2001) for the removal of cadmium from wastewater streams.

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

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

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

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

Adsorption

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

Ainsworth et al. (1994) examined the sorption behavior of cadmium on freshly prepared and aged hydrous ferric oxide (HFO). Their results indicate that HFO effectively removes cadmium from solution at pH above about 6.7. In general, the pH-dependent adsorption behavior parallels the change in aqueous speciation from Cd^{2+} to cadmium hydroxide species (see Fig. 1.1), although adsorption occurs at pH values where cadmium hydroxide species are unexpected in bulk solution. Aging times of up to 21 weeks showed little effect on the sorption behavior of cadmium onto HFO. HFO aged in the presence of Cd^{2+} ions showed some desorption hysteresis suggesting that cadmium is incorporated into the metal oxide structure during recrystallization. Martínez and McBride (1998) suggest that coprecipitation of cadmium with amorphous iron oxides results in more reduced concentrations than can be achieved through surface adsorption alone. However, Ford et al. (1997) report that during long-term aging of hydrous iron oxides, cadmium desorbs or is released suggesting minimal incorporation of cadmium into the goethite or hematite structures.

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

Redox Chemistry

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

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

Colloidal Transport

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

Site Characterization

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

Table 1.1 Natural Attenuation and Mobilization Pathways for Cadmium

Attenuation Processes	Mobilization Processes	Characterization Approach
Precipitation of insoluble carbonates, sulfides, and hydroxides. In general, pH > 8 will drive precipitation reactions resulting in Cd concentrations below the MCL.	Dissolution of carbonates at low pH; oxidative dissolution of sulfides at low to neutral pH and high Eh; degradation of organic matter; complexation/stabilization in the presence of DOC.	Evaluation of cadmium concentration in the aqueous phase. Determination of total Cd in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Evaluation of long-term storage capacity.
Sorption (reversible) to iron hydroxides, organic matter, carbonates, sulfides (pH > 6 to 8). Substitution for Zn in minerals.	Desorption at low pH; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides. Oxidation of metal sulfides.	Evaluation of cadmium speciation in the aqueous phase. Determination of total Cd in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Batch and column testing to determine Cd uptake capacity of site-specific aquifer materials at variable geochemical conditions.

Aqueous Measurements

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

Solid Phase Measurements

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

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

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

Long-Term Stability and Capacity

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

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

Tiered Analysis

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

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

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

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

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

Tier III - Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Cd and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized Cd be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage.

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

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

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Lead

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Occurrence and Distribution

Lead is distributed in low concentrations in sedimentary rocks and soils. The average concentration of lead in shales, sandstones, and carbonate rocks is 20, 7, and 9 mg kg^{-1}, respectively (Turekian and Wedepohl, 1961). Kabatas-Pendias and Pendias (1984) report background soil concentrations of 17-26 mg Pb kg^{-1} in the U.S. Anthropogenic enrichment of lead in near-surface soils stems largely from airborne deposition of particles derived from fossil fuel combustion (e.g., gasoline and coal). Lead is a common metal contaminant at hazardous waste sites, especially at battery crushing and recycling facilities (USEPA, 1991). Indeed, lead is the most commonly recycled metal: roughly 50% of lead production is secondary lead. Approximately 70% of world-lead goes to lead-acid storage batteries. Natural lead enrichment occurs around hydrothermal deposits and base metal ores, most frequently as the mineral galena (PbS), but also as the oxidation products of lead sulfide ores such as anglesite ($PbSO_4$) and cerussite ($PbCO_3$).

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

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

Plume Characteristics

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

Remedial Technologies

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

Regulatory Aspects

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

Geochemistry and Attenuation Processes

Aqueous Speciation

Lead is known to form stable aqueous complexes with OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and HS^-. In pure water, lead is mainly present as Pb^{2+} below a pH of about 7. With increasing pH, the species $PbOH^+$, $Pb(OH)_2^0$, and $Pb(OH)_3^-$ become dominant over Pb^{2+} (Figure 2.1). Lead carbonato complexes ($PbCO_3^0$, $Pb(CO_3)_2^{2-}$), lead chloride complexes ($PbCl^+$, $PbCl_2^0$), lead sulfate complexes ($PbSO_4^0$, $Pb(SO_4)_2^{2-}$), and lead sulfide complexes ($PbHS^+$, Pb_2S_2) are typically considered in aqueous speciation modeling efforts (e.g., Hem and Durum, 1973; Hem, 1976; Marani et al., 1995; Pierrard et al., 2002; Rozan et al., 2003). In general, complexation of lead with chloride and sulfate is most important at near-neutral to low pH; carbonate complexation is most important at near-neutral to moderately alkaline conditions; and, hydroxyl species dominate lead complexation at high pH (Figure 2.2). Inorganic speciation of lead in site-specific water will depend on pH, total lead concentration, and the relative and absolute abundances of the major anions: chloride, sulfate, and carbonate.

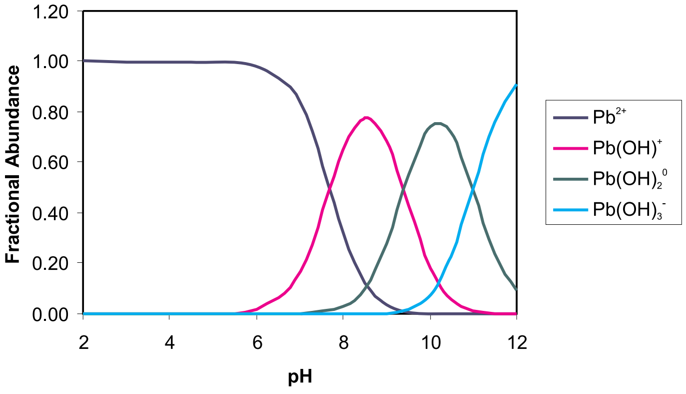

Figure 2.1 *Pb(II) species distribution in pure water at 25 °C.*

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

Reed et al. (1995) took advantage of lead partitioning to organic compounds in column-scale soil flushing studies. For soils contaminated with Pb(II) (500 mg kg^{-1} from $Pb(NO_3)_2$), $PbSO_4$ (10,000 mg kg^{-1}), $PbCO_3$ (10,000 mg kg^{-1}), and Pb-naphthalene (400 mg kg^{-1}), they documented Pb recoveries of 100%, 100%, 100%, and 72%, respectively, using 0.01 M EDTA as the soil-flushing solution. These results demonstrate the degree to which lead can be mobilized by organic ligands such as EDTA.

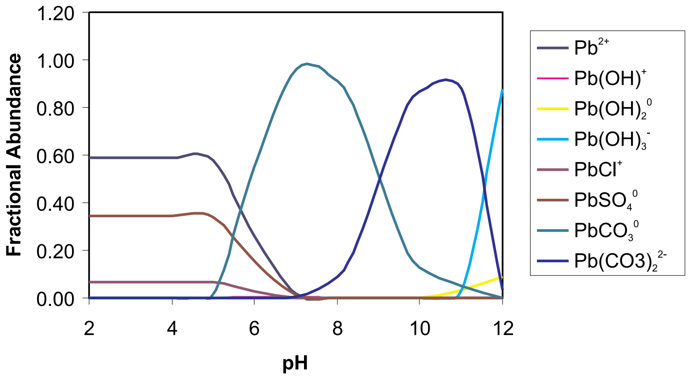

Figure 2.2 *Species distribution of lead in solution with 100 mg L^{-1} chloride, 100 mg L^{-1} sulfate, and 100 mg L^{-1} total inorganic carbon, based on thermodynamic data in MINTEQA2 (Allison et al., 1990).*

Solubility

An Eh-pH diagram for lead is shown in Figure 2.3. Inspection of this diagram indicates that at the specified conditions lead is stable in solids across the stability field of liquid water. At low pH and oxidizing conditions, lead sulfate is stable. At near-neutral to moderately alkaline pH, lead carbonates are stable, and at pH > 12.5 lead hydroxide is stable. In sulfidic environments, lead sulfide (galena) is stable over a wide pH range. The Pb(IV) phase, plattnerite, is stable at moderately alkaline to alkaline pH and at highly oxidizing redox potentials.

Solution pH plays a dominant role in governing lead solubility in aqueous solution. In general, the aqueous solubility of lead is low at near neutral to alkaline pH. Lead is expected to be mobile in low pH, oxidizing conditions. Hem and Durum (1973) found that at pH>7, the equilibrium solubility of lead was below 0.05 mg L^{-1} when $Pb(OH)_2$ and $PbCO_3$ were assumed to be the solubility-controlling phases. Equilibrium solubility of greater than 1000 mg L^{-1} lead was estimated at pH 4 in the absence of any sulfate. Lead is usually not a metal of concern at mining-related sites where acid mine drainage is produced. This is because the weathering of metal sulfides, in addition, to generating acidity also produces high concentrations of sulfate, which results in the precipitation of anglesite (Zänker et al., 2002).

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

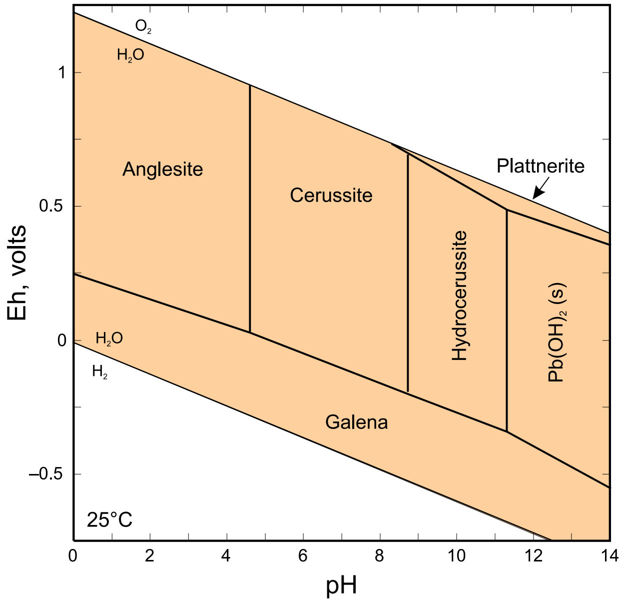

Figure 2.3 *Eh-pH diagram for lead (total Pb = 10^{-5} molal, total C = 10^{-3} molal, total S = 10^{-3} molal; all organic lead complexes are suppressed; activity coefficients for all species are set equal to 1).*

Important lead-bearing mineral phases include: lead hydroxide ($Pb(OH)_2$), cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), anglesite ($PbSO_4$), galena (PbS), lead oxide (PbO), and chloropyromorphite ($Pb_5(PO_4)_3Cl$) in phosphate-bearing systems. In addition, plumbojarosite ($Pb_{0.5}Fe_3(SO_4)_2(OH)_6$) has been identified as an important secondary precipitate and lead sink in weathered mine wastes (e.g., Hochella et al., 1999). Thermodynamic data for most of these phases may be found in a variety of sources (e.g., see Pierrard et al., 2002, and references therein). In carbonate and sulfate systems the most favored mineral species appear to be anglesite, cerussite, and hydrocerussite (Lindsay, 1979; Marani et al., 1995).

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

Marani et al. (1995) point out that the reliability of solubility predictions depends on the choice of the relevant solubility constants used in modeling studies. Unfortunately, such constants are wide ranging for lead. Reasonable agreement between solubility predictions from equilibrium modeling and filterable lead concentrations measured in aged soil-water systems was obtained only with a critical selection of solid phases in the modeling and by appreciating kinetic aspects of the Pb-H_2O system (Marani et al., 1995).

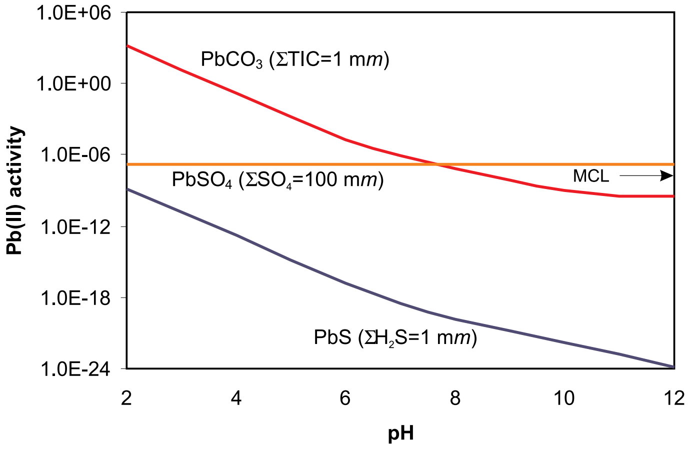

Figure 2.4 *Pb(II) activity in equilibrium with $PbCO_3$ (at total inorganic carbon equal to 0.001 molal), $PbSO_4$ (at total sulfate equal to 0.1 molal), and PbS (at total sulfide equal to 0.001 molal). The solubility trend can be compared to the MCL for lead of 0.015 mg L^{-1} or an activity of ~$7.2x10^{-8}$ m assuming ideal behavior.*

Lead phosphate minerals appear to be highly insoluble lead-bearing phases and remediation strategies for stabilizing lead-contaminated soils have taken advantage of this behavior (e.g., Ruby et al., 1994; Zhang et al., 1997). Hydroxyapatite and sodium phosphate monobasic have been used as a source of soluble phosphate to amend lead-contaminated soils. Reaction between labile lead phases and dissolved phosphate is rapid over a wide range of pH and P/Pb molar ratios and results in the formation of insoluble chloropyromorphite (Zhang and Ryan, 1999).

Adsorption

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

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

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

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

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

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

In reducing systems, adsorption of lead to iron sulfide surfaces is possible. Jean and Bancroft (1986) investigated the pH-dependent adsorption behavior of Pb on several iron sulfide minerals and found that the pH at which 50% of the lead was associated with the pyrite (FeS_2) surface was about 6.0. They suggested that the observed adsorption behavior is controlled by the hydrolysis of Pb^{2+} ions, whereby hydrolyzed species sorb directly on sulfide surface groups as a monolayer.

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

Redox Chemistry

In natural systems lead is present in the +2 oxidation state over relevant conditions of pH and oxidation-reduction potential. Reduction of Pb^{2+} to metallic lead is expected to occur at redox potentials below the stability field of water at pH<6. The oxidized form of lead (Pb(IV)) is not expected in air-saturated solutions based on thermodynamic reasoning. However, the mineral plattnerite (PbO_2) occurs in some natural systems and is associated with other oxidation products such as cerussite and pyromorphite (e.g., Yeates and Ayres, 1892; see Figure 2.3). In general, the geochemical transport processes of lead are not directly tied to redox conditions. However, because lead may form stable precipitates with redox-sensitive elements such as sulfur, lead mobility is indirectly tied to redox conditions. In sulfate-reducing systems, lead is expected to form insoluble PbS precipitates. In moderately reducing but non-sulfidic systems, however, reductive dissolution of hydrous ferric oxides that contain adsorbed lead could result in lead mobilization.

Colloidal Transport

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

Site Characterization

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

Aqueous Measurements

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

Solid Phase Measurements

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

Table 2.1 Natural attenuation and mobilization pathways for lead.

Attenuation Processes	Mobilization Processes	Characterization Approach
Precipitation of insoluble carbonates, sulfides, sulfates, and phosphates. In general, pH>8 will drive precipitation reactions resulting in Pb concentrations to below the MCL.	Dissolution of carbonates at low pH; oxidative dissolution of sulfides at low pH and high Eh; complexation/stabilization in the presence of DOC.	Evaluation of lead speciation in the aqueous phase. Determination of total Pb in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Evaluation of long-term capacity.
Sorption to iron hydroxides (reversible), organic matter, carbonates, sulfides (pH>5).	Desorption at low pH; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides.	Evaluation of lead speciation in the aqueous phase. Determination of total Pb in the solid matrix. Evaluation of solid phase partitioning using sequential extraction methodologies. Batch and column testing to determine Pb uptake capacity of site-specific aquifer materials with variable geochemical conditions.

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

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

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

Pb Isotopes

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

Long-term Stability and Capacity

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

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

Tiered Analysis

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

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

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

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

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

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

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

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Nickel

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Occurrence and Distribution

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

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

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

Plume Characteristics

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

Remedial Technologies

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

Regulatory Aspects

In 2005, nickel was ranked 55 of 275 hazardous substances on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) National Priorities List (NPL) based on frequency of occurrence at NPL sites, toxicity, and potential for human exposure to the substances found at NPL sites (ATSDR, 2005; http://www.atsdr.cdc.gov/cercla/supportdocs/text.pdf). There are currently no primary or secondary drinking water standards (maximum contaminant level or MCL) in place for nickel in potable water sources (USEPA, 2006a; See also http://www.epa.gov/safewater/dwh/t-ioc/nickel.html). However, the health advisory for nickel, an estimate of acceptable drinking water levels for a chemical substance based on health effects information, via consumption of water has been set at 1 mg L^{-1} for one- and ten-day exposures for a child and 0.1 mg L^{-1} for a lifetime exposure for an adult (USEPA, 2006a; http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf). For non-potable water sources, ambient water quality criteria (AWQC) that are protective of aquatic life may serve as alternative cleanup goals. For nickel, current statutes list both acute and chronic criteria for fresh waters as 0.47 mg L^{-1} and 0.052 mg L^{-1}, respectively, for a water hardness of 100 mg L^{-1} (USEPA, 2006b; http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf). Adjustments to these criteria are to be applied for waters with different hardness. An example of where this criterion may apply is a site where contaminated ground water discharges to surface water.

Geochemistry and Attenuation Processes

Aqueous Speciation

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

Solubility

Nickel may be immobilized within ground water through formation of pure nickel precipitates such as hydroxides, silicates, or sulfides (Merlen et al., 1995; Mattigod et al., 1997; Scheidegger et al., 1997; Thoenen, 1999; Scheinost and Sparks, 2000; Peltier et al., 2006) or through coprecipitation with other soil forming minerals such as silicates, iron oxides/sulfides, or carbonates (Manceau et al., 1985; Manceau and Calas, 1986; Huerta-Diaz and Morse, 1992; Ford et al., 1999a; Hoffmann and Stipp, 2001). Predicted nickel concentrations in the absence of sulfide for several potential pure nickel precipitates are shown in Figure 3.1. These data suggest that phyllosilicate and layered double hydroxide (LDH) precipitates (incorporating aluminum) may result in dissolved nickel concentrations below most relevant regulatory criteria over a pH range typical for ground water.

These data also point to the limited capability of pure nickel carbonates and hydroxides in controlling dissolved nickel concentrations to sufficiently low values except under very alkaline conditions. In the presence of dissolved sulfide, the precipitation of a nickel sulfide may plausibly control the concentration of dissolved nickel. The Eh-pH conditions under which these solubility-limiting phases may form is shown in Figure 3.2. According to these data, nickel-bearing phyllosilicate and/or LDH precipitates possess large stability fields indicating their relative importance to controlling nickel solubility under a range of conditions. These calculations point to the importance of dissolved aluminum and silicon concentrations in ground water relative to the potential sequestration of nickel via precipitation (Ford et al., 1999b; Scheinost et al., 1999). As discussed below (see Adsorption section), the formation of these nickel-bearing precipitates may be facilitated through initial adsorption onto clay minerals within the aquifer.

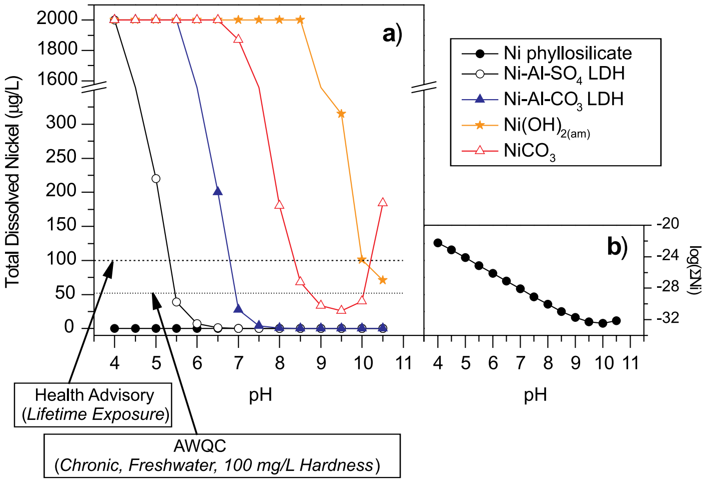

Figure 3.1 *(a) Predicted solubility of various Ni precipitates that could form in aerobic ground water with concentrations of Al and Si controlled by the solubility of the clay mineral, kaolinite. (Note y-axis break to expand lower end of scale.) (b) Expansion of dissolved Ni data for equilibrium with Ni phyllosilicate; plotted on logarithmic scale. Nominal ground-water composition: 0.005 mole/L NaCl, 0.001 mole/L K_2SO_4, 0.001 mole/L $MgNO_3$, 0.001 mole/L $CaCO_3$, and 34 µ mole/L Ni (2000 µg Ni/L). Model predictions using Visual MINTEQ Version 2.50 (Based on MINTEQA2 described in Allison et al. (1991); available at http://www.lwr.kth.se/English/OurSoftware/vminteq/) with solubility constants added for Ni phyllosilicate, Ni-Al-SO_4 LDH, and Ni-Al-CO_3 LDH (Peltier et al., 2006); total dissolved Ni concentrations modeled individually for each Ni solid phase by setting kaolinite as an 'infinite' solid and the Ni solid phase as a 'possible' solid for each pH titration.*

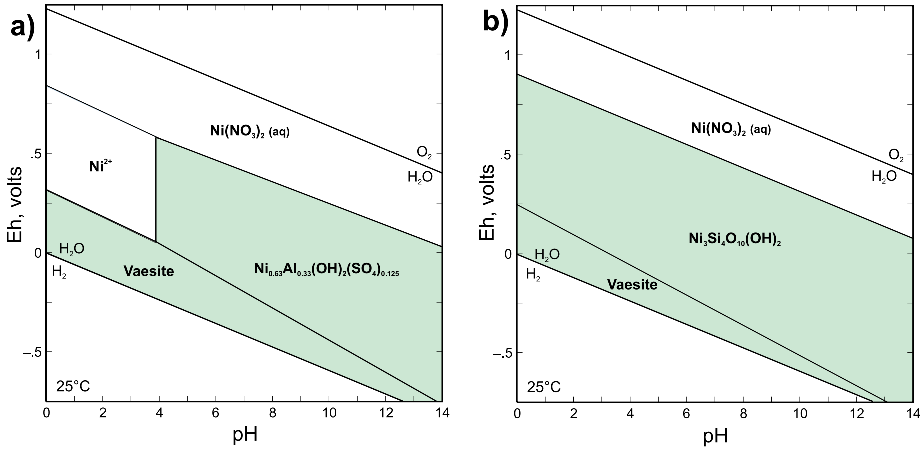

Figure 3.2 *Eh-pH diagrams for nickel at 25 °C. (a) System Ni-H_2O-Ca-Al-NO_3-HCO_3-SO_4 (2 mg Ni/L; 40 mg Ca/L; 3 mg Al/L; 6 mg NO_3/L; 60 mg HCO_3/L; 100 mg SO_4/L). Stability fields for solids are shaded green (Vaesite = NiS_2). (b) Same system plus 3 mg Si /L. Thermodynamic data for $Ni_3Si_4O_{10}(OH)_2$ and $Ni_{0.63}Al_{0.33}(OH)_2(SO_4)_{0.125}$ are from Peltier et al. (2006). [Note that the solubility of the Ni-Al-SO_4 LDH was adjusted to correct for charge imbalance for the chemical structure published in Peltier et al. (2006).]*

Attenuation of nickel may also occur via coprecipitation during the formation of (hydr)oxides or sulfides of iron. These minerals have been observed to form at the boundaries between oxidizing and reducing zones within ground-water plumes. There are numerous laboratory and field observations that demonstrate the capacity of these precipitates for nickel uptake (Schultz et al., 1987; Huarta-Diaz and Morse, 1992; Coughlin and Stone, 1995; Ford et al., 1997; Ford et al., 1999a). Under these circumstances, the solubility of nickel will depend on the stability of the host precipitate phase. For example, iron oxide precipitates may alternatively transform to more stable forms (Ford et al., 1997), stabilizing coprecipitated nickel over the long term, or these precipitates may dissolve concurrent with changes in ground-water redox chemistry (e.g., Zachara et al., 2001).

Adsorption

Adsorption of nickel in soil environments is dependent on pH, temperature, and type of sorbent (minerals or organic matter), as well as the concentration of aqueous complexing agents, competition from other adsorbing cations, and the ionic strength in ground water. Nickel has been shown to adsorb onto many solid components encountered in aquifer sediments, including iron/manganese oxides, clay minerals (Dähn et al., 2003; Bradbury and Baeyens, 2005), and solid organic matter (Nachtegaal and Sparks, 2003). Sorption to iron/manganese oxides and clay minerals has been shown to be of particular importance for controlling nickel mobility in subsurface systems. The relative affinity of these individual minerals for nickel uptake will depend on the mass distribution of the sorbent minerals as well as the predominant geochemical conditions (e.g., pH and nickel aqueous speciation). For example, the pH-dependent distribution of nickel between iron and manganese oxides [hydrous ferric oxide (HFO) and a birnessite-like mineral (nominally MnO_2)] for a representative ground-water composition is shown in Figure 3.3a. Based on the available compilations for surface complexation constants onto these two solid phases (Dzombak and Morel, 1990; Tonkin et al., 2004), one would project the predominance of nickel sorption to MnO_2 at more acidic pH and the predominance of HFO (or ferrihydrite) at more basic pH. With increasing mass of MnO_2, the solid-phase speciation of nickel will be progressively dominated by sorption to this phase. There are examples of the relative preference of nickel sorption to manganese oxides over iron oxides for natural systems (e.g., Larsen and Postma, 1997; Manceau et al., 2002; Kjoller et al., 2004; Manceau et al., 2006). As shown in Figure 3.3b, nickel adsorption may be inhibited (or nickel desorption enhanced) through the formation of solution complexes with organic ligands such as EDTA or natural organic matter (e.g., Bryce and Clark, 1996; Nowack et al., 1997). These dissolved compounds may be present as natural components within ground water or as co-contaminants within a contaminant plume (e.g., Means et al., 1978).

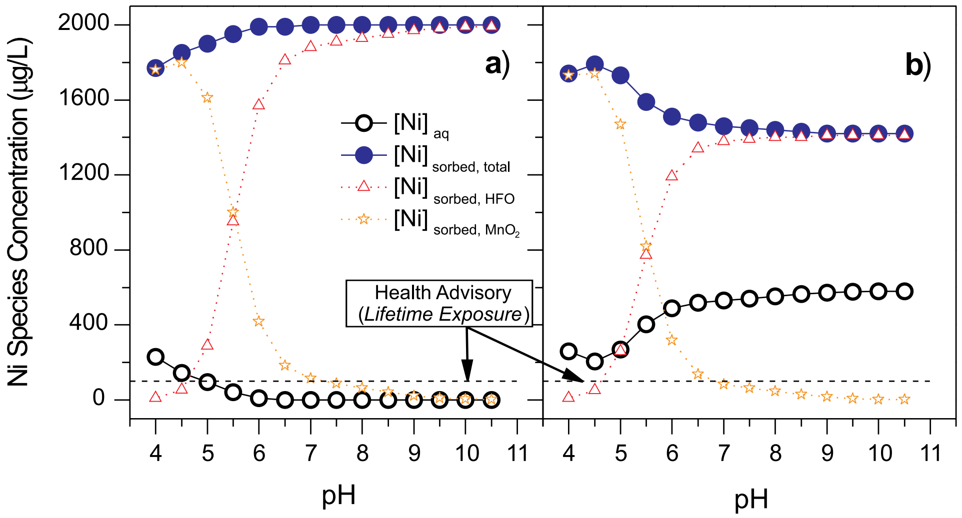

Figure 3.3 *(a) Nickel sorption as a function of pH in the presence of an hypothetical aquifer sediment with iron and manganese oxides reflective of the crustal abundance of these elements (Schulze, 2002; assumed 30% porosity with 185.0 g HFO/L and 1.66 g MnO_2/L). (b) Same conditions as in (a), but with 10 µM EDTA added. Nominal ground-water composition: 0.005 mole/L NaCl, 0.001 mole/L K_2SO_4, 0.001 mole/L $MgNO_3$, 0.001 mole/L $CaCO_3$, and 34 µ mole/L Ni (2 mg Ni/L). Model predictions using Visual MINTEQ Version 2.50 (Based on MINTEQA2 described in Allison et al. (1991); available at http://www.lwr.kth.se/English/OurSoftware/vminteq/) with available surface complexation parameters derived from Dzombak and Morel (1990) and Tonkin et al. (2004); kaolinite set as an 'infinite' solid for pH titration.*

Table 3.1 Natural attenuation and mobilization pathways for nickel.

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

As previously noted, adsorption of nickel onto mineral surfaces may serve as a precursory step to the formation of trace precipitates that reduce the potential for desorption with changes in ground-water chemistry. This may be realized through the nucleation and growth of surface precipitates on clay mineral surfaces due to continued uptake of nickel (Scheckel and Sparks, 2000; Scheckel et al., 2000; Scheckel and Sparks, 2001; Dähn et al., 2002). This type of process may compete with other adsorption processes, such as ion exchange, depending on the prevailing ground-water chemistry and characteristics of the clay mineral (Elzinga and Sparks, 2001).

Site Characterization

Overview

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

Aqueous Measurements

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

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

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

Solid Phase Measurements

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

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

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

Long-term Stability and Capacity

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

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

Tiered Analysis

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

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

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

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

It is recommended that identification of nickel chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the in-situ distribution of dissolved nickel and mineralogy and prevents loss of nickel from aqueous samples (e.g., due to oxidation and precipitation of ferrous iron in anoxic ground water).

The demonstration of concurrence between conceptual and mathematical models describing nickel transport will entail development of site-specific parameterization of the chemical processes controlling nickel solid phase partitioning.

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

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

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Copper

Richard T. Wilkin

Occurrence and Distribution

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

It is believed that the ancient civilizations of Mesopotamia (region of modern Iraq) made use of native copper and gold, possibly as far back as ca. 8700 BC. Indeed the exploitation of natural deposits of copper and gold, which are soft metals that can be hammered into shape without heat, marked the transition from the Stone Age to more modern ways of life (Diamond, 1997). Typical copper-bearing minerals include native copper, sulfides (chalcopyrite, $CuFeS_2$; bornite, Cu_5FeS_4; chalcocite, Cu_2S; covellite, CuS; digenite, Cu_9S_5), sulfosalts (tetrahedrite, $Cu_{12}Sb_4S_{13}$), carbonates (malachite, $Cu_2(OH)_2CO_3$; azurite, $Cu_3(OH)_2(CO_3)_2$), and oxides (tenorite, CuO). In the US, the principal copper mining states are Arizona, Utah, and New Mexico. In 2004, domestic mine production of copper was about 1.16 million tons, or about 8% of world mine production. While the US is the world's second-largest producer of copper, it is the world's largest copper-consumer. The principal modern use of copper is as an electrical conductor. Alloys of copper (e.g., brass and bronze) are used in jewelry, sculptures and for minting coins. Copper also has broad uses as an agricultural poison and as an algaecide in water purification.

Plume Characteristics

Copper has five possible oxidation states (0, +1, +2, +3, and +4). Under most conditions, copper is present in aqueous solution as the divalent cation, Cu^{2+}, or as Cu(II) hydroxide or carbonate complexes. However, copper is not especially mobile in aquatic environments due to the relatively low solubility of Cu(II)-bearing solids and high affinity of copper for mineral and organic surfaces. Certain organic compounds are able to keep copper soluble by ligand complexation. Hence, copper does not typically enter ground water except under conditions of low pH or high ligand concentrations. Where present, copper contamination in soils and ground water stems primarily from mining activities, metal production, wood production, fertilizer production, and combustion of fossil fuels and wastes (e.g., Bocheńska et al., 2000; Zagury et al., 2003).

Copper is not included on the CERCLA Priority List of Hazardous Substances, which is based on the frequency of occurrence of specific contaminants at National Priorities List (NPL) sites and their potential threat to human health. An internet search showed, however, that in 2005 copper was listed as a potential contaminant of concern (COC) in ground water at 287 NPL sites in EPA Regions 1-10.

Remedial Technologies

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

Regulatory Aspects

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

Geochemistry and Attenuation Processes

Aqueous Speciation

Copper complexes are possible in the +1, +2, +3, and +4 valence states. Copper(III) and (IV) complexes are rare and unstable in water. Cu(I) complexes are present under reducing conditions but in general cuprous ions are highly insoluble in water. Cu(II) is the main oxidation state for soluble complexes of copper in aquatic environments. Cu(II) forms complexes with both hard (e.g., CO_3^{2-}, SO_4^{2-}, OH^-, and Cl^-) and soft (e.g., S^{2-}, I^-) bases (Stumm and Morgan, 1996). The stereochemistry of Cu(II) principally involves distorted tetragonal (coordination number 4) or octahedral (coordination number 6) configurations. Cu(II) complexes are subject to the Jahn-Teller effect that acts to stabilize species with the d^9 electronic configuration that are present in tetragonal or octahedral coordination.

In pure water, Cu^{2+} is the predominant ion below pH 7. Above this pH, the species $CuOH^+$, $Cu(OH)_2^0$, and CuO_2^{2-} become increasingly important. Because of uncertainties in the estimates and measurements of the thermodynamic constants for copper complex formation, the speciation of copper in natural waters is not known in detail (e.g., Boyle, 1979; Leckie and Davis,1979; Baes and Mesmer, 1976). Most models, however, predict that Cu^{2+} is a small fraction of the total copper concentration in freshwater and seawater systems and that complexed forms of copper are dominant.

A survey of references that report hydrolysis constants for Cu^{2+} shows considerable variability in species identified and in their formation constants (see e.g., Baes and Mesmer, 1976; Leckie and Davis, 1979 and references therein). Figure 4.1 shows the pH-dependent distribution of Cu^{2+} hydrolysis species based on the Lawrence Livermore National Laboratory thermodynamic database (thermo.com.v8.r6+), along with the pH-dependent solubility of tenorite (CuO) and the metastable solid, $Cu(OH)_2$, based on data in Hidmi and Edwards (1999). Both CuO and $Cu(OH)_2$ are insoluble at neutral to alkaline pH. Below pH of 6 to 7, dissolution of these phases would yield Cu^{2+} concentrations above the MCL of 1.3 mg L^{-1} ($10^{-4.7}$ molal). Stable complexes of Cu^{2+} with SO_4^{2-} ($CuSO_4^0$) and CO_3^{2-} ($CuCO_3^0$) may contribute significantly to total copper at anion concentrations typically encountered in ground water. In environments with high ammonia concentrations, copper can be significantly bound to ammonia at pH>6.

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

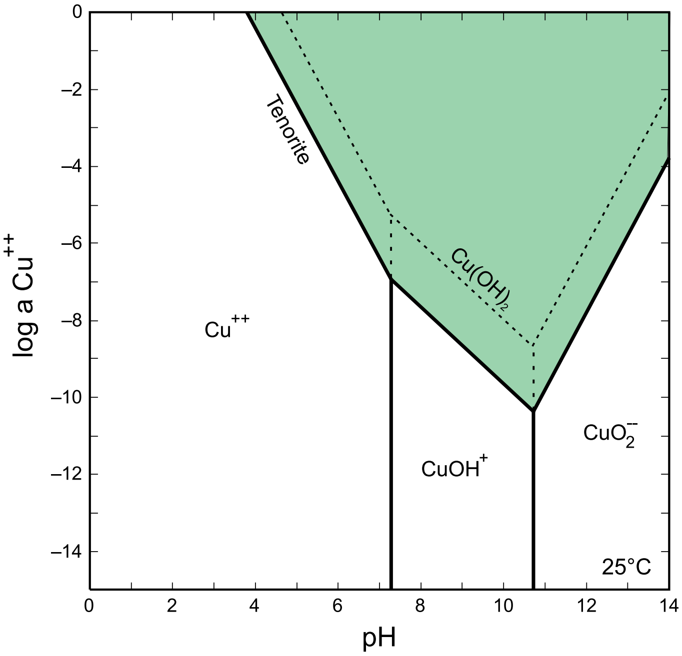

Figure 4.1 *Solubility of copper oxide and copper hydroxide as a function of pH in the system Cu-O-H at 25 °C.*

Solubility

An Eh-pH diagram for copper is shown in Figure 4.2. Inspection of this diagram indicates that at the specified conditions Cu^{2+} is the soluble form of copper at pH<6 and in moderately to highly oxidizing systems. Consequently, upon weathering, copper is likely to be more mobile under acidic rather than alkaline conditions (see, e.g., Paulson and Balistrieri, 1999). Copper hydroxycarbonate (malachite) has a narrow stability field at near-neutral pH and at moderately to highly oxidizing conditions. With increasing inorganic carbon concentrations, the malachite stability field would expand. At neutral to alkaline pH (>7) copper oxides are stable. With progressively more reducing conditions, cuprous oxide and elemental copper develop broad stability fields. Finally, in highly reducing and sulfidic environments, copper sulfides (chalcocite and covellite) are stable over a wide pH range. Aquifer materials usually contain some organic matter as well as sulfate from ground water. Microbial degradation of organic matter can be coupled to sulfate reduction with the production of hydrogen sulfide. Because of the extreme insolubility of copper sulfides, no complexing ligand can compete with hydrogen sulfide or metal sulfide surfaces for copper (Rose, 1989). In addition, there are several fairly common copper-iron-sulfur minerals such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), and cubanite ($CuFe_2S_3$). Note that in solutions with high chloride concentrations (>1 M), the field of soluble copper in Figure 4.2 expands substantially due to the very strong nature of copper chloride complexes.

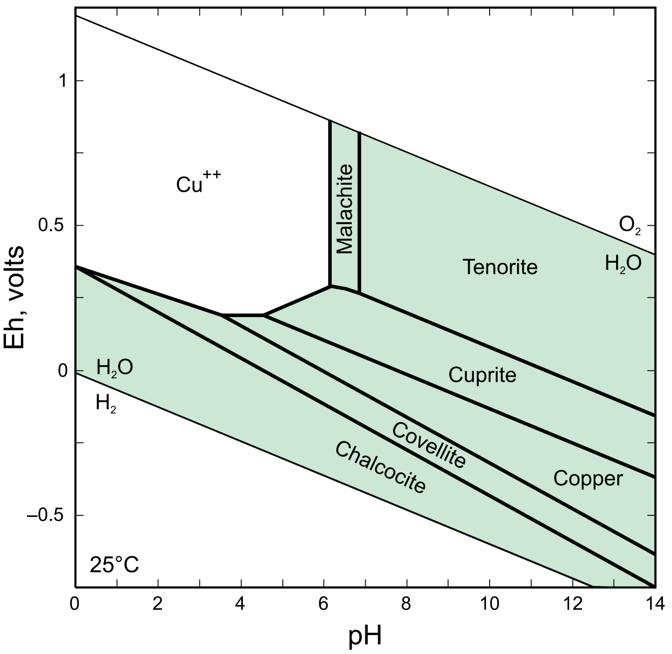

Figure 4.2 *Eh-pH diagram for copper at 25 °C (total inorganic carbon = 10^{-2} molal; total sulfur = 10^{-3} molal; total copper = 10^{-5} molal).*

Cavallaro and McBride (1980) found that in alkaline soils copper was present as $Cu(OH)_2$ and with progressive aging, copper solubility decreased consistent with the formation of $Cu_2(OH)_2CO_3$. In general, they concluded that Cu^{2+} solubility in soil is highly correlated to pH. Dudley et al. (1991) proposed the formation of CuO in soil reacted with an extract of acid mine waste. In both the studies of Cavallaro and McBride (1980) and Dudley et al. (1991), proposed copper phase associations are based on a comparison of observed pH-dependent copper concentrations with solubility estimates based on thermodynamic data. Indeed, Leckie and Davis (1979) suggest that in most soil environments malachite and tenorite are the most important copper-bearing phases, with $Cu(OH)_2$ present as a metastable precursor to malachite and tenorite.

The stability relationships between copper hydroxycarbonates and oxides are shown in Figure 4.3 in terms of pH and CO_2 fugacity. Note that at high pH and CO_2 fugacity, aqueous copper carbonate complexes predominate over hydroxyl complexes. The diagram illustrates that over the pH and f CO_2 conditions in most ground water systems, tenorite and malachite are the expected stable copper minerals.

Adsorption

McBride and Bouldin (1984) examined the solid-phase properties of copper in copper-contaminated soil. They concluded that long-term reaction of copper with calcareous soil failed to convert copper into a form unavailable to plants. Chemical extraction tests suggested that copper was mainly present in a non-exchangeable form easily dissolved by organic chelating compounds. An analysis of pH-dependent solubility data revealed that copper was present as an inorganic form in the soil, possibly tightly adsorbed on surfaces as hydroxyl or hydroxycarbonate species. Greater than 99.5% of the copper in the soil solution was complexed, probably with soluble organic compounds (McBride and Bouldin, 1984). In contrast, Cavallaro and McBride (1978) found that low pH soils are less effective in retaining Cu^{2+} compared to neutral soils and calcareous soils. They concluded that this behavior was in part related to increased competition at low pH for organic functional groups by aluminum and/or protons thus reducing the ability of Cu^{2+} to be adsorbed onto solid organic matter.

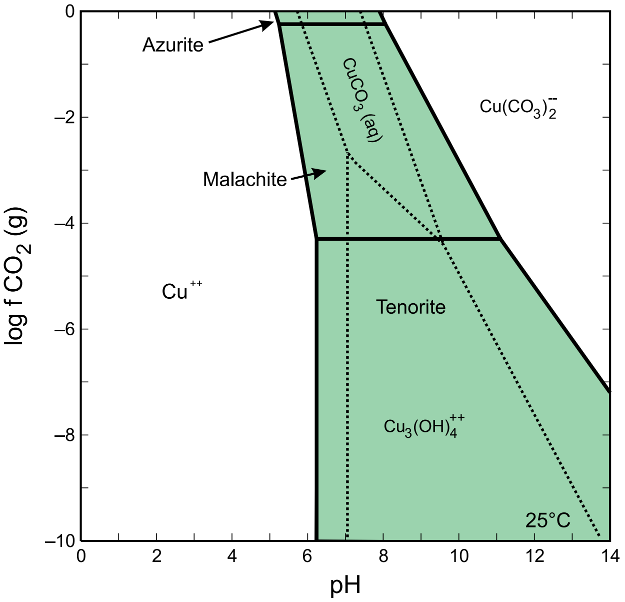

Figure 4.3 *Solubility and speciation of copper as a function of pH and log fugacity of CO_2(gas) at 25 °C. Solid lines separate stable phases and dotted lines separate aqueous species (total copper = 10^{-5} molal). Diagram drawn using thermodynamic data from MINTEQA2.*

Based on the solubility and sorption behavior of copper, it is expected that over a wide range of geochemical conditions copper will be effectively stable in the solid phase of soils and sediment materials. Copper has a strong affinity for the surfaces of iron oxides and hydroxides (e.g., Benjamin and Leckie, 1981; Robertson and Leckie, 1998; Martínez and McBride, 1998), clays (e.g., Pickering, 1980; Farqhar et al., 1997; Morton et al., 2001), sulfides (e.g., Pattrick et al., 1997; Parkman et al., 1999), and organic matter (e.g., Sauvé et al., 1997; Schilling and Cooper, 2004). As well as being less soluble, Cu^{2+} is more strongly adsorbed to mineral substrates than Zn^{2+}, Ni^{2+}, and Cd^{2+}.

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

Redox Chemistry

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

$$Cu^{2+} + e^{-} = Cu^{+} \qquad (\log K = 2.72)$$

In natural systems the stable solid in very reducing conditions is expected to be cuprous sulfide (Cu_2S, chalcocite, see Figure 4.2). As the Eh increases there is a narrow window in which cupric sulfide (CuS, covellite) becomes important. Further increases in Eh can lead to the formation of elemental copper. So in general the solubility and speciation of copper are determined by redox equilibria of sulfur and copper and the strength of available ligands. Experimental studies of Cu(I) complexation by chloride and bisulfide are presented in Xiao et al. (1998), Thompson and Helz (1994), Mosselmans et al. (1999), and Mountain and Seward (1999, 2003). Luther et al. (2002) show that the reduction of Cu(II) to Cu(I) occurs in sulfidic solutions prior to the precipitation of copper sulfides.

Colloidal Transport

Recent studies are consistent in demonstrating that copper in ground water is frequently associated with colloids that appear to be organic in nature (Sañudo-Wilhelmy et al., 2002; Jensen et al., 1999; Freedman et al., 1996; Pauwels et al., 2002). The association between metals and ground water colloids is evident both in uncontaminated groundwater (e.g., Sañudo-Wilhelmy et al., 2002) and in contaminated landfill leachates and in ground water impacted by mining districts (e.g., Jensen et al., 1999; Pauwels et al., 2002). Jensen et al. (1999) found that 86-95% of total copper in landfill leachate was associated with small-size colloidal matter and organic molecules. They concluded that most metals, including copper, present in the colloidal forms would have been sampled in the dissolved fraction if the commonly employed filter size of 0.45 μm had been used, since only negligible amounts of metal were found with colloids >0.40 μm. Pauwels et al. (2002) found that the mobility of copper in ground water impacted by the oxidative dissolution of massive sulfide deposits in the Iberian Pyrite Belt (Spain) was especially enhanced due to complexation with organic matter and/or adsorption onto colloids. For example, measured concentrations of copper were 10^8 to 10^9 times greater than concentrations modeled assuming equilibrium with respect to sulfide minerals (e.g., chalcopyrite).

Site Characterization

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

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

While regulatory requirements stipulate that unfiltered ground-water samples be analyzed to support regulatory decisions at a contaminated site, it may be necessary to also collect filtered samples to help interpret that process(es) controlling contaminant mobility. The use of 0.45 μm pore size filter paper is common as an arbitrary cutoff point to differentiate between dissolved and particulate phases in water samples. However, caution is recommended when using this approach, particularly for Fe and Al and other elements that may be associated with Fe or Al particles (including Cu) that could pass through 0.45 μm filter papers. The use of filter papers with pore sizes less than 0.1 μm will generally provide a better assessment of the dissolved vs. particulate load of a ground water or a surface water sample.

Hickey and Kittrick (1984) examined the chemical partitioning of copper in soils and sediments containing high levels of heavy metals using the selective extraction approach developed by Tessier et al. (1979). In this study, copper was assigned to five operationally defined geochemical fractions: exchangeable, bound to carbonates, bound to Fe- and Mn-oxides, bound to organic matter, and residual. This study concluded that copper was the metal most significantly associated with organic matter. Compared to other heavy metals considered in this study (nickel, and zinc), copper displayed a low potential for mobility and metal bioavailability (Hickey and Kittrick, 1984).

Long-Term Stability and Capacity

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

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

Tiered Analysis

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

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

Table 4.1 Natural attenuation and mobilization pathways for copper.

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

or sulfide. This provides justification for proceeding to Tier II characterization efforts.

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

1) Determination of solution speciation via direct analytical measurements (e.g., Martinez et al., 2001; Sañudo-Wilhelmy et al., 2002) to aid differentiation of uncomplexed (i.e., Cu^{2+}) and complexed (e.g., $CuCl^+$, Cu-organic ligand complexes) forms of mobile Cu in combination with speciation calculations based on characterized ground-water chemistry;
2) Calculation of the saturation state of ground water relative to measured aqueous chemistry complimented by the possible isolation of discrete Cu mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;
3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Cu sorption (e.g., Amonette, 2002; Burton et al., 2005); and
4) Determination of Cu-sediment associations via chemical extractions designed to target specific components within the aquifer sediment (e.g., Lee et al., 2005).

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

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

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

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Chromium

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Occurrence and Distribution

The average crustal abundance of chromium (Cr) is approximately 100 micrograms per gram. Chromium is much less abundant than vanadium and manganese (Mn), which are its nearest neighbors on the periodic table, but more abundant than the other first-row transition elements cobalt (Co), nickel, copper, and zinc. Chromium is a group VI transition metal, whose name refers to the variety of colors associated with its various oxidation states. Only two of these oxidation states are known to occur naturally. In minerals that crystallized in the earth's interior Cr occurs exclusively in the plus 3 oxidation state (Cr(III)). In aquatic systems at pH values above 2 and in the presence of oxygen, Cr(III) is thermodynamically unstable compared to the plus 6 oxidation state (Cr(VI)) and, therefore, is subject to oxidation to Cr(VI).

Minerals containing Cr(VI) are rare. The best known is the lead (Pb) chromate mineral crocoite ($PbCrO_4$), which occurs as spectacular red-orange crystals in the oxidized regions of some Pb deposits. It is from this mineral that Cr was first isolated and identified. Several other Cr(VI) minerals have been identified in evaporite deposits; those from the Atacama Desert in South America account for most of these minerals. These evaporite minerals include chromate (CrO_4^{2-}) or dichromite ($Cr_2O_7^{2-}$) combined with sodium (Na), potassium (K), calcium (Ca), or barium (Ba) with varying amounts of sulfate or other anions.

Chromium(VI) has been found to occur naturally in ground water underlying the arid Paradise Valley in Arizona, USA, at concentrations as high as hundreds to thousands of micrograms per liter (µg L^{-1}) (ones to tens of micromoles per liter, µM) (Robertson, 1975). The ground water was oxic, had alkaline pH values, moderate concentrations of dissolved salts, and was likely very old. More recently, Cr(VI) has been detected in ground water with similar chemical characteristics underlying arid or semi-arid basins in California. As discussed further below, oxic ground water with neutral-to-alkaline pH values and moderate-to-high concentrations of other anions, such as sulfate, possesses the chemical conditions that favor the persistence of Cr(VI) and promote its mobility.

Remedial Technologies

The goal of remediation schemes is to reduce the carcinogenic, soluble, and mobile Cr(VI) to the less toxic and less mobile Cr(III), which forms minimally soluble precipitates. Successful treatment of Cr(VI) hinges upon the formation and stability of Cr(III) precipitates. Ex-situ treatment technologies for ground water commonly use pump-and-treat approaches with chemical reduction of the Cr(VI) to Cr(III) followed by precipitation. In-situ technologies currently used for remediation of Cr(VI) contamination employ some form of chemical reduction and fixation (e.g., geochemical fixation, permeable reactive barriers (PRBs), and reactive zones established through chemical injections). There is fairly extensive performance data available to evaluate the potential for use of PRBs constructed using zerovalent iron (Wilkin and Puls, 2003).

Regulatory Aspects

Cr(VI) is considered teratogenic (Abbasi and Soni, 1984), mutagenic (Paschin et al., 1983) and carcinogenic (Ono, 1988). According to the International Agency for Research on Cancer (IARC), Cr(VI) is considered a powerful carcinogen and its presence in waters is cause for concern. The national primary drinking water standard set by the USEPA for total Cr is 0.1 mg L^{-1} (USEPA, 2006a). The state of California maximum contaminant level in water is 50 µg L^{-1}. No separate drinking water standard for Cr(VI) has been established, but a separate standard has been discussed for some time. For non-potable water sources, ambient water quality criteria (AWQC) that are protective of aquatic life may serve as alternative cleanup goals. For Cr(VI), current statutes list both acute and chronic criteria for fresh waters as 0.016 mg L^{-1} and 0.011 mg L^{-1}, respectively, for a water hardness of 100 mg L^{-1} (USEPA, 2006b). Adjustments to these criteria are to be applied for waters with different hardness. An example of where this criterion may apply is a site where contaminated ground water discharges to surface water.

Geochemistry and Attenuation Processes

Aqueous Speciation

Aqueous speciation of Cr(VI) varies with pH and Cr(VI) concentration (Palmer and Puls, 1994). The dominant aqueous species above pH 6 is CrO_4^{2-}. The dominant species between pH 0 and 6 is $HCrO_4^-$ at Cr(VI) concentrations below approximately 0.003 moles L^{-1} (160 mg L^{-1}) and $Cr_2O_7^{2-}$ at higher Cr(VI) concentrations. The species H_2CrO_4 is dominant only at pH < 0 (i.e., under extremely acidic conditions). In the presence of Ca or iron in the plus

3 oxidation state (Fe(III)), solubility studies indicate the formation of $CaCrO_4^0$ and $FeCrO_4^-$ as solution complexes (Perkins and Palmer, 2000; Baron and Palmer, 1996).

At near-neutral pH values, Cr(III) concentrations in equilibrium with $Cr(OH)_3$ are less than 0.1 µM (approximately 5 µg L^{-1}); concentrations increase with decreasing pH below 7 and increasing pH above 11 (Palmer and Puls, 1994). The dominant solution species below pH 3.5 is Cr^{3+}; at these low pH values Cr(III) can be mobile and appreciable concentrations of Cr(III) may be observed (Seaman et al., 1999). As pH increases, the dominant species changes through a sequence of hydrolysis products: $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, $Cr(OH)_4^-$ (Rai et al., 1987). Oligomers like $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$ may form as metastable species at mildly acidic to near-neutral pH values and moderate Cr(III) concentrations (Baes and Mesmer, 1976).

Cr(III) forms strong complexes with a variety of organic ligands. Once formed, slow exchange of inner-coordination-sphere ligands around Cr(III) may result in the persistence of Cr(III)-organic complexes under conditions where they are thermodynamically unstable This may account for reports of elevated concentrations of Cr(III) at near-neutral pH values and high concentrations of organics in a Cr-contaminated wetland (Mattuck and Nikolaidis, 1996), tannery effluent (Walsh and O'Halloran, 1996), and organic soil or landfill leachates (Li and Xue, 2001).

Solubility

Chromium(VI) forms soluble compounds with the alkali (Na, K) and alkaline earth (Mg, Ca) metal cations that are typically present at the highest concentrations in ground water. It does form a sparingly soluble salt with barium Ba, which is ubiquitous in ground water but usually present at trace concentrations; the mineral hashemite ($Ba(Cr,S)O_4$) is known from at least one location. The importance of $BaCrO_4$ at sites with Cr(VI)-contamination has been suggested by the agreement between ground-water Cr(VI) concentrations and those calculated based on $BaCrO_4$ solubility (Baron and Palmer, 1996). Equilibrium computations suggest that a significant fraction of Cr(VI) could be present as $BaCrO_4$ at neutral and alkaline pH values if there is an adequate source of Ba (Figure 5.1). Barite ($BaSO_4$) was used as the source of Ba used in the computations in Figure 5.1; Ba concentrations in equilibrium with barite are independent of pH in the range shown in Figure 5.1. Another potential source of Ba in ground water is the dissolution of aluminosilicate minerals. These dissolution reactions are typically acid-catalyzed and, therefore, the mass of Ba available from these reactions should increase with decreasing pH. Chromium(VI) also forms sparingly soluble salts with a variety of heavy metal ions, of which Pb ($PbCrO_4$) is the most important by virtue of the fact that it has been identified at Cr(VI)-contaminated sites (Palmer and Wittbrodt, 1991).

Other Cr(VI) compounds can form at very low or very high pH values. A laboratory experimental study showed the formation of Fe(III) hydroxy chromates mixed with hydrous ferric oxide in the pH range 1.5 to 3.5 (Olazabal et al., 1997). $KFe_3(CrO_4)_2(OH)_6$, a chromate analogue to jarosite, has been identified in acidic, Cr(VI)-contaminated soil (Baron et al., 1996). The results of equilibrium calculations, based on thermodynamic data for Cr(VI) species and solids from Baron and Palmer (1998) suggest that this solid is stable below pH 3 (Figure 5.2). Formation of $KFe_3(CrO_4)_2(OH)_6$ in the equilibrium computations was driven by high concentrations of Fe(III), which, in turn, were driven by increased solubility of soil hydrous ferric oxide with decreasing pH. The predicted distribution of Cr(VI) between the aqueous and solid phases at low pH is sensitive to the values assumed for the solubility of hydrous ferric oxide and the total concentrations of K and Cr(VI).

A Cr(VI) analogue of the Ca, aluminum (Al), carbonate mineral ettringite (viz., $Ca_6[Al(OH)_6]_2(CrO_4)_3 \bullet 26H_2O$) was observed in Cr(VI)-contaminated concrete, as was a nearly pure Cr(VI) hydrocalumite (viz., $3[CaO][Al_2O_3][CaCrO_4] \bullet nH_2O$) (Palmer, 2000). Laboratory experiments showed that Cr(VI)-ettringite precipitated from Ca- and Al-containing solutions at pH values greater than 10 (Perkins and Palmer, 2000). In systems where there is an excess of carbonate over the available Ca, Cr(VI)-ettringite is thermodynamically unstable with respect to calcite and gibbsite at high pH. Therefore, Cr(VI)-ettringite and related minerals are most likely to be important in systems at high pH where there is a large excess of Ca over carbonate or where precipitation of calcium carbonate is inhibited.

Concentrations of Cr(III) in aqueous systems are limited by the low solubility of $Cr(OH)_3$ (Rai et al., 1987). Coprecipitation of Cr(III) with hydrous ferric oxide drives Cr(III) concentrations lower and expands the pH range over which Cr(III) concentrations are very low (Palmer and Puls, 1994; Sass and Rai, 1987).

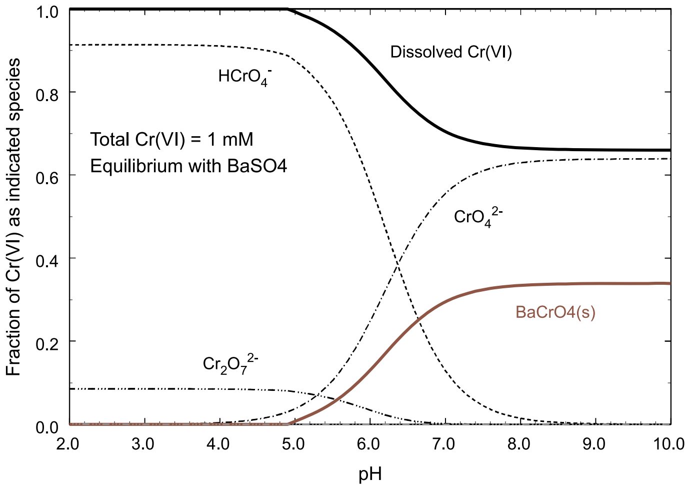

Figure 5.1 *Distribution of 1 mM (millimoles per liter, which equals approximately 52 mg L^{-1}) chromium(VI) plotted as a function of pH in equilibrium with barite. Thermodynamic data for aqueous Cr(VI) species from Baron and Palmer (1998) and for $BaCrO_4$ and $BaSO_4$ from Smith and Martell (1989).*

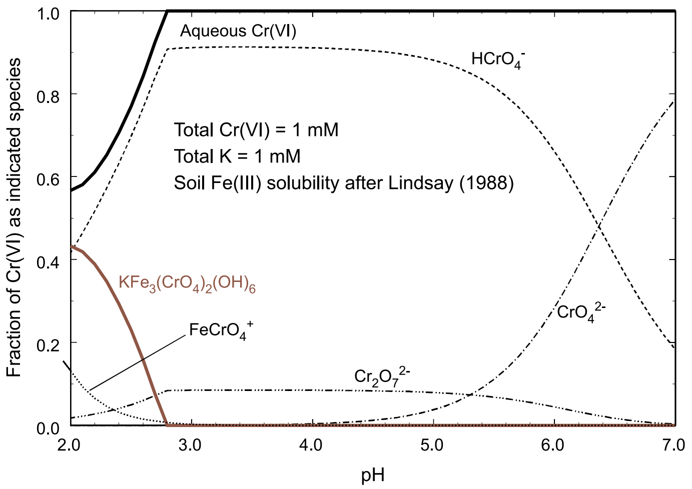

Figure 5.2 *Calculated distribution of 1mM Cr(VI) (approximately 52 mg L^{-1}) in the presence of 1 mM K (approximately 39 mg L^{-1}) and hydrous ferric oxide calculated as a function of pH. Thermodynamic data for aqueous and solid phase Cr(VI) from Baron and Palmer (1998) and for soil hydrous ferric oxide solubility from Lindsay (1988).*

Adsorption

Adsorption of Cr(VI) results from chemical reactions between aqueous Cr(VI) species and sites at mineral surfaces. Adsorption becomes more favorable with decreasing pH because many of the Cr(VI) adsorption reactions consume H^+ and the electrostatic contribution to adsorption onto some important adsorbents becomes more favorable at lower pH values (Dzombak and Morel, 1990). The intensity of binding of Cr(VI) at the mineral-water interface is intermediate between those of strongly binding anions, like phosphate and arsenate, and weakly binding anions like sulfate (Davis and Kent, 1990). As a result, other anions may out-compete Cr(VI) for adsorption sites depending on their concentrations relative to Cr(VI) and the pH. Such competitive effects can give rise to complex dependencies of adsorption on pH and solute concentrations. This effect is illustrated in Figure 5.3. Adsorption of Cr(VI) onto freshly precipitated hydrous ferric oxide (HFO) was determined over a range of pH values and in the presence of different concentrations of sulfate (Leckie et al., 1984). In the absence of sulfate, dissolved concentrations of Cr(VI) decrease with decreasing pH and, therefore, so should the mobility of Cr(VI). As concentrations of sulfate increase, competition for adsorption sites shifts in favor of sulfate and Cr(VI) adsorbs less extensively. Thus, Cr(VI) mobility increases with increasing concentrations of sulfate and, at constant sulfate, it first decreases then increases with decreasing pH (Figure 5.3). Other naturally occurring oxyanions, such as carbonate and silicate, also compete with Cr(VI) for adsorption sites (van Geen et al., 1994; Zachara et al., 1987). In Cr(VI)-contaminated ground water, competitive adsorption with other anions, such as arsenate, phosphate, vanadate (Leckie et al., 1984), or organic acids (Mesuere and Fish, 1992) may produce similar effects. The influence of pH and anion concentration on mobility of Cr(VI) has been demonstrated in field-scale transport experiments in a sand and gravel aquifer whose adsorption properties were dominated by hydrous Fe- and Al-oxide coatings on quartz and feldspar grains (Davis et al., 2000; Kent et al., 1995, 1994). Thus, the mobility of Cr(VI) should be expected to vary with aquifer chemistry.

The affinity of soils and sediments for adsorption of Cr(VI) varies widely depending on composition. Laboratory column experiments have shown that adsorption of Cr(VI) during transport is greatly enhanced by increasing abundance of hydrous ferric oxide in sediments (Martin and Kempton, 2000; Stollenwerk and Grove, 1985). Adsorption of Cr(VI) onto aquifer sediment whose grain surfaces were coated with Fe- and Al-containing hydrous oxides was significantly less extensive than expected from adsorption onto pure hydrous oxides of Fe or Al (Kent et al., 1995). Adsorption of Cr(VI) over a range of pH values onto four different soils varied from essentially no adsorption to extensive adsorption (Zachara et al., 1989); all four soils had high contents of clay-sized minerals and high specific surface areas. Results of these studies show that Cr(VI) adsorption onto soils or sediments cannot be predicted *a priori* and, therefore, must be determined experimentally using site-specific materials.

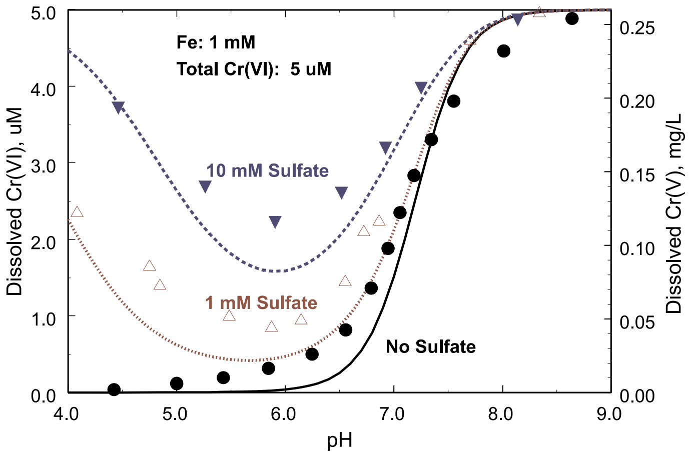

Figure 5.3 *Concentration of dissolved Cr(VI) in equilibrium with Cr(VI) adsorbed on freshly precipitated hydrous ferric oxide. The Fe concentration of 1 mM corresponds to approximately 90 mg FeOOH/L. The 5 µM Cr(VI) concentration corresponds to approximately 260 µg/L. Sulfate concentrations of 1 mM and 10 mM correspond to 96 and 960 mg SO_4/L, respectively Continuous curves calculated from the model for adsorption onto hydrous ferric oxide of Dzombak and Morel (1990). Experimental data from Leckie et al. (1986).*

Redox Chemistry

Reduction of Cr(VI) to Cr(III) is a potentially important mechanism for natural attenuation of Cr in ground water. Research on this topic has contributed to identifying potential Cr(VI) reductants and identifying how the rate and extent of reaction varies with changes in solution and other conditions. Reduction of Cr(VI) in aqueous solution is promoted by low pH and dissolved organic carbon (Stollenwerk and Grove, 1985). Dissolved Fe(II) reduces Cr(VI) rapidly over a wide range of solution conditions (e.g., Buerge and Hug, 1997; Eary and Rai, 1988). The rate of reduction by aqueous Fe(II) decreases with decreasing temperature; the effect of temperature is more pronounced at near-neutral than at low pH (Sedlak and Chan, 1997). Dissolved sulfide (e.g., Pettine et al., 1998), sulfur-containing dissolved organic compounds (Schroeder and Lee, 1975), and hydrogen sulfide gas (Thornton and Amonette, 1999) have been shown to reduce Cr(VI). Aqueous reductants like these are not likely to be of widespread importance in natural attenuation because of the limited extent to which mixing occurs during transport; reductants associated with solids are likely to be much more important in natural attenuation of Cr(VI) (Palmer and Puls, 1994).

Many compounds found in soils and sediments have been shown to be capable of reducing Cr(VI). Reduction of Cr(VI) by Fe(II) associated with surfaces of oxide minerals (e.g., magnetite, ilmenite, and Fe(II)-substituted goethite, White and Peterson, 1996; Bidoglio et al., 1993), silicates (Ilton et al., 1997; Eary and Rai, 1989), and sulfides (Patterson et al., 1997) has been reported. Reduction by Fe(II) associated with minerals has been observed in the presence of dissolved oxygen in laboratory experiments (Ilton et al., 1997) and in field-scale transport experiments (Kent et al., 1994). Laboratory experiments have demonstrated that reduction of Cr(VI) by soil humic and fulvic substances occurs at an appreciable rate at pH 2 but the rate of reduction decreases with increasing pH (Wittbrodt and Palmer, 1996), which is consistent with reduction of Cr(VI) by synthetic, substituted phenols reported by Elovitz and Fish (1994). The rate of reduction by soil humic and fulvic substances decreases with decreasing temperature in the range 15-55 °C (Wittbrodt and Palmer, 1996). The rate of reduction of Cr(VI) by soil organic matter may decrease during the course of the reaction as a result of disappearance of more reactive components of the complex soil organic compounds (Wittbrodt and Palmer, 1996). Soil organic matter may also promote Cr(VI) reduction by enhancing the reductive dissolution of Fe(III) to produce Fe(II) (Wittbrodt and Palmer, 1996). Reduction of Cr(VI) by low molecular weight aliphatic and aromatic organic acids is catalyzed by various titanium-, Al-, and Fe(III)-oxides (Deng and Stone, 1996a, b) representative of solids found in soils and sediments.

The reactivity of Fe(II) at mineral surfaces is subject to passivation as a result of build up of oxidation products at the surface. Reduction of Cr(VI) by magnetite and illmenite was inhibited by build-up of Fe(III) oxides on the surface resulting from reaction between Fe(II)-containing minerals and Cr(VI) or by prolonged exposure of Fe(II) mineral to oxygen (Peterson et al., 1997; White, and Peterson, 1996). Magnetite collected from anoxic reservoir sediments reduced Cr(VI) rapidly but magnetite collected from an oxic soil profile did not reduce Cr(VI), presumably as a result of passivation by Fe(III) oxide coatings on the surface (White and Peterson, 1996). Passive oxide surface coatings can adsorb Cr(VI) but can completely inhibit its reduction (Peterson et al., 1996).

Oxidation of Cr(III) to Cr(VI) is an important process to consider for the long-term performance of a natural attenuation alternative. Oxidation of Cr(III) to Cr(VI) has been observed in some soil and sediment slurries under oxidizing conditions (Palmer and Puls, 1994; Masscheleyn et al., 1992; Bartlett and James, 1979). These studies involved adding Cr(III)-containing solutions to soil or sediment slurries. Oxidation of naturally occurring Cr(III) to Cr(VI) in soils has been reported (Chung et al., 2001), but the form in which Cr(III) occurred in the soils and the mechanism(s) by which it was oxidized were unknown.

Laboratory experimental studies have provided insight into possible mechanisms by which Cr(III) can be oxidized to Cr(VI) in soils and sediments. Oxidation of Cr(III) by dissolved O_2 in homogeneous solution is too slow to be an important process at low temperatures (Nakayama et al., 1981) but may be appreciable at elevated temperatures (Schroeder and Lee, 1975). The potential for solid surfaces to catalyze the oxidation of Cr(III) by dissolved oxygen has not been adequately studied. Various Mn(IV) and Mn(III) oxides can oxidize Cr(III) to Cr(VI) rapidly (Fendorf and Zasoski, 1992; Eary and Rai, 1987; Manceau, and Charlet, 1992). The reaction is inhibited by precipitation of $Cr(OH)_3$ on the Mn oxide surface (Banerjee and Nesbitt, 1999; Fendorf et al., 1992). At near-neutral pH values, the oxidation is not inhibited by Co(II) or Mn(II) but is inhibited by Al (Fendorf et al., 1993), which apparently blocks sites of oxidation either by surface precipitation or competitive adsorption. The oxidation reaction is also inhibited by dissolved organic compounds that form complexes with Cr(III) (Johnson and Xyla, 1991; Nakayama et al., 1981). These inhibitory effects suggest that oxidation requires contact between aqueous Cr(III) and reactive sites at the Mn oxide surface. Thus, while Mn oxides are common constituents of soils and aquifer sediments and, therefore, potentially important oxidants for Cr(III), their ability to oxidize Cr(III) will need to be determined on site-specific materials over ranges of aquifer chemistry that are relevant to field applications.

Colloidal Transport

There is evidence in natural systems of association of chromium with mobile colloidal solids in surface water (e.g., Stolpe et al., 2005) and ground water (e.g., Jensen and Christensen, 1999). In general, these colloids consist of organic macromolecules, iron oxyhydroxides, clay minerals, or sulfide minerals. Increased mobility of chromium-bearing colloidal material may result either from changes in the surface charge on colloids due to changes in subsurface geochemistry (e.g., Grolimund and Borkovec,

2006) or through deflocculation and resuspension of colloidal material through dissolution of cementing agents within the aquifer matrix (e.g., Ryan and Gschwend, 1990; Ryan and Gschwend, 1992). Both processes would be facilitated in aquifers impacted by organic contaminants where microbial activity may be stimulated resulting in the generation of reducing conditions and/or the production of low molecular weight organic compounds that partition to fine-grained sediments. Due to its particle reactivity, mobile forms of Cr(III) may be attributed, in part, to association with mobile colloids. The distance of colloidal transport from an impacted zone is uncertain, since colloid stability may change significantly during transport from reduced to oxidized zones or due to encounter with new sediment surfaces in unimpacted zones. However, identification of this transport mechanism within a chromium plume may play an important role relative to the management of the source zone or the establishment of a monitoring system appropriate for determining the extent of colloidal transport.

Site Characterization

Overview

In most cases the reduction of Cr(VI) to Cr(III) will be the process most likely to provide long-term attenuation and immobilization of Cr in contaminant plumes and, therefore, site characterization should focus on assessing the potential effectiveness of this process. As noted in the previous section, Cr oxidation-reduction chemistry is characterized by disequilibrium. Therefore, assessments based on equilibrium assumptions, such as Eh or pe determinations, will be of little use. Instead, it is recommended that the assessment focus on: 1) identifying solid and solution species capable of reducing Cr(VI), 2) quantifying the capacity for Cr(VI) reduction, 3) determining the quantity of Cr(VI) that could be released over time, 4) assessing possible changes in ground water chemistry that could influence the mobilization of soil- and sediment-bound Cr(VI), 5) assessing the long-term fate of reductants given possible changes in ground-water chemistry, and 6) assessing the potential for re-oxidation of Cr(III).

Assessment of Cr Aqueous Speciation

Identification of the mobile form of chromium within the aquifer is important relative to the development of a conceptual site model of the process(es) controlling immobilization of this contaminant. Chromium may be mobile as a dissolved species or in association with mobile colloidal matter. Generally, the anionic Cr(VI) species is the most mobile form of dissolved chromium in ground water with neutral to basic pH and measurable oxygen (Ball and Izbicki, 2004), although Cr(III) bound to mobile forms of natural organic matter may occur under certain conditions (Li and Xue, 2001). The distribution of these potential species in ground water provides information relative to the dominant process controlling attenuation. Parks et al. (2004) provide a review of several published methods for determining chromium speciation in water samples, including those similar to

Table 5.1 Natural attenuation and mobilization pathways for chromium.

Attenuation Processes	Mobilization Processes	Characterization Approach
Precipitation of metal chromates or precipitation of Cr(III) oxyhydroxide or sulfide	Dissolution of metal chromates due to change in pH; dissolution of Cr(III) oxyhydroxide due to acidification; dissolution of Cr(III) sulfide due to shift from reducing to oxidizing conditions.	Evaluation of Cr speciation in ground water. Determination of total Cr in the solid matrix and suspected components in chromium-bearing mineral. Evaluation of mineral solubility relative to ground-water chemistry and published solubility constants. Determination of Cr(VI) reductants in ground water and aquifer solids.
Co-precipitation of Cr as a trace component in oxyhydroxides or sulfides of iron or manganese	Dissolution of host oxyhydroxide due to decrease in pH or shift from oxidizing to reducing conditions; dissolution of host sulfide due to shift from reducing to oxidizing conditions.	Evaluation of Cr speciation in ground water. Evaluation of host precipitate formation relative to existing ground-water chemistry; determination of host mineral content in aquifer sediments via mineralogical characterization. Evaluation of Cr solid-phase partitioning using sequential extraction methodologies.
Adsorption of chromate to iron oxyhydroxides, iron sulfides, or other mineral surfaces	Desorption at high pH for oxyhydroxides and sulfides; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides or oxidative dissolution of iron sulfides.	Evaluation of Cr speciation in the aqueous phase. Determination of total Cr in the solid matrix. Evaluation of Cr solid-phase partitioning using sequential extraction methodologies. Batch and column testing to determine Cr uptake capacity of site-specific aquifer materials with variable geochemical conditions.

published EPA methods (Table 5.2). These authors stress the importance of sample preservation and processing on the determination of total Cr and Cr(VI) in water samples, particularly in samples that may contain elevated concentrations of colloidal iron oxyhydroxides that may pass through a 0.45 µm filter or precipitate in-situ during storage of improperly preserved samples.

Differentiation of Cr(III) and Cr(VI) species is typically determined via two approaches: 1) chemical separation of the two species by ion-exchange or coprecipitation followed by direct determination of total dissolved chromium and 2) selective determination of Cr(VI) by colorimetry or differential pulse polarography. Colorimetric methods for direct determination of Cr(VI) exist for field measurements and may be employed if there are concerns about the ability to preserve chromium speciation prior to analysis in a laboratory setting. A recent study provides a useful comparison of the relative performance of a field colorimetric method, a field method for species separation followed by laboratory analysis, and EPA Method 218.6 for laboratory separation and quantification of Cr(III) and Cr(VI) by ion chromatography (e.g., Ball and McCleskey, 2003a and 2003b). Ultimately, the method employed for speciation of aqueous chromium will depend on required analytical detection limits and sample preservation requirements, so it is recommended that analytical performance be demonstrated on a site-specific basis.

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

Identifying and Quantifying Cr(VI) Reductants

Ground-water characteristics of direct interest to assessment of Cr(VI) reduction potential include pH and concentrations of dissolved oxygen, Fe(II), sulfide, and organic carbon. Ground-water pH can influence Cr(VI) reduction in two ways. First, from a thermodynamic perspective, the affinity (Morgan, 1967) of many oxidation-reduction reactions involving the Cr(VI)-Cr(III) couple depends on pH. Second, many of the rates of oxidation-reduction reactions depend on pH. The presence of high concentrations of dissolved

Table 5.2 Published USEPA methods for determination of total chromium and speciation in aqueous samples.

Method Name and Number	Source
Chromium, Hexavalent - Chelation Extraction; *7197*	[a] SW-846 Ch 3.3; http://www.epa.gov/epaoswer/hazwaste/test/pdfs/7197.pdf
Chromium, Hexavalent - Colorimetric Method; *7196A*	[a] SW-846 Ch 3.3; http://www.epa.gov/epaoswer/hazwaste/test/pdfs/7196a.pdf
Chromium, Hexavalent - Coprecipitation Method; *7195*	[a] SW-846 Ch 3.3; http://www.epa.gov/epaoswer/hazwaste/test/pdfs/7195.pdf
Chromium, Hexavalent - Differential Pulse Polarography; *7198*	[a] SW-846 Ch 3.3 http://www.epa.gov/sw-846/pdfs/7198.pdf
Determination of Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography, *7199*	[a] SW-846 Ch 3.3; http://www.epa.gov/sw-846/pdfs/7199.pdf
Metals and Trace Elements by ICP/Atomic Emission Spectrometry; *200.7 Rev. 4.4*	[b] EPA/600/R-94/111 (NTIS Order Number PB95-125472)
Trace Elements by ICP/Mass Spectrometry; *200.8 Rev. 5.4*	[b] EPA/600/R-94/111 (NTIS Order Number PB95-125472)
Trace Elements by Stabilized Temperature Graphite Furnace AA Spectrometry; *200.9 Rev. 2.2*	[b] EPA/600/R-94/111 (NTIS Order Number PB95-125472)

[a] *EPA SW-846 Ch 3.3, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (http://www.epa.gov/epaoswer/hazwaste/test/main.htm)*

[b] *Methods for the Determination of Metals in Environmental Samples-Supplement I, EPA/600/R-94/111, May 1994. Available at National Technical Information Service, PB95-125472. (http://www.ntis.gov/products/types/publications.asp?loc=4-4-4)*

oxygen is indicative of conditions unfavorable for Cr(VI) reduction. In contrast, low but detectable dissolved oxygen concentrations can indicate mildly reducing conditions favorable for the accumulation of Cr(VI)-reductants in the sediments. Detectable concentrations of Fe(II) or sulfide are indicative of conditions under which Cr(VI) reduction should occur rapidly. High concentrations of dissolved organic carbon could indicate that organic compounds capable of reducing Cr(VI), either directly or catalyzed by mineral surfaces, may be present.

Detection of Cr(VI) reductants in ground water signals conditions favorable for natural attenuation, but most of the Cr(VI) reduction capacity will likely reside in the sediments (Palmer and Puls, 1994). Potentially important Cr(VI) reductants include sulfides, Fe(II) minerals, and organic matter. Even in the absence of detectable concentrations of reductants in ground water, Cr(VI) reductants may be present in the sediments. For example, sediment-bound Fe(II) can provide a significant capacity for natural attenuation of Cr(VI) even in the absence of detectable concentrations of Fe(II) or sulfide and the presence of low but detectable concentrations of dissolved oxygen (Kent et al., 1994).

In most cases the capacity for Cr(VI) reduction by soils or aquifer sediments will have to be determined experimentally using site-specific materials. Laboratory experiments can be used to assess the Cr(VI) reduction capacity and provide insights into reduction rates by constituents of the sediments. However, it should be noted that exposure to atmospheric oxygen can greatly decrease the Cr(VI) reductive capacity of sediments (e.g., Anderson et al., 1994). Also, rates of reduction measured in laboratory experiments may exceed those achieved during transport. For example, the rate of reduction of Cr(VI) determined in laboratory batch experiments greatly exceeded that during transport in a sand and gravel aquifer because, in the field, the rate of reduction was limited by the rate of mass transfer across sediment layers (Friedly et al., 1995).

Use of Cr Isotopes to Determine Reduction Rates

Recent work suggests that in-situ Cr(VI) reduction rates may be determined through the assessment of chromium stable isotope ratios ($^{53}Cr/^{52}Cr$) in ground water (Ellis et al., 2002). Cr(VI) reduction causes an enrichment of the lighter isotopes in the reduced product at any given instant. Faster reduction of lighter isotopes of Cr(VI) as compared to heavier isotopes resulted in measurable changes in the isotopic composition of dissolved Cr(VI) along flow paths where reduction was occurring. Thus, the extent of Cr(VI) reduction could be assessed along a flow path provided the isotopic composition of the initial source is known. Additional work indicates that sorption reactions occurring within the fringe of contaminant plumes may contribute to the observed isotope fractionation, but this work also indicated that sorption would exert little impact in more mature portions of the plume where sorption may play a less dominant role (Ellis et al., 2004). Theoretical calculations support the mechanism of proposed isotopic fractionation between Cr(VI) and Cr(III) (Schauble et al., 2004; Ottonello and Zuccolini, 2005a; Ottonello and Zuccolini, 2005b) suggesting that characterization of chromium stable isotope ratios may prove a useful tool for assessing in-situ rates of Cr(VI) reduction.

Assessment of Cr Solid-Phase Speciation

Various chemical extraction procedures have been proposed for quantifying soil- and sediment-bound Cr(VI) contamination. Studies in which the effectiveness of different extraction techniques were compared showed that a method involving a heated carbonate-hydroxide solution was the most effective for recovering soluble and insoluble forms of Cr(VI) (James et al., 1995; Vitale et al., 1997). For sparingly soluble Cr(VI) salts, the method was effective at quantifying $PbCrO_4$ but only partially effective at quantifying $BaCrO_4$, which may be an important form of Cr(VI) at some sites (Palmer and Puls, 1994). This method has been adopted by the USEPA (Method 3060A; http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3060a.pdf) for determination of Cr(VI) in contaminated soils and waste materials. It should be noted that Vitale et al. (1997) demonstrated that this method may not be appropriate for solid materials containing sulfide precipitates that reduce Cr(VI) to Cr(III) upon dissolution during extraction. Figure 5.1 suggests that a mildly acidic (pH 3-4) acid leach in the presence of sufficient sulfate to precipitate Ba as $BaSO_4$ might effectively dissolve $BaCrO_4$, but this has not been tested. Very low pH values should be avoided because of the potential for causing Fe(III) concentrations to increase sufficiently to precipitate chromian jarosite (Figure 5.2). At least one potential artifact that could result in overestimating sediment-bound Cr(VI) has been noted. Storing soils so that they are partially saturated (with water) may result in oxidation of native Cr(III) to Cr(VI); drying the soils prior to storage apparently eliminates this possible artifact (Chung et al., 2001). Korolczuk (2000) has examined an adaptation of the heated carbonate-hydroxide extraction method that employs voltammetric determination of extracted Cr(VI) in organic-rich soils containing predominantly Cr(III) solid species. This approach was more reliable for Cr(VI) detection than use of the colorimetric procedure described in Method 3060A.

Various extraction schemes have been employed to determine the chemical speciation of the total chromium content of contaminated soils or sediments. The intent of this solid-phase characterization approach is generally to identify the solid-phase partitioning reactions that govern chromium mobility in the subsurface. However, as noted by Szulczewski et al., (1997), there are limitations to the selectivity of various solutions proposed to extract chromium from labile and recalcitrant pools of solid species within soils and sediments. These authors as well as Wilkin et al. (2005) have made use of x-ray absorption spectroscopy to assist in defining the chemical speciation of chromium in contaminated soils and aquifer sediments, but little work has been conducted to date to better design and assess the accuracy of chemical extractions to determine the chemical speciation of chromium in solid matrices. Thus, currently Method 3060A provides the most thoroughly tested approach for assessing the presence of Cr(VI) in soils and sediment.

Long-Term Stability and Capacity

Changing aquifer chemical conditions will influence the processes that control the mobility and natural attenuation of Cr(VI). Changes in ground-water pH and dissolved salt concentrations can change the solubility of Cr(VI) compounds (Figures 5.1 and 5.2) and the extent to which Cr(VI) adsorbs on the sediments (Figure 5.3). Acidification of natural attenuation zones can cause the Cr(VI) reductive capacity of the sediments to decrease (e.g., Anderson et al., 1994) or to increase (e.g., Wittbrodt and Palmer, 1996; Stollenwerk Grove, 1985). Acidification can also increase the mobility of Cr(III) (e.g., Walter et al., 1994). Invasion of oxygen into reducing zones can result in oxidation of Cr(VI)-reductants. Establishment of completely oxic conditions may result in production of Mn oxides or other compounds capable of re-oxidizing Cr(III) previously sequestered in the sediments.

Laboratory experimental studies conducted during the site assessment phase will provide insight into the impact of anticipated changes in aquifer chemistry on many of these processes. However, the long-term performance of natural attenuation under changing aquifer chemical conditions will be difficult to predict with certainty. Therefore, long-term monitoring of chemical conditions in and around zones in which attenuation processes are active is recommended. It is recommended that long-term monitoring include the critical water quality parameters identified above. If chemical conditions become increasingly oxidizing, then it is recommended that long-term monitoring be supplemented with periodic assessment of the Cr(VI) reduction capacity of the sediments.

Tiered Analysis

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

Tier I. Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate Cr partitioning to aquifer solids within the plume. Rapid movement of contaminants along preferred flow paths in the unsaturated and saturated zones can by induced by hydrologic events such as heavy rains (e.g., McCarthy et al., 1998; Camobreco et al., 1996). It will be important to determine that such hydrogeologic features do not result in contaminants bypassing zones where natural attenuation is occurring. If natural attenuation processes are active throughout the plume, then there should be an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by metal chromates or chromium oxyhydroxides or sulfides. Since identification of the chemical speciation of chromium in water samples and aquifer sediments is critical towards determining the attenuation mechanism(s), it is recommended that precautions be taken to preserve chromium speciation during collection, preservation, and processing of collected samples (See recommendations and application of these methods in Wilkin et al., 2002 and Ford et al., 2005). Identification of active sequestration to prevent chromium migration in ground-water provides justification for proceeding to Tier II characterization efforts.

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

1) Determination of chromium solution speciation via direct analytical measurements in combination with speciation calculations based on characterized ground-water chemistry (e.g., Jensen and Christensen, 1999);
2) Calculation of the saturation state of ground water relative to measured aqueous chemistry (e.g., Wilkin et al., 2005) complimented by the possible isolation of discrete Cr mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;
3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Cr sorption (e.g., Amonette, 2002);

4) Identification of chromium association(s) with the various solid phase components of aquifer solids through combination of chemical extractions with microscopic/spectroscopic confirmation of phase associations, and;
5) Demonstration of concurrence between the site conceptual model and mathematical model(s) that describe arsenic removal mechanism(s).

It is recommended that identification of chromium chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the in-situ mineralogy and speciation of chromium. The demonstration of concurrence between conceptual and mathematical models describing arsenic transport will entail development of site-specific parameterization of the chemical processes controlling chromium solid-phase partitioning.

Tier III. Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Cr and the capacity of the aquifer to sustain continued uptake. The impact of potential hydrologic changes, such as a shift in flow direction caused by the onset of pumping at nearby sites, needs to be determined. A well-constrained ground-water flow model of the site should be capable of evaluating the impact of such changes. It is recommended that the stability of immobilized Cr be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage. For example, changes in ground-water redox potential due to oxygen intrusion or the occurrence of anaerobic microbial processes can exert a significant influence on Cr partitioning to iron sulfides or iron oxyhydroxides, respectively. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of Cr mobilization as a function of ground-water redox chemistry representative of existing and anticipated site conditions. This may involve the use of microcosm tests that stimulate in-situ microbial populations toward the development of redox conditions considered deleterious for continued Cr immobilization. It is recommended that the capacity for Cr uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that co-precipitation of Cr with iron sulfide occurs due to microbial degradation of organic compounds coupled with sulfate reduction within the aquifer, it is recommended that the mass distribution of organic carbon, sulfate and ferrous iron to support this reaction within the aquifer be determined. This site-specific capacity can then be compared to Cr mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized Cr and sufficient capacity within the aquifer to sustain Cr attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction may be necessary.

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

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Arsenic

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Occurrence and Distribution

The types of arsenic wastes at Superfund sites include byproducts of wood preserving, arsenic waste disposal, pesticide production and application, and mining (Table 1 in USEPA, 1997). Mandal and Suzuki (2002) provide a review of anthropogenic sources of arsenic in terrestrial systems. The sources of arsenic in soils are diverse, and they may be derived from organic or inorganic forms. For example, Foster et al. (1998) examined the chemical speciation of arsenic in mine wastes to show that the waste material was chemically complex and composed of a combination of arsenic in native mineral forms and sorbed to common weathering products. Jackson and Bertsch (2001) examined the types of aqueous chemical species of arsenic released from leaching of organo-arsenic materials used in agricultural applications. The aqueous species of arsenic released during the weathering of arsenic compounds in anthropogenic sources may be distinct from the subsequent speciation of arsenic in ground water. Leached species may be unstable in the ground-water environment, but serve as intermediates that control the overall release of arsenic from source zones.

Arsenic in soil and ground water is derived from natural and/or anthropogenic sources (USEPA, 1997). Natural sources of arsenic are derived from a wide array of geologic materials, including igneous, metamorphic and sedimentary rocks (Korte and Fernando, 1991; Welch et al., 2000; Smedley and Kinniburgh, 2002). Arsenic may subsequently be accumulated during secondary mineral formation in overburden materials and soils. In contrast, anthropogenic sources are typically derived from the land application of arsenical pesticides and herbicides and from disposal of arsenic-bearing wastes generated during processing of ore materials for production of commercial products (USEPA, 1995).

Natural sources of arsenic may also pose a health risk in ground water due to changes in site geochemistry that promote mobilization. An example of this scenario is the mobilization of naturally occurring arsenic during transport of landfill leachate through the ground-water aquifer (Hounslow, 1980). In this case, arsenic is mobilized via desorption induced by competitive interactions with dissolved constituents or due to dissolution of host mineral phases as a result of microbial degradation of organic compounds within the contaminant plume. In order to evaluate the potential for down gradient attenuation of mobilized arsenic, it is recommended that site characterization be sufficient to identify the potential sinks for arsenic and the chemical conditions that would result in uptake onto aquifer solids.

Plume Characteristics

Hounslow (1980) and Smedley and Kinniburgh (2002) provide an assessment of geochemical triggers that may lead to arsenic mobilization in subsurface systems. In general these include: 1) desorption at high pH under oxidizing conditions and/or due to the influx of dissolved ions that compete for sorption sites on aquifer minerals, 2) desorption/dissolution due to a change to a reducing chemical environment, and 3) mineral dissolution. The first process is a result of the influx of dissolved constituents that compete for or displace arsenic adsorbed to mineral surfaces without a concomitant change in sorbent stability. The second process is a result of a change in the ground-water chemistry to a condition under which the sorbent material is no longer stable. This may be a result of a change in redox, pH or other factors leading to dissolution of the sorbent phase. The third process is a result of a shift in arsenic mineral stability due to a change in ground-water chemistry. In this instance, arsenic may represent a major or minor component within the solid, e.g., orpiment or arsenic-rich pyrite, respectively. While site-specific mechanisms may differ between naturally occurring versus contaminant sources of arsenic, these general arsenic mobilization processes apply under both scenarios.

Remedial Technologies

Technologies for the remediation of arsenic in soil involve treatments to effect containment, immobilization, or separation/concentration within the solid matrix. The separation/concentration process is followed by some secondary immobilization treatment (USEPA, 1995; USEPA, 1997). Technologies for the treatment of arsenic in ground water are based on ex-situ or in-situ approaches. Pump-and-treat technologies make use of processes common to water and wastewater treatment for removal of dissolved arsenic (USEPA, 2002). In-situ treatment technologies are less common, but there is emerging research based on the application of permeable reactive barriers for arsenic removal from ground water. This technology is based on installation of reactive solid material into the subsurface to intercept and treat the contaminant plume (Lackovic et al., 2000; Su and Puls, 2001; Cheng et al., 2005).

Regulatory Aspects

Arsenic is the second most common contaminant of concern (COC) for sites listed on the Superfund National Priorities List (USEPA, 2002). Of the 1209 sites on the National Priorities List for which a Record of Decision has been signed, there are 380 and 372 sites with arsenic as a COC in ground water and soil, respectively. The maximum contaminant level for arsenic in drinking water was recently revised from 0.05 mg L^{-1} to 0.01 mg L^{-1} (USEPA, 2001; USEPA, 2006a; http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf). This may impact site-specific cleanup goals at hazardous waste sites for locations where ground water is the primary source of potable water. For non-potable water sources, ambient water quality criteria (AWQC) that are protective of aquatic life may serve as alternative cleanup goals. For arsenic, current statutes list both acute and chronic criteria for arsenic in fresh waters as 0.34 mg L^{-1} and 0.15 mg L^{-1}, respectively (USEPA, 2006b; http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf). Contaminant cleanup goals vary widely for arsenic in soil depending on the use of total or leachable metals as the cleanup criterion and the potential impact and intended use of ground water supplies (USEPA, 2001).

Geochemistry and Attenuation Processes

Aqueous Speciation

In oxidizing environments, the predominant form of arsenic in solution is arsenate, $H_nAsO_4^{n-3}$. The arsenate oxyanion may be protonated to various degrees as a function of pH, but it is commonly present as the negatively-charged $H_2AsO_4^{1-}$ or $HAsO_4^{2-}$ within the pH range of natural waters (Cullen and Reimer, 1989; Nordstrom and Archer, 2003). However, the neutral ($H_3AsO_4^0$) or the fully deprotonated form (AsO_4^{3-}) may exist at acid or alkaline pH extremes that may occur at contaminated sites.

The speciation of arsenic may be more complex in reducing environments. In general, arsenite, $H_nAsO_3^{n-3}$, is the predominant arsenic species, but mononuclear ($H_xAsO_yS_z^{(3+x-2y-2z)}$) and polynuclear thioarsenic species may also form in sulfate-reducing zones in which iron is depleted (Clarke and Helz, 2000; Wilkin et al., 2003; Bostick et al., 2005; Hollibaugh et al., 2005). The distribution of various reduced arsenic species under relevant geochemical conditions for an arsenic contaminated site is shown in Figure 6.1. These model results suggest that arsenite would predominate under most reducing environments. However, thioarsenic species may become significant in sulfate-reducing zones that are depleted in iron. These conditions may be encountered in organic-rich ground water derived from contaminated sites (Vroblesky and Chapelle, 1994). The aqueous concentration of thioarsenic species may remain high in sulfide-dominated systems due to the solubility of orpiment at circumneutral pH (Webster, 1990). The detection of the species controlling aqueous arsenic speciation in reducing environments may be complicated by the need to employ different sample preservation techniques in the absence or presence of aqueous sulfide.

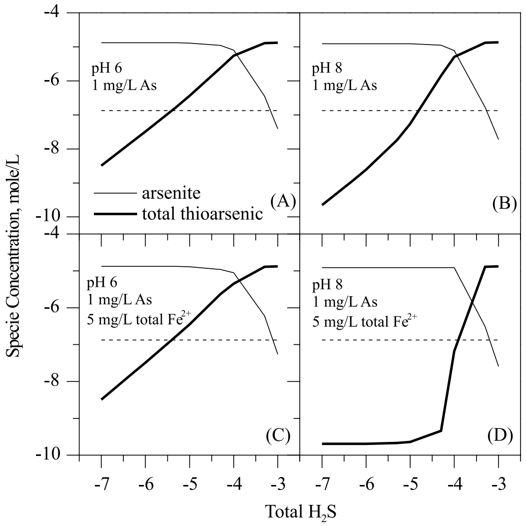

Figure 6.1 *The distribution of arsenite and thioarsenic species in a reducing ground water. The sum of all possible thioarsenic species is shown for simplicity. The dashed line indicates the current MCL for arsenic in drinking water (10 ppb). Model results were generated using MinteqA2 following modification of the database to include mononuclear thioarsenic equilibrium expressions (Wilkin et al., 2003). Calculations were carried out with a background electrolyte of 0.1 M* $NaNO_3$*, and mackinawite (FeS) was allowed to precipitate in systems with* Fe^{2+}*.*

Solubility

The precipitation of pure phase arsenic minerals is not likely in ground-water systems. Examination of solubility trends for phases such as As_2O_5, As_2O_3, and As_2S_3 indicates that these phases would form only under extreme conditions. Metal arsenates are relatively insoluble (e.g., $Ca_3(AsO_4)_2$ and $Ba_3(AsO_4)_2$), but formation of these phases is limited by the typically lower concentrations of dissolved metals and arsenic encountered in ground water downgradient from contaminant source areas. The stability fields of scorodite [$Fe(III)AsO_4 \cdot 2(H_2O)$] and possible arsenic sulfides are shown in Figure 6.2 as a function of pH and Eh for concentrations of total dissolved As, Fe, and S that may be encountered within a contaminant plume. There is also recent evidence for the microbially-mediated formation of ferric/ferrous iron arsenites under certain geochemical environments (Morin et al., 2003). Under reducing conditions, the stability fields of pure arsenic sulfides are quite narrow for relatively high total concentrations of arsenic in ground water, although site-specific conditions may support precipitation of sulfides (e.g., O'Day et al., 2004). In addition, while the precipitation of scorodite seems feasible, this process is typically limited by the consumption of dissolved iron during the formation of iron oxides or iron sulfides. Thus, the immobilization of arsenic via precipitation of pure As-bearing mineral phases is typically limited. However, coprecipitation with other common soil/sediment minerals such as iron oxides and iron sulfides is a likely sink for arsenic in ground water. For this process, arsenic uptake is concurrent with formation of metastable phases of Fe-bearing minerals that can occur proximate to transitions from oxidizing-to-reducing conditions (or vice versa) within the subsurface (e.g., Ford et al., 2005; Ford et al., 2006; Wilkin and Ford, 2006). This process is generally distinct from sorption to pre-existing mineral phases in that arsenic may subsequently be transferred to more stable mineral phases over time (e.g., Moore et al., 1988; Ford, 2002; Lowers et al., 2007). Given the uncertainty in the rates of transformation of metastable minerals to more stable forms, it is currently not possible to reliably estimate the importance of this stabilization process in ground-water systems. However, it is recommended that this process be considered in the context of the dynamics of site-specific geochemistry and the required timeframe for attainment of remedial goals.

Adsorption

The primary forms of inorganic arsenic in both oxidizing and reducing ground water are oxyanions or thiooxyanions (Ferguson and Gavis, 1972; Wilkin et al., 2003; Bostick et al., 2005). Adsorption of arsenic species at mineral surfaces occurs as a result of a set of chemical reactions between aqueous species and surface sites (Dzombak and Morel 1990; Davis and Kent, 1990). Adsorption of both As(III) and As(V) onto most minerals exhibits a strong pH dependence because: 1) most adsorption reactions between As(III) and As(V) and mineral surface sites have H^+ as a reactant, 2) arsenic speciation varies with pH (Figure 6.2), and 3) the electrostatic contribution to the free energy of adsorption of As species onto most minerals varies with pH. In addition to pH, the extent to which As(III) or As(V) adsorbs at mineral surfaces will be influenced by the concentrations of other anions, which compete for surface sites, and cations, the adsorption of which can influence the electrostatic contribution to anion adsorption.

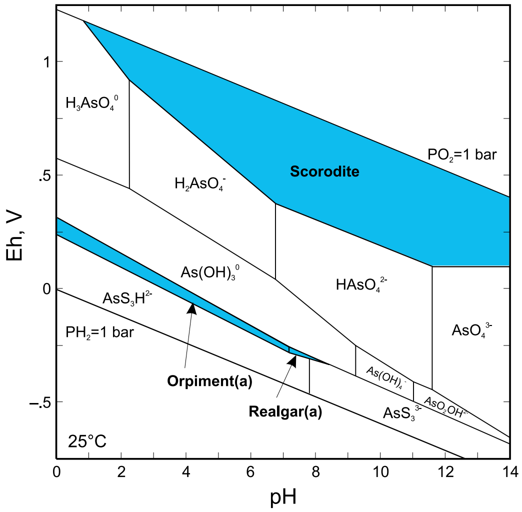

Figure 6.2 *Eh-pH diagram for arsenic at 25°C. System As-H_2O-Fe-S, with $\Sigma As=10^{-5}$ (750 µg L^{-1}), $\Sigma Fe=10^{-4}$ (5.6 mg L^{-1}), and $\Sigma S=10^{-3}$ (32 mg L^{-1}). Solid stability fields are shaded blue. Orpiment(a) and Realgar(a) are poorly crystalline forms of As_2S_3 and AsS, respectively. Arsenopyrite and crystalline forms of As_2S_3 and AsS are suppressed.*

Arsenic sorption has been demonstrated for a wide range of minerals common to soils and sediments with iron oxides and sulfides appearing to play a dominant role in oxidizing and reducing environments, respectively (Goldberg and Glaubig, 1988; de Vitre et al., 1991; Morse, 1994; McNeill and Edwards, 1997; Manning et al., 1998; Chiu and Hering, 2000; Wolthers et al., 2005). The relative distribution of inorganic species of arsenic in relation to the distribution of potential Fe-bearing minerals as a function of pH and Eh in the absence of significant sulfate reduction is shown in Figure 6.3. For near-neutral pH under oxidizing conditions, sorption of arsenate onto iron oxides such as goethite (α-FeOOH) would likely predominate. Under iron-reducing conditions, sorption of arsenate or arsenite to reduced Fe-bearing minerals such as siderite ($FeCO_3$), magnetite [$Fe(III)_2Fe(II)O_4$], or green rust phases [$Fe(II)_6Fe(III)_2(OH)_{18} \cdot 4(H_2O)$] may predominate. However, arsenic may remain mobile in Fe-reducing systems in which reduced Fe-bearing minerals do not precipitate, resulting in a loss of sorption capacity within the aquifer sediment (Swartz et al., 2005; Polizzotto et al., 2005; Polizzotto et al., 2006). For reduced systems in which iron- and sulfate-reduction processes are significant, arsenic may sorb to iron sulfides such as pyrite (Figure 6.4). Sorption of arsenic to iron (or other metal sulfides) may be the dominant mechanism for arsenic mobilization under sulfate-reducing conditions that are undersaturated with respect to precipitation of a pure arsenic sulfide (Wilkin and Ford, 2006).

The extent to which inorganic arsenic will partition to mineral surfaces will be governed by competition with other anions in solution and the net surface charge that develops as a function of site-specific geochemistry. There are several commonly occurring anions in natural waters that could compete with arsenic sorption to mineral surfaces. These competitive reactions will be active for all arsenic aqueous species in oxidized and reduced systems. There is evidence to support that arsenic desorption may occur due to competition with other inorganic and organic anions in solution or due to increases in ground-water pH (Peryea, 1991; Jackson and Miller, 2000; Meng et al., 2000; Redman et al., 2002).

Redox Chemistry

Microbial interactions in aqueous systems can impact arsenic mobility via direct and indirect mechanisms. Experimental evidence suggests that the speciation of arsenic can be directly influenced via microbially-mediated reduction-oxidation (redox) reactions (Ahmann et al., 1994; Zobrist et al., 2000). Common outcomes of these interactions are 1) the conversion of inorganic arsenic between its oxidized or reduced oxyanionic forms and 2) methylation-demethylation of arsenic (Cullen and Reimer, 1989; Anderson and Bruland, 1991; Maeda, 1994). The extent to which these

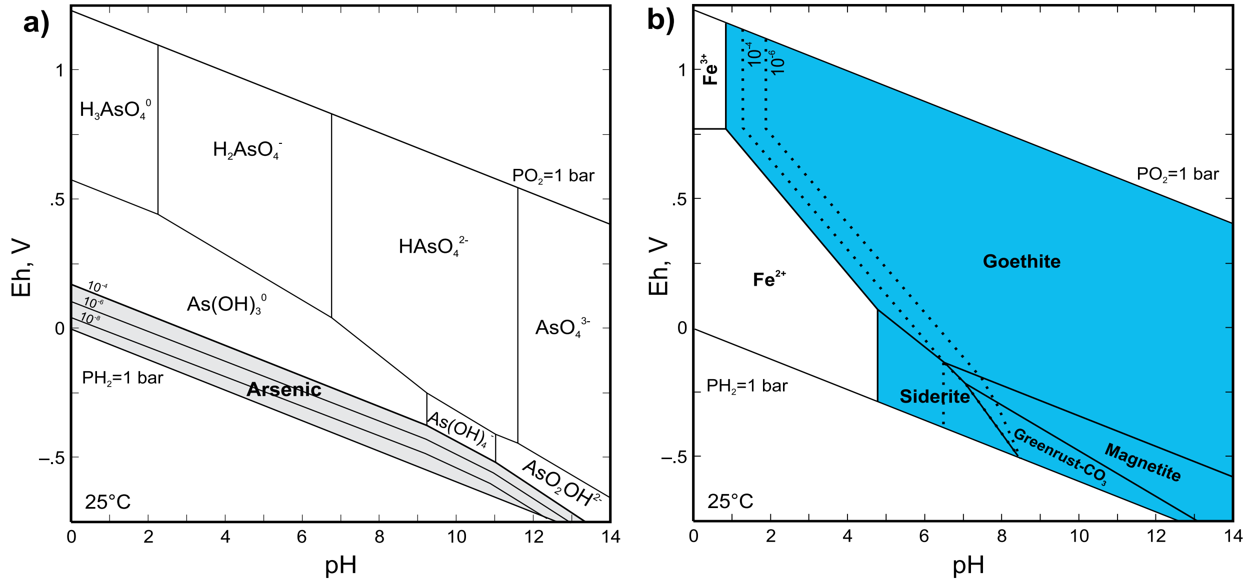

Figure 6.3 *Eh-pH diagrams for arsenic and iron at 25°C for iron-reducing systems. These paired diagrams show the relative distribution of potentially adsorbing arsenic species (left) relative to representative types of Fe-bearing sorbents (right) that are predicted to occur as a function of Eh and pH. (a) System As-H_2O, with ΣAs contoured from 10^{-8} to 10^{-4}; region for elemental arsenic is shaded gray. (b) System Fe-C-H_2O (no sulfur) with ΣFe contoured from 10^{-2} to 10^{-6} and $\Sigma C=10^{-3}$; Hematite and Wüstite are suppressed.*

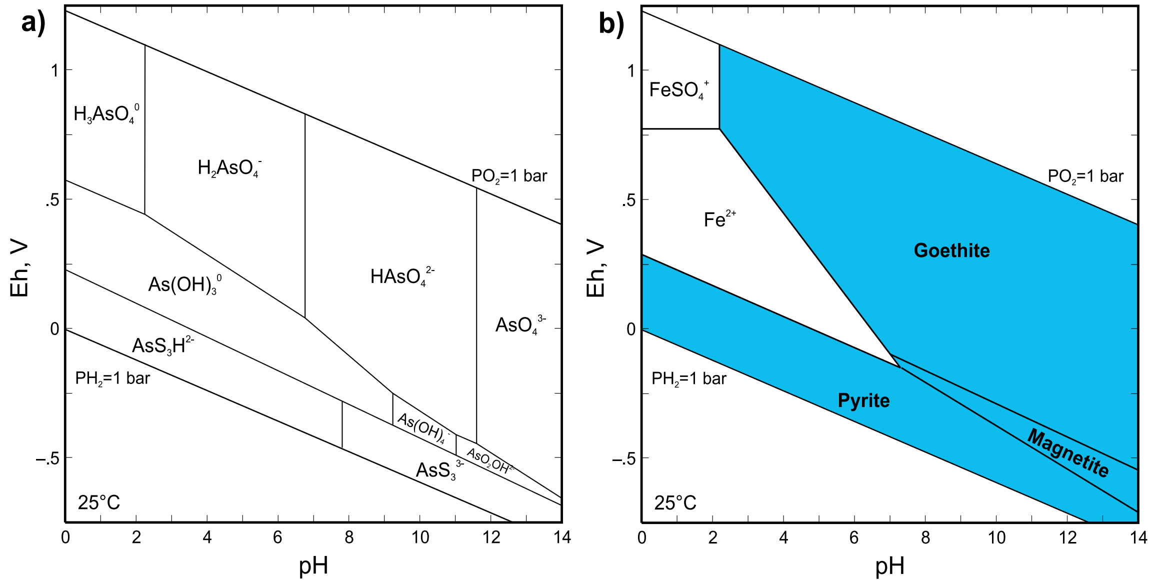

Figure 6.4 *Eh-pH diagrams for arsenic and iron at 25°C for coupled iron- and sulfate-reducing systems. These paired diagrams show the relative distribution of potentially adsorbing arsenic species (left) relative to representative types of Fe-bearing sorbents (right) that are predicted to occur as a function of Eh and pH. (a) System As-S-H_2O, with $\Sigma As=10^{-5}$ and $\Sigma S=10^{-3}$; all solids suppressed to show stability fields for the aqueous species. (b) System Fe-C-S-H_2O with $\Sigma Fe=10^{-4}$, $\Sigma C=10^{-3}$, and $\Sigma S=10^{-3}$; Hematite is suppressed.*

processes influence on arsenic mobility in intermediate and deep ground-water systems is not well known. However, these processes could play a more significant role in shallow systems with zones of ground-water discharge-recharge where biological activity may be more pronounced. More commonly, microbial interactions govern arsenic mobility by controlling the redox chemistry of major elements with which arsenic is associated, e.g., iron, sulfur, and carbon (Moore, 1994; Harrington et al., 1998; McGeehan et al., 1998; Jones et al., 2000). The development of iron- and/or sulfate-reducing zones in ground-water contaminant plumes governs the precipitation-dissolution of iron- and sulfur-bearing minerals. These reactions influence arsenic mobility through production or loss of sorptive material within the aquifer (Ford, 2005).

Recent studies have increased awareness of the role of microorganisms in catalyzing the oxidation of As(III). Chemoautotrophic microorganisms that can oxidize As(III) to As(V) using oxygen have been isolated from arsenopyrite-bearing rock (Santini et al., 2000). Chemoautotrophic microorganisms that can oxidize As(III) under anaerobic conditions using nitrate, nitrite, and, possibly, Fe(III) have also been identified (Oremland et al., 2002). Laboratory experiments have shown that these microorganisms can oxidize millimolar concentrations of As(III) over a period of several hours under both aerobic and anaerobic conditions. Arsenic-oxidizing chemoautotrophic anaerobes were shown to be responsible for maintaining As(V) concentrations up to 160 uM in the anoxic hypolimnion of a lake whose sediments were heavily contaminated with As from industrial activities (Senn and Hemond, 2002). The dominance of As(V) over As(III) in other anoxic water bodies underscores the potential importance of microbial As(III) oxidation (Senn and Hemond, 2002).

Microbial reduction of As(V) to As(III) is likely to be important in some systems. Anaerobes whose dominant metabolic process involves coupling As(V) reduction to oxidation of organic compounds or hydrogen have been isolated from natural and polluted water or sediments (Ahmann et al., 1994; Hoeft et al., 2002). Laboratory studies have shown that these organisms can reduce As(V) adsorbed to hydrous ferric or aluminum oxides (Zobrist et al., 2000) or precipitated with Fe(III) or Fe(II) (Ahmann et al., 1997). Field studies have demonstrated the importance of these microorganisms in reducing As(V) to As(III) associated with As-contaminated lake sediments (Ahmann et al., 1997); As(V) metabolism under anaerobic conditions was shown to be responsible for at least 14 percent of the carbon mineralization in hypersaline Mono Lake, California, where arsenic concentrations up to 200 uM result from hydrothermal inputs (Oremland et al., 2000). Arsenic(V) reducers have been found in freshwater, alkaline, and hypersaline environments but, thus far, only circumstantial evidence points to their occurrence in acidic environments (Oremland et al., 2001).

Colloidal Transport

Laboratory studies suggest that certain conditions within the subsurface may develop that enhance arsenic transport via mobile colloids. Increased mobility of arsenic-bearing colloidal material may result either from changes in the surface charge on colloids due to changes in subsurface geochemistry (e.g., Puls and Powell, 1992; Tadanier et al., 2005) or through deflocculation and resuspension of colloidal material through dissolution of cementing agents within the aquifer matrix (e.g., Ryan and Gschwend, 1990; Ryan and Gschwend, 1992). Both processes would be facilitated in aquifers impacted by organic contaminants where microbial activity may be stimulated resulting in the generation of reducing conditions and/or the production of low molecular weight organic compounds that partition to fine-grained sediments. Due to the affinity of arsenic to the surfaces of iron oxyhydroxides that are commonly present as mineral coatings on aquifer sediments, mobilization of these colloid-sized solids could potentially contribute to arsenic mobility. The distance of colloidal transport from an impacted zone is uncertain, since colloid stability may change significantly during transport from reduced to oxidized zones or due to encounter with new sediment surfaces in unimpacted zones. However, identification of this transport mechanism within an arsenic plume may play an important role relative to the management of the source zone or the establishment of a monitoring system appropriate for determining the extent of colloidal transport.

Site Characterization

Determining the processes controlling arsenic mobility in ground water and forecasting the capacity and longevity for attenuation is dependent on understanding the chemical processes controlling partitioning of arsenic onto aquifer solids. The aqueous and solid phase speciation of arsenic provides clues to the processes controlling solid-liquid partitioning, and, therefore, changes in mobility that may accompany chemical perturbations within the aquifer. Table 6.1 indicates possible natural attenuation and mobilization pathways for arsenic.

Aqueous Measurements

Determination of arsenic chemical speciation in ground water provides a basis for both assessing the factors contributing to arsenic mobilization and the potential for arsenic partitioning to aquifer solids within and down gradient from the contaminant plume. The presence of arsenic as arsenite or thioarsenic species suggests that reductive processes influence arsenic mobility. In contrast, the predominance of the arsenate species in ground water suggests that desorption processes due to elevated pH or competition from other anions for sorption sites may be controlling arsenic mobility. Significant concentrations of methylated or other organo-arsenic species point to the potential influence of microbial processes on arsenic mobility. Thus, knowledge of aqueous arsenic speciation within the context of site ground-water geochemistry within and outside of the boundaries of the contaminant plume is important relative to determining the current conditions controlling arsenic mobility (or immobility) as well as estimating the potential for changes in arsenic mobility that may coincide with geochemical changes that occur as the aquifer returns to pre-contamination conditions.

Table 6.1 Natural attenuation pathways for arsenic.

Attenuation Processes	Mobilization Processes	Characterization Approach
Precipitation of metal arsenates or arsenites or precipitation of arsenic sulfides	Dissolution of metal arsenates/arsenites due to change in pH; dissolution of arsenic sulfides due to increase in pH or shift from reducing to oxidizing conditions.	Evaluation of arsenic speciation in ground water. Determination of total As in the solid matrix and suspected components in arsenic-bearing mineral. Evaluation of mineral solubility relative to ground-water chemistry and published solubility constants.
Co-precipitation of arsenic as a trace component in oxyhydroxides or sulfides of iron or manganese	Dissolution of host oxyhydroxide due to decrease in pH or shift from oxidizing to reducing conditions; dissolution of host sulfide due to shift from reducing to oxidizing conditions.	Evaluation of arsenic speciation in ground water. Evaluation of host precipitate formation relative to existing ground-water chemistry; determination of host mineral content in aquifer sediments via mineralogical characterization. Evaluation of arsenic solid phase partitioning using sequential extraction methodologies.
Adsorption to iron oxyhydroxides, iron sulfides, or other mineral surfaces	Desorption at high pH for oxyhydroxides and sulfides; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides or oxidative dissolution of iron sulfides.	Evaluation of arsenic speciation in the aqueous phase. Determination of total As in the solid matrix. Evaluation of arsenic solid phase partitioning using sequential extraction methodologies. Batch and column testing to determine As uptake capacity of site-specific aquifer materials with variable geochemical conditions.

The total concentration of arsenic in aqueous samples can be assessed by a number of methods depending on the required sensitivity to meet data quality objectives (Melamed, 2004; Melamed, 2005). Colorimetric detection based on the molybdenum blue method has been employed to measure inorganic arsenic for concentrations of approximately 2 μg L^{-1} and higher (Johnson, 1971; Woolson et al., 1971; Johnson and Pilson, 1972). Determination of total arsenic may also be achieved using silver dithyldithiocarbamate as a colorimetric reagent following conversion of arsenic to arsine gas (Aggett and Aspell, 1976). However, these methods typically require conversion of all arsenic species in a sample to a single aqueous or gaseous species prior to colorimetric determination. These methods have been applied in the field and commercial kits are available (e.g., Steinmaus et al., 2006). The colorimetric methods suffer from analytical interferences (Stauffer, 1983; Frenzel et al., 1994) and in some cases require the use of hazardous substances for test application.

More commonly, total arsenic is determined by element-specific atomic absorption/emission or mass spectrometry (Eaton et al., 1998). Samples can be introduced either directly into the spectrometer or following conversion of arsenic to a hydride gas. These methods are less prone to analytical interferences, but complex sample matrices can interfere with the atomization or hydride conversion steps. In addition, both atomic and mass spectrometry may suffer from spectral interferences either from other elements within the sample or from molecular species that absorb at similar energy or possess the mass employed for quantification (Feldmann et al., 1999).

There are generally two approaches to analytical determination of aqueous arsenic speciation: 1) chemical separation of individual species in the field and subsequent determination of total arsenic in each fraction and 2) preservation of the in-situ arsenic speciation followed by chemical separation and quantification of each specie in the laboratory. Numerous studies suggest that field separation of the various arsenic species can be achieved for drinking water supplies via the use of exchange resins that selectively pass or retain specific species (e.g., Wilkie and Hering, 1998; Le et al., 2000; Yalcin and Le, 2001). While this method is attractive, there are limitations in species separation (Miller et al., 2000) and potential interferences from competing cations or anions in contaminated water. This latter factor has not been sufficiently addressed for the complex chemistry frequently encountered in contaminant plumes. Thus, it is recommended that method validation be performed on a site-specific basis for all ground-water compositions that may be encountered.

The use of chemical and/or physical methods to preserve in-situ arsenic speciation has been investigated for a range of sample holding times (e.g., Haswell et al., 1985; Palacios et al., 1997; Eaton et al., 1998; Hall et al., 1999; Gallagher et al., 2004). One recurring observation from all studies is the importance of steps taken to prevent the precipitation of hydrous ferric oxide in samples collected from Fe-rich anoxic water in order to prevent the loss of arsenic from solution. A recent study provides a comprehensive review of previously published research along with the results of a contemporary study conducted using water samples from numerous sources (McCleskey et al., 2004). The analysis presented in this study reconciles many of the inconsistencies from historical studies that examined the use of various chemical reagents for preservation of arsenic species in water. The authors concluded that acidification and storage of the sample at 4° C in a container that excludes light effectively preserves the As(III)/As(V) ratio for adequate periods for a wide range of chemical compositions of non-sulfidic ground water. In sulfidic waters, it appears that most of the methods for preservation of both total and individual arsenic species are inadequate either due to susceptibility of thioarsenic species to oxygen exposure or the precipitation of arsenic sulfides upon acidification (Smieja and Wilkin, 2003). However, preservation approaches have been developed for sulfidic waters that support reliable measurement of total arsenic (Smieja and Wilkin, 2003; Samanta and Clifford, 2006). Samanta and Clifford (2006) also demonstrate that anion exchange may be used for field separation of arsenite and thioarsenic species in reduced water when these are the dominant arsenic species. Regardless of the method of preservation employed, it is recommended that performance validation for site-specific water chemistry be undertaken through use of ground-water samples spiked with known standards in the field. The use of controlled laboratory solutions provides an inadequate test for the complexity of water chemistries that are typically encountered within contaminated ground-water systems.

Arsenic speciation in preserved aqueous samples can be quantified following chemical separation or masking of the various species. The molybedenum blue colorimetric method has been employed on natural samples to quantify As(III) and As(V) following manipulation of the oxidation state of As(III) (Johnson and Pilson, 1972). This method may be employed in the field, but is subject to interferences from the complex chemical matrices commonly encountered in contaminated ground water. More commonly, aqueous speciation is achieved through chromatographic separation of the various species followed by determination of arsenic by atomic absorption/fluorescence or mass spectrometry (Cabon and Cabon, 2000; Gomez-Ariza et al., 2000).

Solid Phase Measurements

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

Bulk solid phase arsenic concentration can be determined directly on the solid sample by X-ray fluorescence spectrometry, neutron activation analysis, or following chemical digestion and analysis of arsenic in the resultant liquid phase. Neutron activation analysis is not commonly employed due to the scarcity of neutron sources required to irradiate the sample. X-ray fluorescence is the most attractive approach due to the relative ease of sample preparation, but there are potential spectral interferences. For example, the presence of elevated concentrations of lead can interfere with arsenic quantification due to overlap of the As Kα and the Pb Lα fluorescence peaks (Wegrzynek and Holynska, 1993). There are approaches to correct for this interference provided the Pb Lβ fluorescence peak is measurable and free from interference. In addition, it is recommended that sample preparation via fusion with lithium metaborate be avoided due to the possible loss of arsenic through volatilization at the fusion temperature (Alvarez, 1990). There are various chemical digestion methods for determination of total arsenic (Kane, 1995; Chen and Ma, 1998), but these procedures do not always provide complete recovery. In addition, arsenic is a relatively volatile element (Yang et al., 1998), so sample heating to improve recovery can lead to losses without the appropriate precautions. Both approaches to quantifying total solid phase arsenic can be reliably applied provided the analyst is aware of the possible analytical artifacts.

There have been many applications of sequential extraction schemes to assess the speciation of solid phase arsenic (e.g., Moore et al., 1988; McLaren et al., 1998; La Force et al., 2000; Lumsdon et al., 2001). This approach has been employed primarily due to the inability to apply conventional laboratory techniques such as X-ray diffraction or infrared spectroscopy for detection of trace constituents within a soil/sediment and the limited availability of more advanced element-specific spectroscopies such as X-ray absorption spectroscopy at a synchrotron radiation facility. However, the lack of validated procedures and reference materials to test the ability of the various chemical extractants that have been employed limits the validity of selective extraction schemes. There are documented instances that clearly show selective extractants are incapable of targeting arsenic associated with specific solid components within a soil/sediment (e.g., Gruebel et al., 1988; Wilkin and Ford, 2002). There is no single extraction protocol that can be recommended to chemically speciate solid phase arsenic. It is recommended that protocols be developed on a site-specific basis with knowledge of the prevailing aqueous geochemistry and mineralogy of the ground-water aquifer (e.g., Ford et al., 2005).

Long-Term Stability and Capacity

The long-term stability of arsenic immobilized onto aquifer solids will depend on the prevailing ground-water chemistry over time relative to the conditions that existed at the time of immobilization. If there are significant changes in ground-water chemistry following immobilization, then the potential exists for remobilization of arsenic with the establishment of a new mobile plume. A general example of this type of situation would be if arsenic was originally immobilized through partitioning to mineral sulfides within aquifer sediments under sulfate-reducing conditions. Arsenic associated with sulfide minerals may be re-mobilized due to sulfide oxidation if the aquifer were to return to more oxidizing conditions. There are several examples of field studies that document the potential for release of arsenic bound to aquifer solids subsequent to changes in ground-water chemistry (Table 6.2). The examples provided in Table 6.2 provide general perspectives of factors that may increase arsenic mobility relative to the original mode for immobilization. While these examples are not exhaustive of all possible situations, they do point to the importance of establishing a monitoring program that is designed to consider the potential impact of changes in site geochemistry relative to the conditions under which arsenic was attenuated within the aquifer. Ultimately, the evolution of biogeochemical conditions in the subsurface will dictate the success of the MNA remedy.

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

Tiered Analysis

Determination of the viability of arsenic remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. The goal of site assessment is to demonstrate the process(es) controlling arsenic sequestration onto aquifer solids and the long-term stability of solid phase arsenic as a function of existing and anticipated ground-water chemistry. A recent technical review highlights limited instances where natural attenuation was chosen as a component of the remedy for cleanup of arsenic in ground water (Reisinger et al., 2005). However, as noted in the review, site characterization conducted to support selection of natural attenuation as a remedy at these sites did not fully identify the site-specific immobilization process and the long-term stability of the sequestered arsenic. The following tiered analysis structure for site characterization provides a technically defensible approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I - Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate As partitioning to aquifer solids within the plume. If natural attenuation processes are active throughout the plume, it is anticipated that this would be reflected in an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by metal arsenates/arsenites or arsenic sulfides. Since identification of the chemical speciation of arsenic in water samples and aquifer sediments is critical towards determining the attenuation mechanism(s), it is recommended that precautions be taken to preserve arsenic

Table 6.2 Examples of arsenic mobilization due to shifts in ground-water chemistry.

Location and Setting	Original Conditions (Arsenic Immobile)	Altered Conditions (Arsenic Mobilized)
Unconsolidated aquifer consisting of glacial outwash, glaciomarine clay, and till overlying bedrock; New Hampshire [a]	Arsenic bound to poorly crystalline iron hydroxides in glaciomarine clay under oxidizing conditions (Eh ~ 400 mV)	Reductive dissolution of iron hydroxides due to microbially driven Fe-reducing conditions stimulated by organic carbon in landfill leachate
Suwannee Limestone, Upper Floridan consolidated aquifer; Florida [b]	Arsenic hosted in pyrite that is most abundant in high porosity zones; anoxic aquifer	Oxidative dissolution of pyrite due to injection of oxygenated water
Unconsolidated, glacial outwash aquifer consisting of coarse(quartz) sand and gravel with Fe and Al oxide and/or silicate mineral coatings; New Hampshire [c]	Arsenic adsorbed to mineral coatings under oxidizing conditions	Adsorbed arsenic mobilized due to desorption in the presence of elevated phosphate derived from sewage disposal via land application coupled with reductive dissolution of Fe-bearing mineral coatings

[a] *Delemeos et al., 2006;* [b] *Price and Pichler, 2006;* [c] *Kent and Fox, 2004*

speciation during collection, preservation, and processing of collected samples (See recommendations and application of these methods in Wilkin et al., 2002, Ford et al., 2005, and Wilkin, 2006). Identification of active sequestration to prevent arsenic migration in ground-water provides justification for proceeding to Tier II characterization efforts.

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

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

It is recommended that identification of arsenic chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the in-situ mineralogy and speciation of arsenic. The demonstration of concurrence between conceptual and mathematical models describing arsenic transport will entail development of site-specific parameterization of the chemical processes controlling arsenic solid phase partitioning.

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

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

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Selenium

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Occurrence and Distribution

Selenium contamination can be derived from weathering of natural deposits as well as discharge from mining, smelting, and coal/oil combustion. Most soils contain between 0.1 to 2 mg kg^{-1}, but soils originating from the Upper Cretaceous marine sedimentary rocks (shale) show elevated concentrations of selenium in about 80,000 km^2 of land in the 17 western states of the United States (Nolan and Clark, 1997). In California, shale materials in the Coastal Ranges along the entire western margin of the San Joaquin Valley contain excessive and varied amounts of selenium with median values as high as 6.5 to 8.7 mg kg^{-1} (Presser and Barnes, 1984). Complex interactions among irrigated agricultural practices and physical and chemical processes have contributed to high selenium concentrations (20 to 1000 µg L^{-1}) in ground water underlying low-altitude agricultural areas of the western San Joaquin Valley (Deverel et al., 1984; Seiler, 1997).

Incidences of waterfowl mortality and reproductive failure at Kesterson Reservoir, San Joaquin Valley, California was discovered in 1983 and was attributed to elevated selenium concentrations in irrigation drainage (Ohlendorf et al., 1986). More follow-up studies have revealed that elevated selenium concentrations in water from irrigation projects in the Western USA are largely caused by application of irrigation water to soils derived from shales of Cretaceous age (Naftz, 1996).

There are 21 former uranium mill sites designated under the Uranium Mill Tailings Radiation Control Act (Federal Register, 1995) that show ground-water contamination with toxic elements including selenium, arsenic, manganese, molybdenum, uranium, vanadium, and zinc. Contamination of groundwater with selenium also occurs from surface coal mining in Wyoming (Blaylock et al., 1995). Waste rock from phosphorite mining in southeastern Idaho contains selenium, cadmium, vanadium, and other metals. Selenium concentrations in the hundreds of parts per million have been found in soils, plants, and seeps in close proximity to some mine waste dumps. Mortality of livestock due to selenosis poisoning has been linked to the contamination of water and vegetation by mine waste (Piper et al., 2000).

Plume Characteristics

The general patterns in subsurface selenium transport that may be anticipated under differing geochemical conditions are represented by a series of field investigations that have been conducted in aquifers with redox chemistry grading from oxic to strongly reducing. For oxic conditions (8 mg L^{-1} O_2, pH ~5, no detectable Fe^{2+} or sulfide), the field study conducted by Kent et al. (1995) demonstrated that selenium (as selenate) transport will likely be dominated by adsorption reactions with aquifer sediment. While adsorption will tend to retard selenium transport, this process will not likely prevent plume expansion. For mildly reducing conditions (0.032 mg L^{-1} O_2, pH ~6, 17-28 mg L^{-1} Fe^{2+}, ≤0.034 mg L^{-1} sulfide), Kent et al. (1994) presented results that indicated little selenate attenuation due to insufficient conditions to support either biotic or abiotic reduction of selenate to less mobile forms. In contrast to selenium transport behavior within the oxic zone of this aquifer, there was little retardation of selenium transport relative to a conservative tracer (bromide). In the absence of conditions insufficient for selenium reduction to Se(0) or more reduced forms, the higher pH and greater concentrations of anions that compete for adsorption sites on aquifer minerals resulted in conservative transport of selenate within the suboxic portion of the aquifer. For highly reducing conditions (≤0.006 mg L^{-1} O_2, pH ~7, ≤25 mg L^{-1} Fe^{2+}, ≤0.5 mg L^{-1} sulfide), field studies conducted in the shallow aquifer underlying a wetland system at the Kesterson Reservoir, California demonstrated significant attenuation of selenium (White et al., 1990; Benson et al., 1991; White et al., 1991). This attenuation apparently resulted from reduction of selenate and/or selenite to Se(0) or more reduced forms upon interaction with biotic/abiotic components of the aquifer sediments in the reducing ground water. These observations generally indicate that the attenuation of selenium will be correlated with the extent of its reduction within an aquifer.

Remedial Technologies

Active removal of selenium from ground water may be achieved either through above ground or subsurface (in-situr) treatment processes. Examples of these approaches include 1) above-ground treatment operations where selenium is removed via adsorption, ion exchange, or chemical reduction, 2) phytoremedation for shallow ground-water systems either through crop planting or the construction of wetland systems that intercept ground-water discharge, and 3) installation of permeable reactive barriers in the subsurface to intercept a migrating plume.

For above ground treatment operations, layered double hydroxide precipitates have been used as sorbents for removing both selenate and selenite from water (O'Neil et al., 1990). Magnesium-aluminum and zinc-aluminum layered double hydroxides show high affinity for both selenate and selenite (You et al., 2001) with uptake of these anions via exchange with structural interlayer anions. Chemical reduction, primarily through stimulation of microbial processes, has been employed for selenium removal from contaminated water. An algal bacterial selenium removal facility was designed and constructed at the Panoche Drainage District in California during 1995-1996 to remove selenium and nitrate from drainage water (Green et al., 2003). Mass removals of total soluble selenium of 77% or greater were achieved over a three-year period. Selenate was removed by assimiliatory and dissimiliatory bacterial reduction. Laboratory tests have shown the benefit of using rice straw to promote selenate removal from drainage water through microbial reduction of selenate to selenite and subsequently to colloidal Se(0) (Zhang and Frankenberger, 2003). In another study, a flow-through wetland system was constructed consisting of ten unlined cells that were flooded continuously. The global mass balance showed that on average 59% of the total inflow selenium was retained within the wetland cells, whereas selenium outputs included outflow (35%), seepage (4%), and volatilization (2%) (Gao et al., 2003a). The major selenium removal mechanism was the reduction of selenate to Se(0) and immobilization into the organic phase of the sediments (Gao et al., 2003b). However, it has been noted that in some wetland systems, biological volatilization of selenium may account for 10-30% of the selenium removed from contaminated water (Allen, 1991; Hansen et al., 1998; Zhang and Frankenburger, 1999).

The use of phytoremediation as a treatment technology involves removal of selenium from contaminated water either through absorption into the plant mass or volatilization following uptake and conversion to organic species (Banuelos et al., 2002). Potential crops tested for the phytoextraction of selenium in central California include two moderate selenium accumulators, Indian mustard and canola (Banuelos et al., 1993). Selenium hyperaccumulators have been identified, e.g., *Astragalus bisulcatus,* which can accumulate up to 0.65% (w/w) selenium. Pickering et al. (2003) have identified high concentrations of the nonprotein amino acid Se-methylseleno-cystein in young leaves of this hyperaccumulator, but in more mature leaves, selenate predominates. Another selenium hyperaccumulator, *Stanleya pinnata* (Brassicaceae) is a perennial that responded favorably to repeated cutting in the greenhouse, a trait that could prove valuable in field-scale phytoremediation (Parker et al., 2003).

The use of zerovalent iron [Fe(0)] for removal of selenium in aqueous systems has been demonstrated in both laboratory and field applications. Earlier studies show that selenate can be reduced to a lower oxidation state by metallic iron in water (Baldwin et al., 1981). Murphy (1988) reported that selenate may be removed by Fe(0) through the formation of Se(0). Selenium in the form of selenocyanate ($SeCN^-$) in oil refinery wastewater and artificial wastewater could be removed using Fe(0) through the formation of Se(0) and ferrous selenide (FeSe). The possible chemical reaction between $SeCN^-$ and Fe(0) included deselenation of $SeCN^-$ and electrochemical reduction of Se(0) to Se(-II) (Meng et al., 2002). Morrison et al. (2002) have demonstrated selenium removal from ground water using Fe(0) in a field installation at a uranium mill tailings repository. Three treatment cells [Cercona foamed Fe(0) plates, steel wool, and Peerless granular Fe(0)] were operated for passive removal of selenium along with arsenic, manganese, molybdenum, uranium, vanadium, and zinc from ground water (Morrison et al., 2002). Significant removal was achieved in the treatment cell using Cercona foamed Fe(0) plates (reduction from 202 µg L^{-1} to 6 µg L^{-1} dissolved Se), and the cell performed for more than three years.

Regulatory Aspects

Selenium was ranked number 144 out of a total of 275 on the CERCLA Priority List of Hazardous Substances in 2001, which was prepared by the Agency for Toxic Substances and Disease Registry, Centers for Disease Control and Prevention. The USEPA has set the maximum contaminant level (MCL) at 0.05 mg L^{-1} for drinking water (USEPA, 2006a; http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf). The USEPA has found selenium to potentially cause the following health effects when people are exposed to it at levels above the MCL: hair or fingernail loss, numbness in fingers or toes, nervous and circulatory systems problems, and kidney and liver damage. For non-potable water sources, ambient water quality criteria (AWQC) that are protective of aquatic life may serve as alternative cleanup goals. For selenium, current statutes list the chronic criterion for fresh waters as 0.005 mg L^{-1} with recommendation for an acute criterion pending review (USEPA, 2006b; http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf). An example of where this criterion may apply is a site where contaminated ground water discharges to surface water.

Selenium (Se) is an essential nutrient for humans and vertebrates, but is only required in small amounts and has a very narrow range between deficient and toxic levels (National Research Council, 1983). It is found in the enzyme glutathione peroxidase that inhibits the oxidative role of peroxides and hydroperoxides, thereby protecting immunocomponent cells and slowing down aging processes. Selenium also plays an important role in anticarcinogenic activity and prevention of heavy metal toxic effects. Selenium detoxifies mercury in humans via possible formation of 1: 1 Hg-Se compounds (Kosta et al., 1975). Selenium yeast can both prevent the accumulation of arsenic in the human body and rectify the damages (Wang et al., 2001). Selenium supports efficient thyroid hormone synthesis and metabolism and protects the thyroid gland from damage by excessive iodide exposure (Zimmermann and Kohrle, 2002). Epidemiological studies have indicated an inverse relationship between selenium intake and the incidence of certain cancers; blood or plasma levels of selenium are usually lower in patients with cancer than those without this disorder (Whanger, 2004). An endemic human disease referred to as Keshan disease in certain regions of China was caused by selenium deficiency (Chen et al., 1980). Keshan disease is a juvenile cardiomyopathy that presents as congestive heart failure in infants and young children. This disease has been virtually eliminated by supplying sodium selenite pills to those at risk. Another selenium deficiency disease has been also reported in areas of China and referred to as Kaschin-Beck disease, which is an osteoarthropathy, a generative articular disease caused by oxidative damage to cartilage that leads to deformation of bone structure (Ge and Yang, 1993).

In contrast, excess selenium is very toxic and can cause selenium poisoning (selenosis) in humans and animals. Consumption of feed containing greater than 5 mg of Se kg^{-1} leads to selenium poisoning in animals (Anderson et al., 1961; National Research Council, 1980). Selenium toxicity disorders in livestock known as "alkali disease" and "blind staggers" were widely recognized in the 1930s in South Dakota in areas of high soil selenium (Magg and Glen, 1967). Sheep grazing in areas of phosphate mining operations in southeastern Idaho have died as a result of high selenium concentrations in forage and water (Fessler et al., 2003). Selenium toxicity also has been reported in some regions of Australia as a result of livestock feeding on selenium accumulative plant species that contain selenocystathionine (Tinggi, 2003). Endemic selenium poisoning of humans characterized by loss of nails and hair was reported in Yutangba of central China in the 1960s, which was associated with the use of carbonaceous shales (stone coal) high in selenium in the form of elemental selenium (Zhu et al., 2004).

Geochemistry and Attenuation Processes

Aqueous Speciation

Selenium is a metalloid exhibiting physical and chemical properties between that of metals and nonmetals. It chemically resembles sulfur and exists in organic and inorganic chemical forms. Inorganic species include selenide [Se(-II)], elemental selenium [Se(0)], selenite [Se(IV)], and selenate [Se(VI)]. Organic species include methylated compounds, selenoamino acids, selenoproteins and their derivatives. The speciation of selenium is greatly influenced by the pH and redox conditions of the environment (Figure 7.1). For example, Se(-II) exists in a reducing environment as hydrogen selenide (H_2Se) and as metal selenides. Reduction of selenate to selenite and Se(0) has been shown to decrease its mobility in saline, mildly alkaline groundwater (White et al., 1991). When dissolved in water, H_2Se can oxidize to elemental selenium. Elemental selenium is stable in a reduced environment, but it can be oxidized to selenite and to selenate by a variety of microorganisms (Sarathchandra and Watkinson, 1981).

Various strains of bacteria have been identified to facilitate selenate reduction in soil and sediment systems. Two microbial processes, namely methylation of selenium and reduction of both selenate and selenite to Se(0), have a major influence on the fate and mobility of this element in the environment (Dungan and Frankenberger, 1999; Dungan et al., 2003). Methylation of selenium, and subsequent selenium volatilization, leads to dissipation of soil selenium to the atmosphere. Environmental factors such as the existing microbial community, pH, temperature, moisture, and organic amendments control the rate of selenium volatilization from seleniferous soils (Frankenberger and Karlson, 1989; Zhang and Frankenburger, 1999). Under flooding conditions, part of the methylated selenium may be transported in water, thus decreasing selenium volatilization to the atmosphere (Zhang and Frankenburger, 1999). The addition of organic amendments to soils has been reported to stimulate indigenous microbes to methylate selenium (Abu-Erreish et al., 1968; Frankenberger and Karlson, 1989); whereas, organic substrates added to ponded sediments have been found to accelerate the reduction of selenate and selenite to Se^0 (Tokunaga et al., 1996) and similar effects were reported in laboratory batch experiments (Zhang et al., 2003).

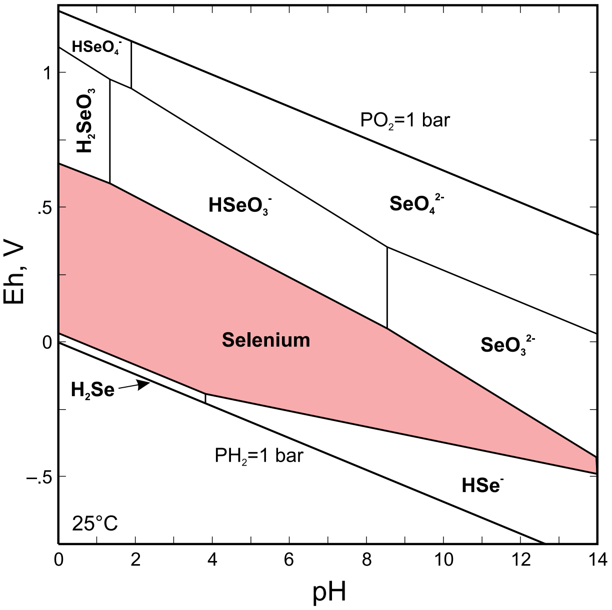

Figure 7.1 *Eh-pH diagram for selenium at 25 °C using thermodynamic data from Séby et al. (2001). $\Sigma Se=10^{-5}$ (790 µg L^{-1}). Solid stability field for elemental selenium is shaded pink.*

Mechanisms for selenium reduction by microbes are complex as it occurs under both aerobic (Lortie et al., 1992) and anaerobic conditions (Oremland et al., 1989; Oremland et al., 1990; Tomei et al., 1992). Both dissimilatory and detoxification mechanisms are possible (Oremland, 1994). The occurrence of sequential reduction of selenate to selenite and then to Se(0) is suggested after amendment of contaminated soils with barley straw under field capacity moisture conditions (Camps Arbestain, 1998). The rates of selenate to selenite reduction in waste waters is proportional to their respective concentrations in solution and also to the amount of the microbial biomass (Rege et al., 1999). A recent study has documented the occurrence of both intracellular and extracellular Se(0) granules in three phylogenetically and physiologically distinct bacteria that are able to respire selenium oxyanions, suggesting that this phenomenon appears to be widespread among such bacteria (Oremland et al., 2004). The metal sites of selenate reductase from *Thauera selenatis* have been characterized

(Maher et al., 2004); the enzyme was found to contain Se in a reduced form (probably organic) and the Se is coordinated to both a metal (probably Fe) and carbon. Assessment of Se(IV) and Se(0) reduction in anaerobic estuarine sediment microcosms demonstrated the sequential formation of Se(0) and ultimately Se(-II) during incubation with elemental selenium and/or lactate as electron donors for microbial reduction (Herbel et al., 2003). Dissolved Se(-II) did not accumulate in sediment pore water during incubation due precipitation with ferrous iron to form $FeSe_{(s)}$, which was determined via solid phase characterization using X-ray absorption spectroscopy.

Solubility

Selenium has the potential of forming precipitates for all of its oxidation states (Seby et al., 2001; see Figure 7.2). For selenate and selenite, this includes precipitates with common major cations in ground water (Ca, Mg) as well as transition metals (Fe, Mn) or heavy metals that may be anticipated in contaminant plumes (Rai et al., 1995; Sharmasarkar et al., 1996). These phases are anticipated to primarily be significant in situations where selenium concentrations are highly elevated. Reduction to form elemental selenium [Se(0)] can result in very low concentrations of dissolved selenium. In general, it has been observed that selenium reduction to insoluble Se(0) results in immobilization and stabilization of this element in the soil matrix, since the re-oxidation reaction of Se(0) to soluble selenate and selenite is relatively slow (Tokunaga et al., 1994; Zawislanski and Zavarin, 1996). Abiotic reduction of selenite to Se(0) was also suggested in sulfate-reducing bacteria (SRB) biofilms (Hockin and Gadd, 2003). Elemental selenium and elemental sulfur were found to precipitate outside SRB cells. Further reduction to selenide [Se(-II)] can lead to precipitation of metal selenides, including ferrous iron and manganese selenides, similar to the formation of metal sulfides under sulfate-reducing conditions.

While not commonly observed, it is anticipated that many suboxic geological environments contain green rust, which is a mixed ferrous, ferric hydroxide that also contains interlayer anions such as sulfate and carbonate in its structure (Feder et al., 2005). Identification of green rusts in sediments and soils is hampered by the rapid oxidation of green rusts by atmosphere oxygen, and for this reason, they have not been commonly reported. However, recent thermodynamic and spectroscopic studies give direct evidence for the existence of green rusts in soils (Hansen et al., 1994; Trolard et al., 1997; Feder et al., 2005). Due to high reactivity, green rust minerals are envisioned as potential reducing agents of a number of contaminants such as nitrate, chromate, and selenate. Direct evidence for the formation of reduced selenium species in anoxic sediments via abiotic redox reactions with sulfate green rust was provided using X-ray absorption near-edge spectroscopy (XANES) and Fourier-transform extended X-ray absorption fine structure (EXAFS) spectroscopy (Myneni et al., 1997). The mechanism of selenate reduction was described by the following equation:

$$HSeO_4^- + 4Fe_4^{II}Fe_2^{III}(OH)_{12}SO_4 \bullet 3H_2O \rightarrow HSe^- + 8Fe_3O_4 + 4SO_4^{2-} + 8H^+ + 32H_2O \qquad (2)$$

in which sulfate green rust was oxidized to form magnetite, whereas selenate was reduced to Se(0) and subsequently to selenide (herein referred to as the 'adsorption-reduction' pathway). In addition, a laboratory study has demonstrated that a significant fraction of dissolved selenate can be coprecipitated with Fe(II) and Fe(III) ions to form Fe(II)-Fe(III) hydroxyselenate green rust with simultaneous reduction of an equal amount of selenate anions to selenite anions (Refait et al., 2000). In the subsurface environment, selenate reduction by coprecipitation and adsorption pathways can occur when selenium-contaminated sediment becomes reducing (Pickering et al., 1995). In the coprecipitation-reduction pathway, reductive dissolution of Fe(III) oxides precipitates green rust with selenate followed by selenate reduction to Se(0) and selenide. Reduction of selenium oxyanions to Se(0) has also been observed in the presence of iron sulfides (Bruggeman et al., 2005) and ferrous hydroxide (Zingaro et al., 1997).

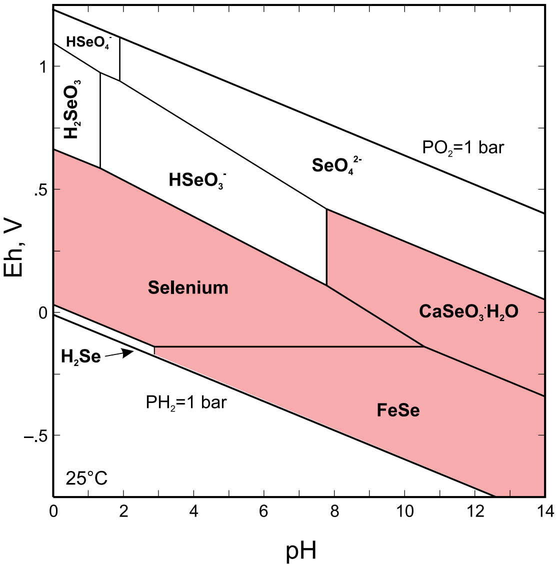

Figure 7.2 *Eh-pH diagram for selenium at 25 °C using thermodynamic data from Séby et al. (2001). System Se-H_2O-Fe-Ca, with $\Sigma Se=10^{-5}$ M (790 µg L^{-1}), $\Sigma Fe=10^{-4}$ M (5.6 mg L^{-1}), and $\Sigma Ca=10^{-2}$ M (400 mg L^{-1}). Solid stability fields for elemental selenium, hydrous calcium selenite, and ferrous selenide are shaded pink. $FeSe_2$ was suppressed (data not available in the Séby et al. review); however, the stability field of the diselenide would be intermediate between elemental selenium and FeSe.*

Adsorption

A comprehensive summary of selenate and selenite adsorption behavior on individual soil minerals (Fe, Al, and Mn oxides, kaolinite, and calcite) and whole soils throughout the United States is documented in Zachara et al. (1994). This research demonstrated the importance of Fe and Al oxide surfaces for selenium adsorption onto aquifer sediments and highlighted the dependence of the extent of adsorption on the pH of ground water and the presence of anions that compete for adsorption sites. Additional review of the published literature is provided below.

Selenate has been shown to behave like sulfate with minimal adsorption and high mobility (Goldberg and Glaubig, 1988; Neal and Sposito, 1989); whereas, selenite behaves analogously to phosphate, with greater adsorption than selenate (Neal et al., 1987; Barrow and Whelan, 1989a; Zhang and Sparks, 1990). Adsorption of selenite on goethite decreases with increasing pH, with decreasing selenite concentration, and with competing anions such as phosphate, silicate, citrate, molybdate, carbonate, oxalate, and fluoride (Balistrieri and Chao, 1987). More selenite is adsorbed onto montmorillonite than on kaolinite (Frost and Griffin, 1977). Selenite adsorption in seleniferous soils are decreased in the presence of sulfate, nitrate, and phosphate (Pareek et al, 2000). Selenite sorption by aluminum hydroxides is adversely affected by organic acids (Dynes and Huang, 1997). Selenite selectively adsorbs at the carbonate (CO_3^{2-}) site on calcite ($CaCO_3$) via ionic exchange, forming a two-dimensional solid-solution of the form $Ca(SeO_3)_x(CO_3)^{1-x}$ at the interface; under identical chemical conditions, selenate adsorption is inhibited (Cheng et al., 1997). An earlier study showed selenate substitution in calcite also occurred (Redder et al., 1994). Desorption of selenate is faster and more nearly complete than selenite after adsorption and incubation in soil (Barrow and Whelan, 1989b).

Mechanisms of selenium adsorption have been studied from both macroscale batch and microscale spectroscopic approaches. The presence of either selenate or selenite lowers the electrophoretic mobility and decreases the point of zero charge of amorphous iron hydroxide (am-$Fe(OH)_3$)and goethite (α-FeOOH), suggesting inner-sphere complexation for both selenate and selenite species (Su and Suarez, 2000). Both in situ attenuated total reflection – Fourier transform infrared (ATR-FTIR) and diffuse reflectance infrared Fourier transform (DRIFT) spectra show bidentate complexes of selenate with am-$Fe(OH)_3$ and the DRIFT spectra of selenite on goethite show bridging bidentate complex of selenite. These results are consistent with an earlier in situ extended x-ray absorption fine structure (EXAFS) spectroscopic study (Manceau and Charlet, 1994) that shows selenate forms an inner-sphere binuclear bridging surface complex on hydrous ferric oxide and goethite. On the contrary, an earlier EXAFS study (Hayes et al., 1987) concluded that selenate forms an outer-sphere surface complex on goethite. A recent combined data set of Raman and ATR-FTIR spectra indicate that both inner- and outer-sphere surface complexes of selenate occur on goethite, as predominantly monodentate inner-sphere surface complexes at $pH < 6$, and as predominantly outer-sphere surface complexes at $pH > 6$ (Wijnja and Schulthess, 2000).

Site Characterization

The conditions that favor the mobility of selenium in the environment with respect to adsorption are alkaline pH, high selenium concentrations, oxidizing conditions, and high concentrations of additional anions that strongly adsorb. Most of the reductive capacity in aquifers resides in the sediments (Barcelona and Holm, 1991). It is thus critical to assess the predominant ground-water chemistry across the plume as well as the biogeochemical characteristics of the aquifer sediments that may lead to selenium attenuation. Table 7.1 provides a summary of potential attenuation processes that may be active within an aquifer along with a general approach to site characterization to identify the active attenuation process(es).

Aqueous Measurements

The mobility of selenium depends mainly on the different chemical forms in which it is present. Information on the chemical speciation of selenium in ground water provides part of the context for understanding the processes that may control its attenuation within the aquifer. Measurements that can be used to assess the chemical speciation of selenium include determination of its total dissolved concentration along with quantification of individual chemical species (inorganic or organic) that may occur within the plume. Published USEPA methods that may be employed for the determination of the total dissolved concentration of selenium are documented in Table 7.2. Of these methods, only the gaseous hydride technique can differentiate between inorganic chemical selenium species, namely selenate [Se(VI)] and selenite [Se(IV)], since only selenite forms a gaseous hydride that is detected using this technique. In this case, selenate may be inferred by the difference between measured selenite and total dissolved selenium. However, as previously reviewed, there are other inorganic (e.g., HSe^-) and organoselenium species that may occur within ground water. Thus, additional speciation methods may be needed in order to properly characterize the distribution of dissolved selenium species.

There are several documented approaches to determine the chemical speciation of selenium in water. These approaches can be classified into two general categories: 1) those that use a chemical/mass specific detector following chromatographic separation of individual aqueous species (hyphenated techniques), and 2) those that provide direct and indirect detection of individual species prior to or following chemical conversion of individual species within the sample (e.g., voltammetric techniques). Recent comprehensive reviews are available for hyphenated techniques that employ atomic absorption/fluorescence spectrometry (Capelo et al., 2006) or inductively coupled plasma-mass spectrometry (B'Hymer and Caruso, 2006). For the latter technique, Tirez et al. (2000) provide a useful overview of possible isobaric (similar ion mass) and polyatomic interferences (due to argon bonding to sample matrix elements within plasma) that can bias analytical results for individual chemical species of selenium. There are several published procedures that employ voltammetry for the detection of selenium in natural water samples (Locatelli and Torsi, 2000; Ochsenkuhn-Petropoulou and Tsopelas, 2002; Bertolina et al., 2006). As outlined by Ochsenkuhn-Petropoulou and Tsopelas (2002), not all aqueous selenium species

Table 7.1 Natural attenuation and mobilization pathways for selenium.

Attenuation Processes	Mobilization Processes	Characterization Approach
Biotic (microbial) or abiotic reduction by reduced Fe-bearing minerals of selenate/selenite to elemental Se(0) and/or selenide with precipitation as a metal selenide.	Cessation of microbial processes via changes in nutrient supply within the ground-water flow path; reduction in the mass of reduced Fe-bearing minerals within the aquifer due to changes in redox conditions or supply of soluble iron. Oxidation of Se(-II) or Se(0) upon exposure to oxygen or other oxidants.	Determination of water chemistry, microbial populations, and/or sediment mineralogy linked to selenium reduction along with spatial and temporal variability of required chemical/microbial components relative to selenium transport pathway(s). Determination of total concentration and selenium chemical speciation in aquifer sediments.
Precipitation of metal selenates or selenites	Dissolution of metal selenates/selenites due to increased pH	Evaluation of selenium speciation in ground water. Determination of total Se in the solid matrix and suspected components in arsenic-bearing mineral. Evaluation of mineral solubility relative to ground-water chemistry and published solubility constants.
Adsorption to iron oxyhydroxides, iron sulfides, or other mineral surfaces	Desorption at high pH for oxyhydroxides and sulfides; adsorption inhibition in the presence of DOC or competing anions. Reductive dissolution of iron hydroxides or oxidative dissolution of iron sulfides.	Evaluation of selenium speciation in the aqueous phase. Determination of total Se in the solid matrix. Evaluation of selenium solid phase partitioning using single or sequential extraction methodologies. Batch and column testing to determine Se uptake capacity of site-specific aquifer materials with variable geochemical conditions.

Table 7.2 Published USEPA methods for determination of selenium in aqueous samples.

Method Name and Number	Source
Inductively Coupled Plasma-Atomic Emission Spectrometry, *6010B, Revision 2*	December 1996 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6010b.pdf
Inductively Coupled Plasma-Mass Spectrometry, *6020, Revision 0*	September 1994 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6020.pdf
Selenium (Atomic Absorption, Furnace Technique), *7740, Revision 0*	September 1986 [a]
Selenium (Atomic Absorption, Gaseous Hydride), *7741a, Revision 1*	September 1994 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/7741a.pdf
Selenium (Atomic Absorption, Borohydride Reduction), *7742, Revision 0*	September 1994 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/7742.pdf

[a] *Available electronically at http://web1.er.usgs.gov/nemi/method_summary.jsp?param_method_id=5239.*

are electrochemically active [e.g., selenate and $(CH_3)_2Se$]. Thus, this analytical approach requires the development and testing of sample preparation schemes that can separate individual electrochemically active and inactive species and convert the latter to active forms. Given this analytical limitation, a potential advantage of this approach is that the instrumentation can be deployed in the field setting, facilitating rapid screening analyses.

It is important to insure that the *in-situ* speciation of aqueous selenium is maintained following sample collection prior to analysis. Gómez Ariza et al. (2000) provide a recent review of studies conducted to assess appropriate methods for selenium species preservation in natural water samples. In general, this review suggests that acidification followed by sample storage at ≤4 °C is adequate to prevent changes in the oxidation state of selenite/selenate and/or selenium loss via coprecipitation with ferric (hydr)oxides due to air exposure over reasonable time periods. More stringent collection, handling, and storage requirements may be necessary for ground-water samples with significant concentrations of organoselenium species. Alternatively, it may be possible to carry out separation of the various selenium species within the field using solid phase extraction (SPE) immediately following sample collection. There are several published reviews of the use of solid phase extraction media that may be employed to selectively extract individual selenium species from water samples (Bueno et al., 2002; Camel, 2003; Wake et al., 2004). Subsequent analysis of the retained selenium species can then be achieved in the laboratory following elution of the species off the SPE material. This approach may be necessary for water samples containing selenium species that are not amenable to chemical preservation within the native ground-water sample.

Solid Phase Measurements

Determination of the chemical speciation of selenium within aquifer sediments may be required for determination of the mechanisms active in its sequestration from ground water. This analysis may include determination of the oxidation state of selenium within the whole solid matrix or individual components, as well as the determination of its presence as a discrete solid phase (e.g., elemental selenium) or its association with specific mineral components (e.g., iron oxides or sulfides). The following review provides a summary of approaches that have been used to assist in identification of the solid phase associations controlling selenium solubility within a contaminant plume.

There are several examples within the literature of the determination of the distribution of selenium oxidation states within a solid matrix following partial or complete dissolution of the solid (e.g., Ferri et al., 1998; Ochsenkuhn-Petropoulou and Tsopelas, 2002; de Leon et al., 2003). However, there has been insufficient assessment of the potential for selenium species transformation that may occur with use of aggressive extraction procedures designed to achieve complete sample dissolution (especially oxidation state) in order to recommend this analytical approach. Determination of selenium oxidation state for extracts that are non-selective for various mineralogical associations within the aquifer sediment may not provide sufficient detail to identify specific partitioning mechanisms. In these instances, the use of extraction solutions that are intended to target specific mineralogical associations may provide a necessary compliment to determination of the distribution of selenium oxidation states within the whole solid matrix. Again, there are numerous examples of the use of single or sequential extraction procedures to determine the mineralogical speciation of selenium in soils and sediments. The following provides a synopsis of the most commonly employed procedures.

Sequential extraction procedures (SEP) employed for characterization of aquifer sediments can be categorized into two types: 1) procedures designed to quantify the abundance of various mineralogical components (e.g., iron oxides, carbonates, organic matter), and 2) procedures designed to quantify the abundance of specific trace element phase associations. The first SEP types have a longer history of development and application and are considered as an appropriate supplement to other analytical methods (e.g., X-ray diffraction, thermal analysis) used to define soil/sediment mineralogy. There are examples in the literature where this type of SEP has been used to infer selenium speciation in soil/sediments (e.g., Tokonaga et al., 1991). However, the chemical extractants employed in these procedures are not designed to specifically recover selenium from specific solid phase associations. In the absence of suitable standard reference materials (soils/sediments) and the general failure to include matrix spike analyses with reference compounds that represent various selenium solid phase species anticipated in soils/sediments (e.g., selenate/selenite adsorbed to reference soil minerals, elemental selenium, organoselenium compounds), the use of this approach is not likely to provide useful characterization information.

Sequential extraction procedures designed to target specific selenium solid phase associations (i.e., type two SEPs) have been developed and applied for characterization of soils and sediments. A recent study by Wright et al. (2003) provides a comprehensive review and analysis of the utility of these procedures. Ultimately, these authors demonstrated the non-selectivity of existing SEPs and provided analysis of an alternative SEP designed to target selenium in the following solid phase associations: 1) weakly adsorbed selenate, 2) strongly adsorbed selenite, 3) elemental selenium [Se(0)], and 4) selenium associated with the organic fraction. The authors provide a comprehensive analytical assessment of potential analytical artifacts and extraction phase selectivity through the use of model reference compounds incorporated into either a ‘synthesized’ reference soil or spiked into real soils/sediments for analytical performance analysis. Wright et al. (2003) point out that all procedures are not capable of uniquely identifying selenium in either an iron-selenide precipitate (e.g., $FeSe_{(s)}$) or selenium incorporated into iron sulfides (e.g,, mackinawite or pyrite). Velinsky and Cutter (1990) suggest the use of extractants designed to target dissolution of iron sulfides as a means for assessing the amount of coprecipitated selenium, but this avenue requires additional testing to properly assess its reliability. Chu et al. (2006) also point to the potential use of carbon disulfide as a stand-alone extractant to target the most labile form of elemental selenium. Finally, it is also important to circumventing possible analytical artifacts at the stage of selenium detection in the extraction solution due to interferences from either 1) reagents employed in the extraction and sample pre-treatment for analysis (Wright et al., 2003) or 2) sample matrix components that were liberated from the soil or sediment (Bujdoš et al., 2000).

Recently, X-ray absorption spectroscopy/microscopy employing synchrotron radiation sources have been employed to provide direct assessment of the *in-situ* speciation of selenium in soils/sediments. The synchrotron X-ray fluorescence microprobe (SXRFM) provides the capability of mapping elemental distributions at a spatial resolution which, in some cases, approaches 1 µm. The application of SXRFM for mapping selenium distribution within both natural and laboratory-constructed soil aggregates illustrates the potential usefulness of this tool for site characterization (Tokunaga et al., 1994; Strawn et al., 2002). In addition, X-ray absorption spectroscopy has been employed to identify the *in-situ* chemical speciation of selenium (including selenium oxidation state and bonding environment) in both experimental and natural materials (Tokunaga et al., 1994; Strawn et al., 2002; Herbel et al., 2003; Templeton et al., 2003). The advantage of these techniques is the ability to characterize the solid phase speciation of selenium at relatively low concentrations in soils/sediments with minimal sample handling that may perturb the characteristics of the as-collected sample. However, these methods are not routinely available, which limits their utility as a regular component of a site characterization effort.

Selenium Isotope Fractionation

A review of the use of selenium isotope measurements for the determination of selenium reduction processes active within an aquifer or the determination of selenium sources within a plume is provided in Johnson and Bullen (2004). The six stable isotopes, ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, and ^{82}Se, are present in abundances of 0.889, 9.366, 7.635, 23.772, 49.607, and 8.731%. Reduction of selenate and selenite, either through biotic or abiotic processes, may result in enrichment of lighter isotopes in the reduction products and a complementary enrichment of the heavier isotopes in the remaining unreduced selenium due to kinetic isotope fractionation processes (Johnson and Bullen, 2004). Since reduction of selenium results in breaking a bond with oxygen, the kinetic effect is a result of the smaller expense of energy by the microbe to reduce the lighter isotope. The current state of knowledge relative to the extent of selenium isotope fractionation as a result of abiotic-biotic oxidation/reduction processes is summarized in Table 7.3 (Johnson and Bullen, 2004). This summary is in part derived from recent studies designed to assess the importance of biotic (Herbel et al., 2000; Ellis et al., 2003) and abiotic (Johnson and Bullen, 2003) reduction processes that are anticipated to be active in reducing subsurface environmentals. Currently available data indicate that reduction of the selenium oxyanions, selenate and selenite, is the main source of fractionation observed in ground-water systems.

Determination of selenium isotope fractionation can be carried out using either thermal ionization mass spectrometry (TIMS; Johnson et al., 1999) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Rouxel et al., 2002). Both methods are susceptible to measurement bias due to changes in selenium speciation and mass distribution that may occur during sample preparation due to the susceptibility of selenium to redox transformations and volatilization. Therefore, it is recommended that a 'double spike' technique be employed to correct for these analytical inaccuracies (Johnson et al., 1999; Johnson and Bullen, 2004). With this method, a reference sample with known ^{82}Se/^{74}Se ratio is added to the sample and its recovery is monitored along with evaluation of the natural ratio of ^{80}Se/^{76}Se originally in the sample. In addition, the MC-ICP-MS method is also susceptible to bias due to the formation of polyatomic species with identical masses that form within the argon plasma (e.g., $ArCl^+$ and ArC^+; Rouxel et al., 2002). It should be noted that a representative inter-laboratory standard is not commercially available, although the National Institute of Standards and Technology does market a reference meteorite standard (Canyon Diablo

Table 7.3 Review of selenium isotope fractionation ranges for abiotic-biotic processes during reduction and oxidation (Johnson, 2004). NM = not measured

Reduction	*Abiotic*	*Biotic*	**Oxidation**	*Abiotic*	*Biotic*
Se(VI) → Se(IV)	7-12 ‰	3-5 ‰	Se(IV) → Se(VI)	0 ‰	NM
Se(IV) → Se(0)	6-13 ‰	6-9 ‰	Se(0) → Se(IV)	0 ‰	NM
Se(0) → Se(-II)	0 ‰	NM	Se(-II) → Se(0)	Small	NM

Troilite; SRM 3149). Typically, a provisional standard is generated via mixtures of synthetic solutions with known selenium isotope content, and this reference is used to monitor analytical performance. Isotopic measurements may be performed on the native ground water or chemical extracts used to determine the selenium isotope distribution in on whole or selective fractions of aquifer solids.

Long-term Stability and Capacity

The long-term stability of selenium immobilized onto aquifer solids will depend on the prevailing ground-water chemistry over time relative to the conditions that existed at the time of immobilization. If there are significant changes in ground-water chemistry following immobilization, then the potential exists for remobilization of selenium with the establishment of a new mobile plume. A general example of this type of situation would be if selenium was originally immobilized through partitioning to mineral sulfides within aquifer sediments under sulfate-reducing conditions. Selenium associated with sulfide minerals may be re-mobilized due to sulfide oxidation if the aquifer were to return to more oxidizing conditions. Alternatively, there is evidence that elemental selenium may be re-oxidized to selenite/selenate, resulting in re-mobilization of selenium in ground water (Tokunaga et al., 1996; Zawislanski and Zavarin, 1996; Losi and Frankenberger, 1998). However, as demonstrated by Dowdle and Oremland (1998) the oxidation of elemental selenium is a slow, microbially-controlled process with rates that are 3-4 orders of magnitude lower than microbial reduction of selenate/selenite.

The capacity to sustain continued removal of selenium from ground water will be dictated by the evolution of ground-water chemistry through time and the continued activity of relevant microbial processes. For situations in which adsorption or abiotic precipitation reactions control selenium attenuation, significant changes in pH or increases in the concentration of competing anions (e.g., sulfate) in ground water can cause reversal of adsorption reactions or dissolution of precipitates (e.g., metal selenates/selenites). Likewise, a change to more oxidizing conditions can cause destabilization of reduced mineral phases (e.g., sulfides) that may sequester selenium during the original attenuation reaction. For situations in which microbial reduction controls selenium attenuation, changes in the availability of required substrates/nutrients as well as potentially competing electron acceptors can reduce the capacity of the aquifer to sustain continued attenuation prior to consumption of the total mass of selenium within the plume. There is laboratory and field evidence that increases in ground-water nitrate can inhibit or slow down selenium reduction (Oremland et al., 1989; Benson, 1998). While these examples are not exhaustive of all possible situations, they do point to the importance of establishing a monitoring program that is designed to consider the potential impact of changes in site geochemistry relative to the conditions under which selenium is attenuated within the aquifer. Ultimately, the evolution of biogeochemical conditions in the subsurface will dictate the success of the MNA remedy.

Tiered Analysis

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

Tier I Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate Se partitioning to aquifer solids within the plume. Rapid movement of contaminants along preferred flow paths in the unsaturated and saturated zones can be induced by hydrologic events such as heavy rains (e.g., McCarthy et al., 1998; Camobreco et al., 1996). It will be important to determine that such hydrogeologic features do not result in contaminants bypassing zones where natural attenuation is occurring. If natural attenuation processes are active throughout the plume, then an observed increase in solid phase concentrations within regions of the plume with higher aqueous concentrations is anticipated, e.g., near the source term. This field partitioning data may be supplemented by geochemical modeling that incorporates measured water chemistry (e.g., pH, Eh, and major ion chemistry) throughout the plume to assess the potential for solubility control by metal selenates/selenites or elemental selenium. Since identification of the chemical speciation of selenium in water samples and aquifer sediments is critical towards determining the attenuation mechanism(s), it is recommended that precautions be taken to preserve selenium speciation during collection, preservation, and processing of collected samples (See recommendations and application of these methods in Wilkin et al., 2002 and Ford et al., 2005). Identification of active sequestration to prevent selenium migration in ground-water provides justification for proceeding to Tier II characterization efforts.

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

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

It is recommended that identification of selenium chemical speciation in aqueous and solid matrices be conducted using samples collected in a manner that preserves the *in-situ* mineralogy and speciation of selenium. The demonstration of concurrence between conceptual and mathematical models describing selenium transport will entail development of site-specific parameterization of the chemical processes controlling selenium solid phase partitioning.

Tier III Once the attenuation mechanism(s) has been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Se and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized Se be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage. For example, changes in ground-water redox potential due to oxygen intrusion or the occurrence of aerobic microbial processes can exert a significant influence on Se attenuated in its elemental form [Se(0)]. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of Se mobilization as a function of ground-water redox chemistry representative of existing and anticipated site conditions. This may involve the use of microcosm tests that stimulate *in-situ* microbial populations toward the development of redox conditions considered deleterious for continued Se immobilization. It is recommended that the capacity for Se uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that co-precipitation of Se with iron sulfide due to microbial degradation of organic compounds coupled with sulfate reduction occurs within the aquifer, it is recommended that the mass distribution of organic carbon, sulfate and ferrous iron to support this reaction within the aquifer be determined. This site-specific capacity can then be compared to Se mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized Se and sufficient capacity within the aquifer to sustain Se attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction may be necessary.

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

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Nitrate

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Occurrence and Distribution

Nitrate (NO_3^-) is a chemical form of nitrogen that is essential for plant growth, but potentially toxic to human and animal life at moderate concentrations. Nitrate is considered to be the most ubiquitous chemical contaminant in aquifers throughout the world with continuously observed increases in contamination (Spalding and Exner, 1993). Results from the USGS National Water Quality Assessment Program showed that in the United States nitrate is detected in 71% of ground water samples, more than 13 times as often as ammonium (NH_4^+), nitrite (NO_2^-), organic nitrogen, and orthophosphate, based on a common detection threshold of 0.2 mg of N L^{-1} (Nolan and Stoner, 2000). According to these authors, shallow ground water (< 5 m deep) beneath agricultural land has the highest median nitrate concentration (3.4 mg of N L^{-1}), followed by shallow ground water beneath urban land (1.6 mg of N L^{-1}) and deeper ground water in major aquifers (0.48 mg of N L^{-1}). Nitrate exceeds the maximum contaminant level (MCL), 10 mg of N L^{-1}, in more than 15% of ground-water samples from 4 of 33 major aquifers commonly used as a source of drinking water (Nolan and Stoner, 2000). Recent analyses of ground-water samples from about 1500 domestic drinking water and public supply wells show that of more than 140 contaminants measured, nitrate most frequently exceeded drinking water standards or human health criteria (Squillace et al., 2002).

A National Research Council report has indicated that there are approximately 300-400 thousand nitrate-contaminated sites in the United States (National Research Council, 1994). Sources of nitrate and nitrite in ground water include atmospheric deposition from fossil fuel burning, runoff from fertilizer use; leaching from animal wastes from confined animal feedlot operations and dairies, septic tanks, and sewage; solid waste disposal (landfills and waste tips); and erosion of natural deposits (Puckett, 1995; Nolan and Stoner, 2000). Organic nitrogen and ammonia are potential nitrate sources because they tend to be converted to nitrate in natural waters.

While nitrate leaching from disturbed forests is a threat to ground water, this source is small compared to agricultural and industrial sources (Keeney, 1986). A survey of eastern U.S. watersheds showed that the total nitrogen levels in streams draining agricultural watersheds were fivefold greater than forested watersheds, while the percentage of total nitrogen was much greater from agricultural than from forested watersheds (Omernik, 1976). Since most native and extensively managed grasslands are nitrogen deficient, very little nitrate will be available for leaching; also many of these grasslands are in the semiarid West where leaching is limited. On the other hand, intensively managed forage and grazed grasslands (with major nitrogen inputs from fertilizer and symbiotic nitrogen fixation) may be the source of considerable ground water nitrate. Grasslands, like croplands, have annual above-ground biomass cycles that leave nitrate in the soil profile susceptible to leaching at times of the year when plant uptake is minimal, usually spring and autumn (Keeney, 1986). Agricultural cropland provides a large nonpoint source relative to other nitrate sources. Nitrogen applications in amounts exceeding the optimum rates are often used to provide maximum economic yields. Excess nitrate in the root zone is leached at times when the soil is vulnerable to substantial rainfall or excessive irrigation. Irrigation combined with high use of nitrogen fertilizers is the primary source of nitrate in ground water (Keeney, 1986).

Most of the areas high in ground-water nitrate are west of the Missouri River where irrigation is a necessity. Aquifers in highly agricultural areas in the southeastern USA reportedly are not contaminated. Vegetative uptake and denitrification in this warm, wet, carbon-rich environment are responsible for the natural remediation of nitrate in shallow aquifers (Spalding and Exner, 1993). In the Middle Atlantic States and the Delmarva Peninsula, localized contamination occurs beneath cropped, well-drained soils that receive excessive applications of manure and commercial fertilizer. Extensive tile drainage has for the most part prevented a nitrate problem in the ground water of the Corn Belt states in that the nitrate-contaminated recharge is diverted by tile drains and subsequently is discharged to surface water (Spalding and Exner, 1993).

Point-source nitrate contamination includes ammonium nitrate as explosives residues in mining operations (e.g., Johnson et al., 2000). Nitrate in ground water can also arise from deposits lain down during geological times. Examples are nitrate found in Pleistocene age loess of semiarid southwestern and western central Nebraska (Boyce et al., 1976) and high levels of geological nitrogen found in the alluvium beneath the San Joaquin Valley, California (Strathouse et al., 1980; Holloway et al., 1998). A large reservoir of bioavailable nitrogen (up to 104 kilograms of nitrogen per hectare, as nitrate) has been previously overlooked in studies of global nitrogen distribution (Walvoord et al., 2003). The reservoir has been accumulating in subsoil zones of arid regions throughout the Holocene. Consideration of the subsoil reservoir raises estimates of vadose-zone nitrogen inventories by 14 to 71% for warm deserts and arid shrublands worldwide and by 3 to 16% globally. Subsoil nitrate accumulation indicates long-term leaching from desert soils, impelling further evaluation of nutrient dynamics in xeric ecosystems. Evidence that subsoil accumulations are readily mobilized raises concern about ground-water contamination as a result of land-use or climate change.

Ground water, due to its direct connection to surface waters, can be a significant source of nitrogen to lakes, impoundments, and estuaries. Increased nitrogen input from ground-water sources has caused overgrowth of aquatic plants and subsequently depletion of dissolved oxygen as plants decay (eutrophication). Although overlooked in many nutrient management plans, ground-water discharges of nitrate to streams may contribute the majority of the total amount of stream nitrogen (Williamson et al., 1998). Ground-water contamination at landfill sites by ammonium can be significant with mean concentrations of about 900 mg NH_4^+-N L^{-1} having been reported for landfill leachates in the United Kingdom (Burton and Watson-Craik, 1998). Ammonium production is a result of amino acid fermentation during decomposition of organic matter in domestic waste disposed under anaerobic conditions. Anaerobic conditions in the waste may persist for many years particularly if the landfill is capped with a low permeability cover to prevent water infiltration and gas exchange. Ammonium attenuation in subsoils and ground water is predominantly due to cation exchange and/or nitrification (biological oxidation) processes (Buss et al., 2004). Currently, more research is being conducted to improve the understanding of nitrogen cycling at the watershed level and to determine where nitrogen attenuation is occurring and to what extent. This information is needed to assist the U.S. Environmental Protection Agency and States with the general development of total maximum daily load (TMDL) for nitrogen, as well as to help States adopt more appropriate nutrient criteria on which TMDLs are based.

Plume Characteristics

Nitrate concentration in ground water is variable and depends on interactions among several factors, including nitrogen loading, soil type, aquifer permeability, recharge rate, climate, and aquifer oxidation state and pH. Factors that generally increase nitrate concentrations in ground water include well-drained soils, fractured bedrock, and irrigation. Factors that mitigate nitrate contamination of ground water include poorly drained soils, greater depth to ground water, artificial drainage systems, intervening layers of unfractured bedrock, a low rate of ground water recharge, and anaerobic conditions in aquifers (Nolan and Stoner, 2000). Vulnerability of ground water to contamination by nitrate does not depend on any single factor, but on the simultaneous influence of factors representing nitrogen loading sources and aquifer susceptibility (Nolan, 2001). Tools have been developed to assess aquifer susceptibility to nitrate contamination based on the factors indicated above (Ceplecha et al., 2004). Research conducted within the North Carolina Coastal Plain illustrates the dependence of nitrate transport on the variability of subsurface hydrogeologic characteristics. The North Carolina Coastal Plain consists of varying permeability surface sediments underlain by relatively impermeable, highly reduced sediments (Gilliam et al., 1974). Nitrate accumulates in the shallow ground water in response to agricultural activities, but because of the reduced zones (up to 15 m thick) it does not reach deep aquifers (Gilliam et al., 1979). It was found that if the water table was artificially raised using flashboard riser-type water-level control structures on tile mains or outlet ditches, denitrification in the subsoils could be enhanced to reduce nitrate concentrations in shallow ground water (Skaggs and Gilliam, 1981).

Remedial Technologies

A recent review of available technologies for remediation of nitrate contamination in ground water has been published by the Interstate Technology Regulatory Council (ITRC, 2000), which is available at http://www.itrcweb.org/Documents/EISBD-1.pdf. Available technologies include: 1) ex-situ, pump-and-treat approaches that extract nitrate from recovered ground water or degrade nitrate to innocuous compounds through above-ground biotic or abiotic chemical reduction processes, and 2) in-situ treatment approaches that degrade nitrate within the plume via phytoremediation, stimulation of native microbial communities for denitrification, or the emplacement of media that achieve biotic and abiotic chemical reduction of nitrate. Examples of field demonstrations of biotic remediation technologies for removal of nitrate from ground water are listed in Table 8.1. In addition, research indicates that abiotic processes may be used to remediate nitrate via ex-situ or in-situ approaches. Technologies that extract nitrate from water via concentration onto solid media (e.g., Tezuka et al., 2004) or into a waste brine have the disadvantage of requiring further treatment or disposal of the process waste stream (e.g., Dorsheimer et al., 1997). Examples of chemical reduction of nitrate via systems with reduced Fe media (Chew and Zhang, 1998, 1999; Alowitz and Scherer, 2002; Chen et al., 2004; Su and Puls, 2004; Chen et al., 2005; Mishra and Farrell, 2005; Yang and Lee, 2005) indicate that the predominant reaction leads to the production of ammonia-nitrogen, although the potential exists to control reaction conditions to favor complete nitrate reduction to dinitrogen gas. There is evidence that zero-valent iron may also stimulate the growth of subsurface denitrifying bacteria (Gu et al., 2002), suggesting the use of this material in permeable reactive barriers for mixed contaminant plumes containing nitrate and other inorganic/organic constituents more amenable to chemical reduction.

The success of these treatment approaches will be influenced by the level of knowledge of the ground-water flow regime as well as the geochemical characteristics within the plume. For technologies based on nitrate extraction, the

Table 8.1 Example field applications of biotic remedial technologies for nitrate removal.

Technology	Application Setting	Approach	Reference
Phytoremediation/ Riparian Buffers/ Constructed Wetlands	Prevent deep percolation of nitrate at an abandoned feedlot high in soil profile nitrate	Planted corn (*Zea mays* L.) and deep-rooted alfalfa (*Medicago* sativa L.)	Schuman and Elliott (1978)
	Cover cropping in the Northern U.S. Corn Belt to decrease nitrate loss from subsurface drainage discharge	Planted autumn-seeded rye (*Secale cereale* L.) following corn harvest	Strock et al. (2004)
	Desert soil at a former uranium ore-processing plant, near Monument Valley, Arizona	Planted fourwing saltbush (*Atriplex canescens*); biological denitrification	McKeon et al. (2005)
	Nutrient interception by a riparian forest adjacent to cropland on Delmarva peninsula	Monitoring network consisting of well transect from crop field through hill slope, adjacent flood plain, and into receiving stream; measured nitrate removal	Jordan et al. (1993)
	Wastewater effluent flowed through shallow ground water of a forested headwater riparian zone within the Appalachian Valley and Ridge physiographic province	Monitored denitrification enzyme activity attributable to riparian zone location, soil horizon, and nitrate amendments	Flite et al. (2001)
In-situ treatment; Permeable Reactive Barriers	Permeable reactive barriers to intercept effluent from septic system infiltration beds, horizontally migrating septic system plume, farm field drainage water, or a shallow sand-and-gravel aquifer	Porous media barrier composed of waste cellulose solids (wood mulch or particles, sawdust, leaf compost); horizontal infiltration beds in vadose zone and vertical wall or buried containerized systems in saturated zone	Robertson and Cherry (1995); Robertson et al. (2000); Robertson et al. (2005)
	Permeable reactive subsurface barriers at two field sites in an agricultural area of southwestern Ontario	Upflow reactors with wood particle carbon source with very high hydraulic conductivities (0.1–1 cm s^{-1})	van Driel et al. (2006)
In-situ treatment; Permeable Reactive Zones via Injection	Stimulation of in-situ biological denitrification via subsurface injection of a carbon source such as ethanol or acetic acid	Network of injection and recovery wells to control ground-water recirculation in subsurface reaction zone; operational parameters influenced denitrification rates and formation clogging	Hiscock et al. (1991); Hamon and Fustec (1991)
	Plumes originating from former waste disposal ponds at the Y-12 plant Complex within the Oak Ridge National Laboratory; acidic sediments, low ground-water pH (pH 3.8 – 4.4), high nitrate (9-154 mM)	Conducted push-pull tests in wells to stimulate and monitor denitrification; injected solutions consisted of neutralized site ground water made anoxic by sparging with 80%N_2-20%CO_2, and amended with either ethanol or glucose as an electron donor	North et al. (2004)
	Sand and gravel aquifer at the Massachusetts Military Reservation, Cape Cod near Falmouth, Massachusetts; nitrate plume from surface disposal of treated sewage	Sodium formate solution injected as a potential electron donor for denitrification; nitrate reduction occurred with buildup of nitrite due to incomplete reduction	Smith et al. (2001)

presence of common anions in ground water may reduce treatment performance for engineered systems based on ion exchange, reverse osmosis, or electrodyolisis. For microbial nitrate reduction (ex-situ or in-situ), geochemical parameters such as low pH and high total dissolved solids, as well as the presence of aerobic conditions or competing electron acceptors such as perchlorate or sulfate may negatively impact the rates and extent of nitrate reduction that can be achieved. It is important to consider these site-specific factors when selecting treatment technologies.

Regulatory Aspects

Nitrate was ranked number 216, nitrite number 212, and ammonia number 160 out of a total of 275 contaminants on the CERCLA Priority List of Hazardous Substances in 2001 (Centers for Disease Control, 1996). The USEPA has set the MCL for nitrate at 10 mg of N L^{-1} (USEPA, 2006; http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf). The USEPA has determined that infants below the age of six months who drink water containing nitrate or nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms of acute exposure include shortness of breath and blueness of the skin, or blue-baby syndrome (methemoglobulinemia). This is due to the conversion of nitrate to nitrite by the body, which interferes with the oxygen-carrying capacity of the child's blood. Chronic exposure to high levels of nitrate/nitrite results in diuresis, increased starchy deposits, and hemorrhaging of the spleen (http://www.epa.gov/safewater/contaminants/dw_contamfs/nitrates.html).

Geochemistry and Attenuation Processes

Aqueous Speciation

Nitrate (with an oxidation number of +5 for nitrogen) is the conjugate base of HNO_3, a strong mineral acid. Common metal nitrate salts are highly soluble in water. Nitrate forms weak coordination complexes with metals and displays minimal sorption to inorganic or organic surfaces. Being an anion, nitrate (NO_3^-) in solution is attracted electrostatically to positively charged surfaces and is repulsed by negative surfaces. Nitrate is not appreciably adsorbed onto aquifer sediments.

Redox Chemistry

Denitrification refers to a microbial respiratory process where nitrate is used as a terminal electron acceptor and is reduced to dinitrogen gas by the following generalized half reaction:

$$2NO_3^- + 12\,H^+ + 10e \rightarrow N_2 + 6H_2O \qquad \text{(Eq. 8.1)}$$

It is an important biological process for the return of fixed nitrogen to the atmosphere. In the above respiratory electron transport process electron donors are usually organic matter or reduced sulfur compounds. Nitrate can also be reduced to ammonium, but this requires highly reducing conditions and organic carbon. The denitrifying bacteria use nitrate, nitrite, or nitrous oxide as terminal electron acceptors for respiratory growth in the presence of gaseous oxygen and under micro-aerobic and anaerobic conditions. Denitrification involves four consecutive steps in which nitrate is reduced to dinitrogen gas by the metalloenzymes, nitrate reductase, nitrite reductase, nitric oxide reductase, and nitrous oxide reductase:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad \text{(Eq. 8.2)}$$

Many denitrifying organisms do not contain or express all of the four reductases needed for complete denitrification so that the interaction of different organisms is needed to reduce nitrate completely into dinitrogen gas.

Anaerobic conditions in the immediate cell environment are essential for denitrification to occur (Table 8.2). This translates to a measured Eh potential of 300 to 350 mV (Reddy and Patrick, 1984). Denitrification is not limited to water-logged soils, it occurs in moist, fine-textured soils as well as in localized micro-anoxic zones within the overall aerobic soil matrix. The optimum temperature range for denitrification is from 20 to 35 °C and the optimum pH is neutral to slightly alkaline, but denitrification will occur over at least pH 5 to 9 (Focht and Verstraete, 1977). Denitrification can be described by a zero-order kinetic reaction at high concentrations of nitrate, and by a first-order reaction at low concentrations (Focht and Verstraete, 1977).

There are two physiologically distinct classes of denitrifying bacteria: heterotrophic denitrifiers, which use organic

Table 8.2 Natural attenuation and mobilization pathways for nitrate.

Attenuation Processes	Mobilization Processes	Characterization Approach
Biotic (microbial) or abiotic transformation of nitrate to other nitrogen species.	Cessation of microbial processes via changes in nutrient supply within the ground-water flow path; reduction in the mass of reduced Fe-bearing minerals within the aquifer due to changes in redox conditions or supply of soluble iron.	Evaluation of N speciation in ground water. Determination of water chemistry, microbial populations, and/or sediment mineralogy linked to nitrate transformation along with spatial and temporal variability of required chemical/microbial components relative to nitrate transport pathway(s).

compounds as electron donors and carbon sources (Equation 8.3 and 8.4); and chemolithoautotrophic (or autotrophic) denitrifiers, which use inorganic compounds (e.g., minerals containing reduced sulfur and iron) as electron donors and CO_2 as a carbon source (Equations 8.5 and 8.6):

Heterotrophic denitrification:

$$4\ NO_3^- + 5CH_2O\ \text{(organic matter)} \rightarrow 2\ N_2 + 5HCO_3^- + H^+ + 2H_2O \tag{Eq. 8.3}$$

$$8\ NO_3^- + 5CH_3COO^-\text{(acetate)} + 3H^+ \rightarrow 4\ N_2 + 10HCO_3^- + 4H_2O \tag{Eq. 8.4}$$

Autotrophic denitrification:

$$14\ NO_3^- + 5FeS_2\ \text{(pyrite)} + 4H^+ \rightarrow 7\ N_2 + 5Fe^{2+} + 10\ SO_4^{2-} + 2H_2O \tag{Eq. 8.5}$$

$$NO_3^- + 5Fe^{2+} + 7H_2O \rightarrow 5FeOOH\ \text{(goethite)} + 0.5\ N_2 + 9H^+ \tag{Eq. 8.6}$$

Because the rate and extent of denitrification are dependent on available carbon supply (Reddy and Patrick, 1984), it is often assumed that denitrification is not important as a nitrate-removal mechanism below the root zone. Denitrification is usually not significant in the subsurface of low organic matter and of sandy soils.

Nitrate was found in the ground water beneath poorly drained soils of the North Carolina Coastal Plain and denitrification was proposed as a nitrogen loss mechanism in the saturated subsoil (Gilliam et al., 1974). Based on nitrate concentration data, nitrogen mass balances, soluble organic carbon, and redox potential measurements, Gambrell et al. (1975) concluded that denitrification could readily occur in the subsurface (1 to 2.5 m) of poorly drained subsoils of the North Carolina Coastal Plain. They attributed this to the high amounts of dissolved organic carbon (the subsoil was overlain by an organic soil), low dissolved oxygen, and low Eh (350 mV at 1 m). The nitrate concentration and nitrate-to-chloride concentration ratios declined sharply with depth. The North Carolina case is relevant to many other riparian and wetland areas that are believed to be significant in denitrification losses at the watershed level. Under certain flow and redox conditions, riparian zones along waterways have demonstrated a natural proficiency to intercept and denitrify nitrate in shallow ground water (Gilliam, 1991; Schipper et al., 1991).

The rate and mechanism of nitrate removal along and between ground water flow paths were investigated using a series of well nests screened in an unconfined sand and gravel aquifer in southwestern British Columbia, Canada (Tesoriero et al., 2000). Intensive agricultural activity in this area has resulted in nitrate concentrations in ground water often exceeding drinking water standards. Both the extent and rate of denitrification varied depending on the ground water flow path. While little or no denitrification occurred in much of the upland portions of the aquifer, a gradual redox gradient was observed as aerobic upland ground water moved deeper into the aquifer. In contrast, a sharp shallow redox gradient was observed adjacent to a third-order stream as aerobic ground water entered reduced sediments. An essentially complete loss of nitrate concurrent with increases in excess dissolved N_2 gas provided evidence that denitrification occurred as ground water entered this zone. Low denitrification rates were observed along the deep flow path (< 0.04 μmol cm^{-3} aquifer yr^{-1}). The estimated denitrification rate for the redoxcline in this aquifer ranged from 0.3 to 0.8 μmol cm^{-3} aquifer yr^{-1}, and an *in-situ* experiment conducted adjacent to the stream suggested potential denitrification rates may be as high as 42 μmol cm^{-3} aquifer yr^{-1}. Electron and mass balance calculations suggested that iron sulfide (e.g., pyrite) deposits and to a lesser degree organic matter were electron donors for denitrification.

Shallow anaerobic ground water not immediately adjacent to streams exhibits variable but generally low rates of denitrification. Natural gradient tracer tests yielded potential denitrification rates ranging from 0.44 to 1.1 μmol cm^{-3} aquifer yr^{-1} for a shallow sand and gravel aquifer on Cape Cod, Massachusetts (Smith et al., 1996). Greater denitrification rates (24 μmol cm^{-3} aquifer yr^{-1}) were estimated from an *in-situ* experiment conducted 3 m below the land surface in a shallow aquifer in Ontario, Canada (Trudell et al., 1986).

Pyrite-bearing aquifers represent important hydrological compartments due to their capacity to eliminate nitrate. In the absence of molecular oxygen, the nitrate is reduced coupled with the microbial oxidation of sulfur in the pyrite by the bacterium *Thiobacillus denitrificans* (Pauwels et al., 1998, Grimaldi et al., 2004). A field tracer test using Br^- coupled with nitrate injection revealed that denitrification rates in a pyrite-bearing schist aquifer varied depending on the medium permeability, with slower the denitrification rate observed in regions of faster ground-water flow velocity (Pauwels et al., 1998). Denitrification was shown to be accompanied by the precipitation of sulfate and iron-bearing minerals, probably jarosite ($KFe_3(SO_4)_2(OH)_6$).

Under anaerobic conditions, the presence of both nitrate and ammonium may facilitate establishment of anaerobic ammonium-oxidizing (anammox) bacteria that directly oxidize ammonium to dinitrogen gas with nitrate (Mulder et al., 1995) and nitrite (Dalsgaard et al., 2003) as the electron acceptor:

$$5NH_4^+ + 3NO_3^- \rightarrow 4N_2 + 9H_2O + 2H^+ \tag{Eq. 8.7}$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \tag{Eq. 8.8}$$

It remains to be seen if ammonium accumulation is an issue of concern where nitrate is a major remediation target.

Chemical reduction of nitrate has been shown to occur in a mixture of dissolved Fe^{2+} and Fe(II)-containing silicates (arfvedsonite and augite), but only after an oxyhydroxide precipitate had formed on the silicate surface (Postma, 1990). Similarly, nitrite has been shown to be reduced to N_2O by adsorbed Fe(II) on the surface of lepidocrocite (γ-FeOOH) at pH > 7 (Sørensen and Thorling, 1991). The Fe(II) associated with a reactive complex formed during Fe^{2+} binding to lepidocrocite, and not the ionic Fe^{2+}, seemed responsible for the reduction of NO_2^- similar to the following reaction, where the first term in the reaction signifies ferrous iron adsorbed to lepidocrocite.

$$6Fe^{2+}_{(ads)} + 2\ NO_2^- + 5H_2O \rightarrow 2Fe_3O_{4(s)} + N_2O + 10H^+ \qquad \text{(Eq. 8.9)}$$

In this reaction, it is presumed that the ferrous iron-lepidocrocite surface complex is converted to surface precipitate similar in nature to the mineral magnetite. The catalytic effect of Fe(III) oxyhydroxide may stimulate Fe(II)-dependent formation of N_2O from NO_2^- (chemodenitrification) in sediments and subsoils.

In sulfate green rust $[Fe(II)_4Fe(III)_2(OH)_{12}SO_4 \bullet nH_2O]$ suspensions, nitrate is stoichiometrically reduced to NH_4^+, and magnetite is the sole Fe-containing product (Hansen et al., 1996).

$$4Fe(II)_4Fe(III)_2(OH)_{12}SO_4 + NO_3^- + 6OH^- \rightarrow NH_4^+ + 8Fe_3O_4 + 4SO_4^{2-} + 24H_2O \qquad \text{(Eq. 8.10)}$$

Recent thermodynamic and spectroscopic studies give direct evidence for the existence of green rusts in soils (Hansen et al., 1994; Trolard et al., 1997). Since microbial processes may be expected only to dominate in environments rich in organic carbon, the green rust-facilitated NH4+ formation may be an important pathway for nitrate removal and nitrogen conservation in certain anoxic subsoils and sediments poor in organic matter.

Site Characterization

Groundwater geochemistry provides information about the source, transformation, and attenuation of nitrate in ground water. In addition, specific soil properties are important parameters determining the potential for natural attenuation of nitrate. For example, nitrate concentrations at the 0.8 to 8 m depth at 15 sites within a beef feedlot were found to decrease as clay content increased (Lund et al., 1974). Other characteristics, such as a clay layer that severely restricted water movement, also decreased soil nitrate concentrations. It was probable that considerable soluble carbon was leached from the feedlot floor to provide energy for denitrification. The presence of ample organic carbon in the soil leads to active denitrification. Studies on the fate of nitrate below organic waste disposal sites (food processing waste lagoons, manure lagoons, feed yard, sewage sludge, and effluent septic tank drainfields) have shown significant denitrification in the vadose zone (Keeney, 1981).

Measurement of Inorganic Nitrogen Species

It is recommended that site characterization include measurement of the various inorganic nitrogen species – largely nitrate, nitrite, and ammonia in ground water. At circum-neutral pH typical of most ground water, ammonia is present predominantly as the ammonium ion (NH_4^+). Nitrogen is a redox sensitive element that is involved in numerous chemical and biological processes. It is anticipated that the fate and transformation of nitrate, nitrite, and ammonia in the subsurface would be reflected by the changes of their concentrations in the aqueous phase of the subsurface environment with time. It is therefore important to monitor their concentrations as an integral part of the overall evaluation of natural attenuation at a site. A summary of available laboratory methods for determination of the various inorganic species of nitrogen in ground water is provided in Table A.1 in USEPA (2002), which is available at http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf.

Although field colorimetric methods are available to quantify nitrate, nitrite, and ammonia, field determination using these methods is not generally needed as long as laboratory measurements can be made within specified holding times. Samples collected for nitrogen speciation are to be preserved by keeping cold (4°C) and measured within specified holding times, generally < 48 h. Depending on the method of analysis, longer holding times are possible by acidifying samples with sulfuric acid and keeping them cold. Prior to analysis, acid-preserved samples are to be brought back to room temperature and neutralized by adding base.

Use of Nitrogen Isotope Ratios for Identifying Sources and Transformation Processes of Nitrate

There are two stable isotopes of nitrogen: ^{14}N (with a natural abundance of 99.6337 atom percentage) and ^{15}N (0.3663) (Junk and Svec, 1958). Enrichment of ^{15}N is expressed on the per mille (‰) basis, and is calculated as:

$$\delta^{15}N‰ = (\text{atom}\%^{15}N_{\text{sample}} - \text{atom}\%^{15}N_{\text{standard}}) \times 1000 / (\text{atom}\%^{15}N_{\text{standard}}) \qquad \text{(Eq. 8.11)}$$

The standard is usually atmospheric nitrogen. Manufactured fertilizers and nitrate in precipitation tend to have ^{15}N concentrations close to natural abundance ($\delta^{15}N‰ = 0$), and soil organic matter nitrogen and hog manure organic nitrogen show greater $\delta^{15}N‰$ values (Kellman, 2005). In bacterially mediated processes the reaction of the light isotopic species is kinetically favored. As a result, the $^{15}N/^{14}N$ ratio of the instantaneously-formed product is lower than the $^{15}N/^{14}N$ ratio of the remaining, unreacted substrate. Ammonia volatilization can also lead to ^{15}N isotope enrichment in the remaining substrate. This "kinetic isotope fractionation" is defined in terms of the isotope enrichment factor, $\varepsilon_{\text{product-substrate}}$ ($\varepsilon_{\text{p-s}}$),

$$\varepsilon_{\text{p-s}} \approx \delta^{15}N_{\text{product}} - \delta^{15}N_{\text{substrate}} \qquad \text{(Eq. 8.12)}$$

For bacterial processes, $\varepsilon_{\text{p-s}}$ is negative or zero (Heaton et al., 2005). If a process can be approximated as a first order reaction, changes in the $\delta^{15}N$ value of the product or substrate of the reaction can be calculated using "Rayleigh" equations (Heaton et al., 2005).

For the substrate,

$$\delta_{s,t} = \delta_{s,0} + \varepsilon_{\text{p-s}}.\ln(f), \qquad \text{(Eq. 8.13)}$$

and for the total accumulated product,

$$\delta_{p,t} = \delta_{s,0} - \varepsilon_{\text{p-s}}.\ln(f)[f/(1-f)] \qquad \text{(Eq. 8.14)}$$

Where $\delta_{s,t}$, $\delta_{p,t}$ are the $\delta^{15}N$ values of the remaining substrate and accumulated product at time t; $\delta s_{,0}$ is the initial

$\delta^{15}N$ value of the substrate; f is the fraction of substrate remaining; and ε_{p-s} is the isotope enrichment factor for the process.

Since the early 1990s, a few published studies have focused on the transport and fate of nitrate in ground water using dual isotope analysis (e.g., $\delta^{15}N$ and $\delta^{18}O$ in dissolved NO_3^-) in combination with other lines of evidence to document *in-situ* microbial denitrification (Aravena and Robertson, 1998; Beller et al., 2004). Analytical procedures have been developed for determination of $\delta^{15}N$ via catalytic reduction of nitrate to N_2 after anion exchange separation and precipitation as $AgNO_3$, and for determination of $\delta^{18}O$ via combustion of nitrate to CO_2 using excess graphite (Aravena and Robertson, 1998). For determination of isotopic signatures of both nitrate and nitrite, a quantitative method has been developed based on bacterial denitrification (Sigman et al., 2001; Casciotti et al., 2002). Widory et al. (2005) used a coupled isotopic approach ($\delta^{15}N$ and $\delta^{11}B$), in addition to conventional hydrogeological analyses, to trace the origin of NO_3^- in ground water. The studied watersheds include both fractured bedrock and alluvial (subsurface and deep) hydrogeological contexts. The joint use of nitrogen and boron isotope systematics in each context deciphers the origin of NO_3^- in the groundwater and allows a semi-quantification of the contributions of the respective pollution sources (mineral fertilizers, wastewater, and animal manure).

To investigate the fate of nitrate in a petroleum-contaminated aquifer, ^{15}N isotope and acetylene-inhibition methods in combination with single-well push-pull tests were used to quantify processes contributing to nitrate consumption (Schurmann et al., 2003). The processes quantified included denitrification, assimilatory nitrate reduction, dissimilatory nitrate reduction to ammonium, and abiotic nitrate reduction. Multiple lines of evidence from chemical composition, stable isotope ($^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{34}S/^{32}S$), and dissolved gas (N_2, Ar, O_2, and CH_4) composition of ground water at a landfill site were used to account for all NH_4^+ loss by combined nitrification and denitrification processes in a system where there were abrupt temporal and spatial changes in redox conditions (Heaton et al., 2005).

There are pitfalls in nitrogen source identification using the nitrogen isotope approach. The heterogeneity of complex watersheds makes source identification difficult; the complexity of the nitrogen cycle and the associated isotope fractionations can make the results ambiguous or unreliable; source identification becomes very difficult when mixing of point and non-point sources occurs; isotopic ratios sometimes are hard to determine in environmental samples due to analytical difficulties. It appears that use of $\delta^{15}N$ to identify sources of nitrogen to ground waters is feasible only in relatively simple systems (e.g., low rainfall, single or dual sources, and minimal nitrogen transformations such as denitrification). Watershed- or ecosystem- level studies using this technique are semiquantitative at best. In most cases where $\delta^{15}N$ can be applied reliably, the sources of nitrogen are obvious or can readily be estimated by other, less expensive means (Keeney, 1986). In one case, nitrogen isotopic data were of little help in determining the relative importance of cyanide and explosive residues as nitrogen sources in surface ponds at three Nevada gold mine sites. The data do, however, provide strong evidence for natural attenuation of non-cyanide nitrogen species by dispersal of ammonia gas or by dispersal of N_2O or N_2 gas produced by denitrification of nitrate (Johnson et al., 2000).

Use of ^1H Nuclear Magnetic Resonance for Identifying Sources of Nitrate

Dissolved organic matter (DOM) originating from a certain source usually carries characteristic marks in its molecular structures that can be recognized by spectroscopic analysis such as nuclear magnetic resonance (NMR). Sources of water-born contaminants, such as nitrate, can be identified by recognition of the characteristics of DOM entrained in the water. Lu et al. (2004) analyzed DOM in ground water collected from a dairy/crop production area (Chino Basin, CA) using ^1H NMR. Results showed that DOM derived from natural soil organic matter has a characteristic resonance at a chemical shift region of 4.0-4.3 ppm, while DOM derived from dairy wastes has a characteristic resonance at a lower chemical shift region of 3.2-3.6 ppm. These signature resonances were then used to distinguish the origins of nitrate in the ground water. It was found that disposal of dairy wastes on croplands was the primary source of nitrate contamination in ground water underlying the Chino Basin dairy area.

Denitrification Enzyme Activity

Denitrification enzyme activity (DEA) experiments can be conducted according to Tiedje (1994) using soils/sediments collected from the aquifer. It is recommended that these tests be conducted with caution due to potential disturbance to intact soil/sediment conditions during retrieval and processing. However, DEA has been shown to be strongly related to annual denitrification rates in temperate zone soils, and is useful for comparisons within a site as well as for the distribution of rates within soil horizons (Groffman and Tiedje, 1989; Schnabel et al., 1996; Flite et al., 2001). The end product of denitrification is N_2 gas, thus, it may be useful to analyze ground water for dissolved N_2 gas at locations where soils/sediments are sampled for DEA experiments. This dissolved gas is a good indicator of denitrification when found in excess of concentrations expected relative to atmospheric trace gases such as Ar (Vogel et al., 1981; Böhlke and Denver, 1995).

Estimation of Denitrifying Capacity

Ground-water denitrification capacity may be evaluated through laboratory microcosm studies using aquifer sediments or through direct *in-situ* tracer tests in discrete locations within the aquifer. However, successful extrapolation of the results from these measurements across the site will depend on the degree of sampling frequency to capture spatial heterogeneity in both horizontal and vertical dimensions of the site with respect to hydrology, soil characteristics, and biogeochemical processes. It is recommended that both approaches be employed for a given site, since there is evidence that measured potentials of nitrate removal derived from laboratory microcosms may overestimate removal capacities in the field (Kellman, 2004). Korom et al. (2005) illustrated the use of *in-situ* mesocosm to determine denitrification rates in aquifer sediments. These authors incorporated information from tracer tests, $\delta^{15}N$ data, and geochemical data to determine that 58% of the denitrification was caused by S(-I) in pyrite as the electron donor with the rest from ferrous iron and organic carbon.

To quantify ground water denitrification in discrete locations of riparian aquifers, Addy et al. (2002) modified and evaluated an *in-situ* method based on conservative tracers and ^{15}N-enriched nitrate. Ground water was "pushed" (i.e., injected) into a mini-piezometer and then "pulled" (i.e., extracted) from the same mini-piezometer after an incubation period. This push–pull method was applied in replicate mini-piezometers at two Rhode Island riparian sites, one fresh water and one brackish water. Conservative tracer pretests were conducted to determine incubation periods, ranging from 5 to 120 h, to optimize recovery of introduced plumes. For nitrate push–pull tests, they used two conservative tracers, sulfur hexafluoride and bromide, to provide insight into plume recovery. The two conservative tracers behaved similarly. The dosing solutions were amended with ^{15}N-enriched nitrate to quantify the mass of denitrification gases generated during the incubation period. The *in-situ* push–pull method detected substantial denitrification rates (mean of 97 µg N kg^{-1} d^{-1}) at a depth of 65 cm in a glacial outwash setting located within 10 m of the stream. At the brackish site, high rates of ground water denitrification were found in marsh locations (mean of 123 µg N kg^{-1} d^{-1}) and minimal denitrification in soils fringing the marsh (mean of 2 µg N kg^{-1} d^{-1}) at a depth of 125 cm. The push–pull method can provide useful insights into spatial and temporal patterns of denitrification in riparian zones. The method is robust and results are not seriously affected by dilution or degassing from ground water to soil air. In conjunction with measurements of ground water flow, this method holds promise for evaluating the influence of site and management factors on the ground-water nitrate removal capacity of riparian zones (Addy et al., 2002; Kellogg et al., 2005).

Attempts have been made to estimate the denitrifying removal capacity of an entire wetland (Maître et al., 2005). The authors developed a methodology that consisted of the following steps: 1) delineating the structure of aquifer formation in the riparian wetland; 2) mapping the spatial variation of the thickness of the different soil horizons constituting the aquifer formation; 3) measuring the DEA for each type of soil horizon; 4) grouping the soil horizons in specific soil-denitrifying classes; 5) mapping the spatial variation of the thickness of each soil-denitrifying class; 6) mapping the spatial variation of the water table position; 7) combining the maps to calculate the volume of the fraction of each soil-denitrifying class that interacts with groundwater; and 8) calculating the denitrifying removal capacity of the whole site.

Long-term Capacity

The long-term capacity of nitrate transformation within the aquifer will depend on the prevailing ground-water chemistry and the dynamics of biotic and abiotic processes controlling conversion of nitrate to other nitrogen species. If there are significant changes in ground-water chemistry over time, then the potential exists for reductions in the aquifer denitrifying capacity relative to nitrate loading from the contaminant plume. For situations in which nitrate transformation is controlled by biotic (microbial) processes, this may be due to reductions in degradable organic carbon (dissolved or associated with aquifer matrix) and nutrients needed to sustain the microbial community. For situations where abiotic components control nitrate transformation, e.g., reduced Fe-bearing minerals, changes to more oxidizing conditions or reductions in the supply of iron to sustain the mass of reactive minerals would likely result in nitrate plume expansion. Ultimately, the evolution of biogeochemical conditions in the subsurface will dictate the success of the MNA remedy.

Since heterotrophic denitrification reactions require that the water is anaerobic ($Eh < 350$ mV) and that considerable organic carbon is present at concentrations greater than the nitrate concentration (Korom, 1992), significant widespread denitrification in aquifers are unlikely to occur. Based on water chemistry data, it was concluded that denitrification cannot be relied upon to decrease elevated nitrate concentrations in the modern, polluted, recharge waters of the English chalk (limestone) aquifer (Howard, 1985). On the other hand, situations exist where denitrification may be occurring in some shallow aquifers. For example, Egboka (1984) studied six ground water flow systems in Ontario, Canada under widely varying land use. Several of the ground waters exhibited low dissolved oxygen and Eh, but there was little consistency in the nitrate to chloride ratio. Nitrate concentrations at the sites that were reducing (low Eh) declined with distance from the nitrate source. Vidon and Hill (2004) observed effective nitrate removal by denitrification in riparian zones with hydric soils as well as in non-hydric riparian zones, and they concluded that a shallow water table is not always necessary for efficient nitrate removal by denitrification.

Chemolithoautotrophic denitrification may occur with pyrite as the electron donor. This is the proposed mechanism derived from a recent study based on the low dissolved organic carbon concentrations (< 1.5 mg L^{-1}) that could not support heterotrophic denitrification, the common occurrence of disseminated pyrite in the aquifer, and the trend of increasing sulfate as ground water flowed from aerobic, unconfined conditions to anoxic, confined aquifer conditions (Beller et al., 2004). In this study, several independent lines of evidence suggested that microbial denitrification was naturally attenuating nitrate in a confined, O_2-depleted region of a bedrock aquifer at a Lawrence Livermore National Laboratory site. The evidence included the following observations: (1) both nitrate and dissolved oxygen concentrations in ground water decreased dramatically as ground water flowed from unconfined to confined aquifer conditions, (2) stable isotope signatures (i.e., $\delta^{15}N$ and $\delta^{18}O$) of ground water NO_3^- indicated a trend of isotopic enrichment that was characteristic of denitrification, and (3) dissolved N_2 gas, the product of denitrification, was highly elevated in nitrate-depleted ground water in the confined region of the aquifer. At this site, long-term nitrate concentrations were relatively high and constant in recharge-area monitoring wells (typically 70 – 100 mg $NO_3^- L^{-1}$) and relatively low and constant in the downgradient confined region (typically < 0.1 – 3 mg $NO_3^- L^{-1}$), suggesting a balance between rates of nitrate loading and removal by denitrification. Autotrophic denitrification with pyrite (or other reduced Fe-S minerals) has been invoked to explain geochemical results of other field studies where low dissolved organic carbon concentrations could not explain apparent nitrate degradation in ground water (Kölle et al., 1985; Böttcher et al., 1990; Postma et al., 1991; Robertson et al., 1996; Pauwels et al., 1998; Aravena and Robertson, 1998; Tesoriero et al., 2000).

Tiered Analysis

Determination of the viability of nitrate remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. It is essential to understand the cause-and-effect relationship between loss of nitrate in ground water and the mechanisms responsible for its loss. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate nitrate reduction within the plume. Rapid movement of contaminants along preferred flow paths in the unsaturated and saturated zones can be induced by hydrologic events such as heavy rains (e.g., McCarthy et al., 1998; Camobreco et al., 1996). It will be important to determine that such hydrogeologic features do not result in contaminants bypassing zones where natural attenuation is occurring. An observed decrease in nitrate concentration in space and time that is attributable to a mass-removal process is anticipated if natural attenuation processes are active throughout the plume. Conditions that would support this initial screening would include evidence of reducing conditions (i.e., low E_H) and abundant electron donors (e.g., elevated total organic matter or the presence of degradable organic co-contaminants). Identification of nitrate removal along ground-water flow paths provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be determined via several approaches: 1) assessment of nitrate disappearance across well transects along the ground-water flow path(s), 2) assessment of *in-situ* rates of nitrate reduction through analysis of changes in the nitrogen stabile isotope fractionation along the ground-water flow path, and 3) *ex-situ* assessment of nitrate reduction rate(s) through the use of microcosm studies. In addition, time-series data may be collected at one or more monitoring points within the plume. This information will allow assessment of the relative timescale(s) for nitrate reduction relative to ground-water seepage velocities and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation need to be identified under this stage of site characterization (e.g., See site characterization approach in Postma et al., 1991.). This effort may require identification of the microbial agents involved in nitrate reduction and their distribution throughout the plume (see Site Characterization section in this chapter). Alternatively, sites at which an abiotic process dominates nitrate reduction may require characterization of aquifer solids to determine the presence of candidate mineral phases such as those discussed previously (see Equations 8.10 and 8.11). If a link is established between the apparent disappearance of nitrate and observed microbial or chemical processes active within the plume, then this provides justification for proceeding to Tier III characterization efforts.

Tier III. Once the nitrate reduction mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the capacity of the aquifer to sustain continued biological reduction. The impact of potential hydrologic changes, such as a shift in flow direction caused by the onset of pumping at nearby sites, needs to be determined. Since the active microbial community will reside within the boundaries of the nitrate plume, potential alterations in the predominant flow path may deliver nitrate to regions of the aquifer in which there is a reduced (or inactive) population of nitrate-reducing bacteria (NRB) to sustain reduction. A well-constrained ground-water flow model of the site relative to observed spatial distributions of nitrate and NRB density will assist in assessing the potential impact of such changes. For sites in which organic co-contaminants are identified as the predominant electron donor for nitrate reduction, it is recommended that an evaluation of the long-term supply of the electron donor be assessed. If engineered remedies for the treatment of co-contaminants are active or planned (e.g., source zone treatment or removal of co-contaminants), then it is expected that the impact these remedies have on the potential supply of electron donor will influence the sustainability of nitrate reduction. This may require evaluation of whether 1) the total organic carbon content and characteristics of treated ground water are sufficient to maintain NRB activity or 2) the available mass of reactive minerals within aquifer sediments is sufficient to sustain chemical reduction. Analysis of the capacity for sustained biological reduction could be conducted through laboratory microcosm studies, whereas assessment of the long-term capacity for chemical reduction may be achieved through assessment of the mass of reactive minerals within the plume flow path and their stability relative to anticipated changes in ground-water chemistry.

For sites in which uncontaminated portions of the aquifer are aerobic (i.e., oxygen is present) or have naturally elevated concentrations of competing electron acceptors such as perchlorate, it is anticipated that evolution of the plume geochemistry may evolve to a condition that will not sustain microbial nitrate reduction. It is recommended that the potential impact of anticipated changes in ground-water chemistry on the rate or sustainability of nitrate reduction be assessed through microcosm studies. Ultimately, the ability to forecast the potential impacts of changes in aquifer chemistry or ground-water flow can be improved through the development of a reaction-transport model that includes site-specific parameterization of the microbial or chemical reduction process and site hydrogeology. If site-specific tests demonstrate sufficient capacity within the aquifer to sustain nitrate reduction, then the site characterization effort can progress to Tier IV. For cases where aquifer capacity is insufficient for plume reduction to required levels, then a determination of the benefits of contaminant source reduction or removal may be necessary.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to a decrease in the rates or capacity for nitrate reduction. The specific chemical parameters to be monitored will include those identified under Tier III that may halt or slow down microbial nitrate reduction within the plume. For example, solution phase parameters that could alter nitrate reduction include the concentrations of dissolved oxygen or competing electron acceptors such as perchlorate. Similarly, a decrease in the concentration of electron donors such as natural organic matter, organic co-contaminants, or reactive minerals could slow or halt nitrate reduction via biological or abiotic processes. Changes in these parameters may occur prior to observed changes in nitrate concentrations and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance reduction capacity perpendicular to the direction of plume advance, or enhancement of natural attenuation processes within the aquifer through the injection of soluble reactive components (see Remedial Technologies section in this chapter).

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Perchlorate

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Occurrence and Distribution

Ammonium perchlorate (NH_4ClO_4) has been used with powdered aluminum and various chemical binders as rocket fuel and in munitions since the mid-1940s. It powers the space shuttle and the U.S. nuclear missile arsenal. There are no ready substitutes. Potassium perchlorate is used in airbags in cars, in the production of leather, fabrics, coloring agents, fireworks (Wilkin et al., 2007), and elsewhere. Perchlorate in the environment is largely associated with the periodic replacement of perchlorate in rockets (ammonium perchlorate has a long, but not infinite, shelf-life) and its subsequent disposal. Naturally-occurring perchlorate from nitrate deposits in Chile has occasionally been released to the environment during mining to recover nitrate for use as fertilizer (e.g., Urbansky et al., 2001). Perchlorate has also been detected in sylvite from New Mexico, as well as in langbenite – a potassium sulfate mineral. The most common co-contaminants found at perchlorate-contaminated sites are nitrate and sulfate (ITRC, 2005). Atmospheric sources of perchlorate have also been implicated as a potential source of perchlorate in arid and semi-arid regions (Rajagopalan et al., 2006). Perchlorate is a powerful oxidant when heated, but the oxidation reaction is kinetically sluggish at low temperatures. The combination of low temperature stability and high temperature reactivity is what makes perchlorate so attractive for explosives and rocket fuel.

Plume Characteristics

Because perchlorate is a large anion with a relatively low diffuse charge it is non-complexing, forms no insoluble minerals, and sorbs poorly to most solids. The solubility of perchlorate salts is typically in the range of 10 - 2000 g L^{-1}. Although perchlorate sorption to soil materials is typically assumed to be negligible, there is some evidence that perchlorate might sorb to soil organics (e.g., Urbansky and Brown, 2003). Partitioning coefficients (i.e., K_d) describing sorption to geologic materials are usually found to equal zero. Few ion exchange resins or filter media effectively remove perchlorate from drinking water or wastewater. Similarly, perchlorate sorbs poorly to most geologic materials, suggesting that perchlorate plumes would likely move at roughly the same speed as ground water in the absence of biodegradation. Perchlorate-rich brines released from industrial applications can be sufficiently dense as to 'sink' in the subsurface analogous to dense non-aqueous phase liquids (Flowers and Hunt, 2000; Motzer, 2001).

Remedial Technologies

A current review of available technologies for remediation of perchlorate contamination in ground water has been published by the Interstate Technology Regulatory Council (ITRC, 2005), which is available via the internet at http://www.itrcweb.org/Documents/PERC-1.pdf. Available technologies include: 1) *ex-situ*, pump-and-treat approaches that extract perchlorate from recovered ground water or degrade perchlorate to innocuous compounds through biotic or abiotic chemical reduction, and 2) *in-situ* treatment approaches that degrade perchlorate within the plume via stimulation of native microbial communities or the emplacement of media that achieve biotic and abiotic chemical reduction of perchlorate, respectively. The success of these treatment approaches will be influenced by the level of knowledge of the ground-water flow regime as well as the geochemical characteristics within the plume. For technologies based on perchlorate extraction, the presence of common anions in ground water may compete for binding sites on ion exchange resins or other solid media used in the treatment process. For microbial perchlorate reduction (*ex-situ* or *in-situ*), geochemical parameters such as low pH and high total dissolved solids, as well as the presence of aerobic conditions or competing electron acceptors such as nitrate or sulfate may negatively impact the rates and extent of perchlorate reduction that can be achieved. It is important to consider these site-specific factors when selecting treatment technologies.

Regulatory Aspects

Introduction of a new analytical method in 1997 by the California Department of Health Services lowered the detection limit for perchlorate from 400 ppb to 4 ppb. Since that time relatively wide occurrences of perchlorate have been detected. As of 2001, forty-four states have perchlorate manufacturers or users (Motzer, 2001). There were 24 sites on the National Priorities List with perchlorate contamination as of September 23, 2004 (USEPA, 2004) with various cleanup actions having been initiated at 12 of these sites (http://www.epa.gov/swerffrr/documents/perchlorate_site_summaries.htm). Perchlorate has been found in the water supplies of over 15 million people in California, Nevada and Arizona and in surface or ground water throughout the United States.

Perchlorate is used to treat Grave's Disease (hyperthyroidism) and in sufficient quantity competes with iodide in the thyroid gland. The perchlorate ion (ClO_4^-) has a charge and radius close to iodide and substitutes for iodide in the thyroid causing a decrease in hormonal output. Perchlorate is apparently not metabolized in the body, nor is it rapidly reduced to chloride in many soil settings.

There are at present no state or federal drinking water standards for perchlorate, but several are being considered. With authority under the Safe Drinking Water Act (SDWA), in March 1998, the U.S. Environmental Protection Agency's Office of Water formally added perchlorate to the drinking water contaminant candidate list (CCL) (Urbansky and Schock 1999). A National Primary Drinking Water Regulation (NPDWR) has not yet been promulgated for perchlorate, but monitoring will continue under the Unregulated Contaminants Monitoring Rule (UCMR). Several states have set action or advisory levels for perchlorate: Nevada – 18 ppb; Arizona – 14 ppb; California and Texas – 4 ppb; Maryland and Massachusetts – 1 ppb. No state governments have set enforceable standards. Current efforts are focused on identifying the specific health risks posed by perchlorate intake (National Research Council, 2005; http://www.nap.edu/catalog/11202.html). Perchlorate compounds do not have reportable quantities under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended, but the USEPA Office of Solid Waste and Emergency Response has issued recent guidance with a Drinking Water Equivalent Level (DWEL) for actions administered under the CERCLA of 24.5 $\mu g\ L^{-1}$ based on an adopted reference dose (RfD) for perchlorate of 0.0007 mg/kg-day (http://www.epa.gov/fedfac/pdf/perchlorate_guidance.pdf).

Geochemistry and Attenuation Processes

Attenuation of perchlorate might be achieved through reduction ultimately to chloride. Specialized microorganisms able to reduce perchlorate to chloride have been identified (Coates and Achenbach, 2004; Achenbach et al., 2001; Coates et al., 1999) that are widespread in the environment. All of the identified perchlorate reducers are facultatively anaerobic or microaerophilic (Coates et al., 1999). Perchlorate-reducing bacteria use as electron donors: hydrogen, organic acids and alcohols, aromatic hydrocarbons, reduced humic substances, hexoses, ferrous minerals and hydrogen sulfide (Chaudhuri et al., 2002). In situ perchlorate biodegradation methods typically use electron donors such as vegetable oils, organic acids, alcohols, or sugars. Anaerobic conditions are required for biodegradation of perchlorate to proceed. Metabolism of electron donors leads to the consumption of free oxygen and nitrate, at which point perchlorate reduction proceeds. Molybdate is apparently important for perchlorate reduction; nitrate occasionally is seen to inhibit perchlorate reduction (Chaudhuri et al., 2002).

Dozens of strains of perchlorate-reducing bacteria have been identified in the environment, their ubiquity, substrate specificity, and wide distribution suggesting both a natural source of perchlorate and the potential for natural attenuation of perchlorate. Perchlorate reduction to chloride proceeds in the general sequence of perchlorate to chlorate to chlorite to hypochlorite to chloride:

$$ClO_4^- \rightarrow ClO_3^- \rightarrow ClO_2^- \rightarrow ClO^- \rightarrow Cl^- + O_2 \qquad \text{(Eq. 9.1)}$$

The first step of perchlorate reduction to chlorite is thought to be the rate-limiting step in the cascade.

The Chilean Perchlorate Deposits

Two lines of evidence suggest that natural perchlorate fluxes into soils might be appreciable and that natural attenuation of very small amounts of perchlorate is perhaps common. The specificity and relative ubiquity of perchlorate reducing microorganisms imply the existence of an undetected, "shadow" flux of perchlorate (Urbansky and Schock, 1999). As noted by Urbansky and Schock (1999),

> *"If it can be shown that perchlorate is produced naturally in the environment and yet levels are very low, we must conclude that natural attenuation is responsible for the dichotomy."*

Presumably, the development of more powerful analytical methods will point to the existence or non-existence of such a flux.

The occurrence of natural perchlorate in the nitrate deposits of the Atacama Desert in Chile points to the existence of a natural process of perchlorate formation – though it says little more. Perchlorate minerals occur along with other oxidized minerals rarely observed elsewhere including nitrates, iodates, chromates and dichromates. There are competing explanations for the origin(s) of the nitrate salts – which have received the most attention - including atmospheric formation (through electrochemical or photochemical means) followed by evaporative concentration (Bohlke et al., 1997; Dasgupta et al., 2005) or fixation by microorganisms (Ericksen, 1983). Ericksen (1983) suggested a photochemical oxidation of atmospheric Cl and O in the atmosphere or at ground level to form the perchlorate deposits, citing as evidence arguments that a similar reaction might take place in the stratosphere. The iodates in Chile might have come from sea spray (much of the iodine in the sea is iodate). The formation path for chromate is less clear as there are few sources of Cr near the area. The dichromate mineral lopezite – $K_2Cr_2O_7$ – appears to be an alteration product of the chromate minerals (Ericksen, 1983). Note that the half cell reaction for reduction of perchlorate to chloride is:

$$ClO_4^- + 8e^- + 8H^+ \rightarrow Cl^- + 4H_2O \quad E_o = 1.29V \qquad \text{(Eq. 9.2)}$$

which means that in acidic solutions perchlorate is in theory a stronger oxidant than oxygen, but not as strong as dichromate (Urbansky and Schock, 1999). In other words, a dichromate mineral once formed might be able to oxidatively form perchlorate from chloride. In the absence of a clearer understanding of how perchlorate came to form in the Atacama Desert, two poorly constrained potential fluxes present themselves:

1. An undefined atmospheric source of perchlorate – perhaps oxidation of chloride to chlorate by OH radicals, followed by further photochemical oxidation by H_2O_2, ozone or HO_2 radical (e.g., Dasgupta et al., 2005),
2. An undefined soil source of perchlorate linked to oxidation of chloride by possibly transient dichromate sources or other unidentified soil processes.

Obviously the above is largely speculation in the absence of a better understanding of mechanisms. Presumably, better analytical methods will allow more precise measurement of actual perchlorate backgrounds and fluxes.

Site Characterization

Site characterization, conceptual evaluation of long-term stability and capacity, and tiered analysis for perchlorate is likely be similar to that done for other contaminants that naturally attenuate through reduction by ambient microorganisms – namely chlorinated solvents. Anaerobic conditions (nitrate reducing or lower) are critical as are sufficient quantities of potential electron donors. In the absence of further research demonstrating otherwise, it is reasonable to assume the presence of perchlorate-reducing bacteria (Wu et al., 2001). A recent publication outlines an approach used to assess the limitations for natural biodegradation of perchlorate at a contaminated site (Kesterson et al., 2005). These authors collected data on the presence of perchlorate-reducing bacteria, availability of electron donors, and the concentrations of competing electron acceptors. While the presence of perchlorate-reducing bacteria in soil and water was determined throughout the site, perchlorate persisted in the subsurface due either to the lack of available electron donors and/or the presence of competing electron acceptors. This work illustrates the importance of collecting site specific data to explicitly demonstrate that natural attenuation of perchlorate by biodegradation is both active and of sufficient magnitude to achieve required mass/concentration reductions in ground water. A general summary is presented in Table 9.1 of the attenuation process anticipated to dominate perchlorate transport in ground water along with a synopsis of the types of information to be collected to support site characterization.

Determining Cl Ground-water Speciation

Determination of the potential extent of perchlorate degradation within a plume can be initially assessed through observation of the mass distribution of chlorine-bearing inorganic ions according to the sequential reaction scheme shown in Equation 9.1. ITRC (2005) provides a review of several published methods for determining perchlorate or the distribution of Cl-bearing inorganic anions in water samples, including those similar to published EPA methods (Table 9.2). Unlike methods based on analyte detection by conductivity, methods employing mass spectrometry are capable of confirming the chemical composition of unknown ions by their molecular weight (mass-to-charge ratio). This may be important for samples with complex matrices containing ions that may co-elute with perchlorate during ion chromatography separation. Preservation studies suggest that filtration and refrigeration (4°C) of samples is sufficient for laboratory analysis within reasonable holding times (Stetson et al., 2006; Wilkin et al., 2007). Comparison of results from these studies suggests that filtration with a pore size less than 0.45 μm may be warranted to eliminate the potential for microbial degradation of perchlorate during storage. Since perchlorate is a common component of many detergents used in field decontamination procedures (such as Alconox, Alcotabs, Liqui-Nox, and Neutrad), it is recommended that equipment rinseate blanks be collected during each sampling event when sampling equipment is reused (ITRC, 2005). Thorne (2004) developed a field colorimetric method that showed good agreement with EPA Method 314.0 over the range of 1–225 μg L^{-1} (slope = 1.11, $R^2 = 0.913$) for well water and bioreactor effluent samples. The method is based on pre-concentration of perchlorate onto a solid-phase extraction cartridge that has been conditioned with a perchlorate-specific ion-pair reagent, followed by elution into an ion-pairing dye that is further treated for absorbance measurement at 640 nm using a standard portable spectrophotometer. No other published literature was available to further document the field performance of this method, but the general simplicity of the method suggests that it may be suitable as a field screening tool when there is an immediate need for analytical data to guide the placement of additional ground-water sampling locations during initial site characterization efforts.

Table 9.1 Natural attenuation and mobilization pathways for perchlorate.

Attenuation Processes	Mobilization Processes	Characterization Approach
Biotic (microbial) or abiotic transformation of perchlorate to other chlorine species	Cessation of microbial reduction processes via changes in electron donor or nutrient supply within the ground-water flow path	Determination of the mass distribution of perchlorate and other Cl-bearing inorganic ions in ground water. Determination of water chemistry, microbial populations, and/or sediment mineralogy linked to perchlorate transformation along with spatial and temporal variability of required chemical/microbial components relative to perchlorate transport pathway(s).

Table 9.2 Published USEPA methods for determination of perchlorate and other Cl-bearing inorganic Ions in aqueous samples.

Method Name and ***Number***	Source
Determination of Perchlorate in Drinking Water by Ion Chromatography; *314.0*	November 1999 http://www.epa.gov/ogwdw/methods/pdfs/met314.pdf
Determination of Perchlorate using Ion Chromatography with Chemical Suppression Conductivity Detection; *9058, Revision 0*	November 2000 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9058.pdf
Perchlorate in Water, Soils and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry; *6850, Revision 0*	January 2007 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6850.pdf
Perchlorate in Water, Soils and Solid Wastes Using Ion Chromatography/Electrospray Ionization/Mass Spectrometry (IC/ESI/MS OR IC/ESI/MS/MS); *6860, Revision 0*	January 2007 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6860.pdf
Determination of Perchlorate in Drinking Water Using Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection; *314.1, Revision 1.0*	EPA 815-R-05-009, May 2005 http://www.epa.gov/ogwdw/methods/pdfs/method_314_1.pdf
Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry, *331.0, Rev. 1.0*	EPA 815-R-05-007, January 2005 http://www.epa.gov/ogwdw/methods/pdfs/met331_0.pdf
Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry; *332.0*	EPA/600/R-05/049, March 2005 http://www.epa.gov/nerlcwww/m_332_0.pdf
Determination of Inorganic Anions by Ion Chromatography; *9056A, Revision 1*	November 2000 http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9056a.pdf

Stable Isotope Techniques

Stable isotopes of chlorine and oxygen within the perchlorate anion can be used to aid in differentiating natural and synthetic sources of contaminant as well as the degree to which perchlorate has been reduced by biotic processes. Specifically, determination of the distribution of the stable isotopes of oxygen (^{18}O, ^{17}O, ^{16}O) can be used to determine the value of $\Delta^{17}O$ (or ^{17}O anomaly), defined by the following equations:

$$\delta^{17}O = (^{17}Cl/^{16}Cl)_{sample}/(^{17}Cl/^{16}Cl)_{reference} - 1 \qquad \text{(Eq. 9.3)}$$

$$\delta^{18}O = (^{18}Cl/^{17}Cl)_{sample}/(^{18}Cl/^{17}Cl)_{reference} - 1 \qquad \text{(Eq. 9.4)}$$

$$\Delta^{17}O = [(1+ \delta^{17}O)/(1+ \delta^{18}O)^{0.525}] - 1 \qquad \text{(Eq. 9.5)}$$

The value of $\Delta^{17}O$ can be used to differentiate between natural sources of perchlorate (e.g., Atacama salt deposits and fertilizer products) versus synthetic perchlorate produced by electrolytic oxidation (Bao and Gu, 2004; Bohlke et al., 2005; Motzer et al., 2006). As discussed by Bao and Gu (2004), chemical reactions and biodegradation of perchlorate will not change the value of $\Delta^{17}O$ of the original perchlorate, which can only occur within a ground-water plume through addition of another source of perchlorate with a different $\Delta^{17}O$ signature. In addition, the values of $\delta^{37}Cl$ (defined as $[(^{37}Cl/^{35}Cl)_{sample}/(^{37}Cl/^{35}Cl)_{reference} - 1]$ relative to Standard Mean Ocean Chloride; Long et al., 1993) from Atacama nitrate ore and from Chilean nitrate fertilizer products are the lowest reported for any common substance on Earth (Bohlke et al., 2005). These measurements have been used to determine the sources of perchlorate in groundwater plumes at several sites of contamination (Bohlke et al., 2005).

Changes in the fractionation of the chlorine stable isotope composition of perchlorate are significant during microbial reduction (Coleman et al., 2003; Sturchio et al., 2003), consistent with preferential reduction of perchlorate containing the lighter chlorine isotope (^{35}Cl). Coleman et al. (2003) observed chlorine isotope fractionation on the order of -15‰ during perchlorate reduction by a microorganism isolated from a swine waste lagoon (*Dechlorosoma suillum* strain PS). Sturchio et al. (2003) also assessed chlorine stable isotope fractionation during perchlorate reduction using *Dechlorosoma suillum* JPLRND isolated from ground water sampled in southern California. In addition, these authors used EPA Methods 300.0 and 314.0 to monitor the speciation of perchlorate, chlorate, chlorite, and chloride throughout incubation observing only minor intermittent concentrations of chlorate (<1.3 % of perchlorate concentration). The overall reaction was dominated by stoichiometric conversion of perchlorate to chloride. Based on these experiments, Sturchio et al. (2003) estimated that chlorine stable isotope fractionation during microbial perchlorate reduction may be detected at levels of biodegradation <2%, which may provide a more sensitive limit of detection than that obtained through direct measurements of changes in perchlorate and chloride concentrations within the groundwater plume.

Stable isotope measurements for this contaminant have been made possible through the development of a highly selective bifunctional anion-exchange resin and sample processing method to extract and concentrate perchlorate from environmental samples (Gu et al., 2000; Gu et al., 2001). As reported by Bohlke et al. (2005), the collection of perchlorate onto the anion-exchange resin can be accomplished in the field with further processing conducted in the laboratory. However, the acquisition of a sufficient mass of perchlorate to support isotopic analyses for ground-water samples with 1-10 μg L^{-1} perchlorate may require significant volumes of water (Duncan et al., 2005). Determination of the various isotopes of chlorine and oxygen is dependent on the conversion of perchlorate to various gaseous products that carry the specific isotope of interest. For example, Bohlke et al. (2005) describe the following procedures: 1) determination of $\delta^{18}O$ following decomposition of perchlorate to carbon monoxide, 2) determination of $\Delta^{17}O$ following decomposition of perchlorate to produce oxygen, and 3) determination of $\delta^{37}Cl$ following decomposition of perchlorate to produce chloride that was subsequently reacted to produce methyl chloride (CH_3Cl; also known as chloromethane). As these authors point out, there are currently no perchlorate isotopic reference materials available for the purpose of assessing performance for a given analytical facility.

Identifying Microbial Populations

Recent work has demonstrated the ubiquity of perchlorate-reducing bacteria at sites with perchlorate contamination in ground water (Waller et al., 2004). These microorganisms reduced perchlorate in microcosm studies with or without supplement of an electron donor (e.g., acetate, molasses), although degradation rates were greater for supplemented microcosms. In order to assess the degree of intrinsic bioreduction of perchlorate at a given site, information is needed to identify the conditions of the microbial process controlling perchlorate reduction throughout the perchlorate plume. Bender et al. (2004) have developed two metabolic primer sets designed to target the chlorite dismutase (*cld*) gene, which can be used to identify perchlorate-reducing bacteria in environmental samples by a qualitative polymerase chain reaction (PCR) approach. False positive identification of perchlorate-reducing bacteria may occur, since the approach targets only a single gene that may be present even though the microorganism lacks other genes necessary to carry out perchlorate metabolism (e.g., genes required for perchlorate reductase). However, subsequent analysis of *cld*-positive samples using perchlorate reductase probes could be carried out in order to eliminate false positive identifications (Bender et al., 2005). This approach may substitute for or supplement for enumeration of perchlorate-reducing bacteria using the Most Probable Number (MPN) procedure (Wu et al., 2001; Kesterson et al., 2005).

Long-term Capacity

Given reducing conditions and labile electron donor masses that substantially exceed the perchlorate source, a critical unknown for determining the long-term capacity for attenuation is likely to be the perchlorate reduction rate relative to the flux of perchlorate and required electron donors and essential nutrients to sustain the metabolic process. Reduction rates for perchlorate remain an area of ongoing research. There is no universally accepted means for estimating perchlorate reduction rates, although the use of stable isotopes of chlorine and oxygen may provide a means to estimate in-situ rates of reduction along a plume flow path. Since there are potentially large uncertainties associated with extrapolating degradation rates determined from laboratory microcosm studies to the field setting, multiple lines of evidence based on field observations will likely provide the most reliable means for assessing the long-term capacity of the aquifer. In general, a default approach might then be to: 1) establish that conditions are reducing; 2) demonstrate that there are more than sufficient electron donors available for perchlorate reduction; 3) fit plume contours over time to estimate a biodegradation rate (possibly supported by microcosm studies demonstrating that perchlorate reduction is possible under the conditions prevailing in the field); and 4) use the derived model to assess long-term capacity for sustaining biological reduction of perchlorate.

Tiered Analysis

Determination of the viability of perchlorate remediation in ground water via monitored natural attenuation will depend upon proper assessment of contaminant loading to the aquifer and prevailing geochemistry and mineralogy within the contaminant plume and the down gradient zone prior to the point(s) of compliance. It is essential to understand the cause-and-effect relationship between loss of perchlorate in ground water and the mechanisms responsible for its loss. The following tiered analysis structure for site characterization provides an approach to evaluate candidate sites and define the potential limitations of MNA as part of a remedy for ground-water cleanup.

Tier I. Site characterization under Tier I will involve demonstration that the plume is static or shrinking, has not reached compliance boundaries, and does not impact existing water supplies. Once this is established through ground-water characterization, evidence is collected to demonstrate perchlorate reduction within the plume. Rapid movement of contaminants along preferred flow paths in the unsaturated and saturated zones can be induced by hydrologic events such as heavy rains (e.g., McCarthy et al., 1998; Camobreco et al., 1996). It will be important to determine that such hydrogeologic features do not result in contaminants bypassing zones where natural attenuation is occurring. In addition, for sites in which the suspected source term may have consisted of a perchlorate brine, it is recommended that the hydrogeologic characterization of the site establish whether perched 'DNAPL-like' plumes exist that could influence both the timeframe for remediation and the required attenuation capacity within the aquifer. If natural attenuation processes are active throughout the plume, then an observed decrease in perchlorate concentration in space and time that is attributable to a mass-removal process is anticipated. Conditions that would support this initial screening would include evidence of reducing conditions (i.e., low E_H), abundant electron donors (e.g., elevated total organic matter or the presence of degradable organic co-contaminants), and the apparent availability of essential nutrients such as molybdate. Identification of perchlorate removal along ground-water flow paths provides justification for proceeding to Tier II characterization efforts.

Tier II. Under Tier II, the apparent rate and mechanism(s) of attenuation are determined. Estimates of a site attenuation rate(s) can be determined via several approaches: 1) assessment of perchlorate disappearance across well transects along the ground-water flow path(s), 2) assessment of *in-situ* rates of perchlorate reduction through analysis of changes in the chlorine stabile isotope fractionation along the ground-water flow path, and 3) *ex-situ* assessment of perchlorate reduction rate(s) through the use of microcosm studies. In addition, time-series data may be collected at one or more monitoring points within the plume. This information will allow assessment of the relative timescale(s) for perchlorate reduction relative to ground-water seepage velocities and determination of whether remediation objectives can be met within the required regulatory time frame. In addition, the mechanism(s) for attenuation need to be identified under this stage of site characterization. This effort may require identification of the microbial agents involved in perchlorate reduction and their distribution throughout the plume (see Site Characterization section in this chapter). If a link is established between the apparent disappearance of perchlorate and observed microbial processes active within the plume, then this provides justification for proceeding to Tier III characterization efforts.

Tier III. Once the perchlorate reduction mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the capacity of the aquifer to sustain continued biological reduction. The impact of potential hydrologic changes, such as a shift in flow direction caused by the onset of pumping at nearby sites, needs to be determined. Since the active microbial community will reside within the boundaries of the perchlorate plume, potential alterations in the predominant flow path may deliver perchlorate to regions of the aquifer in which there is a reduced (or inactive) population of perchlorate-reducing bacteria to sustain reduction. A well-constrained ground-water flow model of the site relative to observed spatial distributions of perchlorate and density perchlorate-reducing bacteria will assist in assessing the potential impact of such changes. For sites in which organic co-contaminants are identified as the predominant electron donor for perchlorate reduction, it is recommended that an evaluation of the long-term supply of the electron donor be assessed. If engineered remedies for the treatment of co-contaminants are active or planned (e.g., source zone treatment or removal of co-contaminants), then it is expected that the impact these remedies have on the potential supply of electron donor will influence the sustainability of perchlorate reduction. This may require evaluation of whether the total organic carbon content and characteristics of treated ground water are sufficient to maintain the activity of perchlorate reducing bactera. This analysis could be conducted through laboratory microcosm studies. For sites in which uncontaminated portions of the aquifer are aerobic (i.e., oxygen is present) or have naturally elevated concentrations of competing electron acceptors such as nitrate, it is anticipated that evolution of the plume geochemistry may evolve to a condition that will not sustain microbial perchlorate reduction. It is recommended that the potential impact of anticipated changes in ground-water chemistry on the rate or sustainability of perchlorate reduction be assessed through microcosm studies. Ultimately, the ability to forecast the potential impacts of changes in aquifer chemistry or ground-water flow can be improved through the development of a reaction-transport model that includes site-specific parameterization of the microbial reduction process and site hydrogeology. If site-specific tests demonstrate sufficient capacity within the aquifer to sustain perchlorate reduction, then the site characterization effort can progress to Tier IV. For cases where aquifer capacity is insufficient for plume reduction to required levels, then a determination of the benefits of contaminant source reduction or removal may be necessary.

Tier IV. Finally, under Tier IV a monitoring plan is established along with contingency plans in the event of MNA failure. It is recommended that the monitoring plan be designed to establish both continued plume stability and to identify changes in ground-water chemistry that may lead to a decrease in the rates or capacity for perchlorate reduction. The specific chemical parameters to be monitored will include those identified under Tier III that may halt or slow down microbial perchlorate reduction within the plume. For example, solution phase parameters that could alter perchlorate reduction include the concentrations of dissolved oxygen or competing electron acceptors such as nitrate. Similarly, a decrease in the concentration of electron donors such as natural organic matter or organic co-contaminants could slow or halt perchlorate biodegradation. Changes in these parameters may occur prior to observed changes in perchlorate concentrations and, thus, serve as monitoring triggers for potential MNA failure. In this instance, a contingency plan can be implemented that incorporates strategies to arrest possible plume expansion beyond compliance boundaries. Possible strategies to prevent plume expansion include pump and treat operations, installation of reactive barriers to enhance uptake/degradation capacity perpendicular to the direction of plume advance, or enhancement of natural attenuation processes within the aquifer through the injection of soluble reactive components (see Remedial Technologies section in this chapter).

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