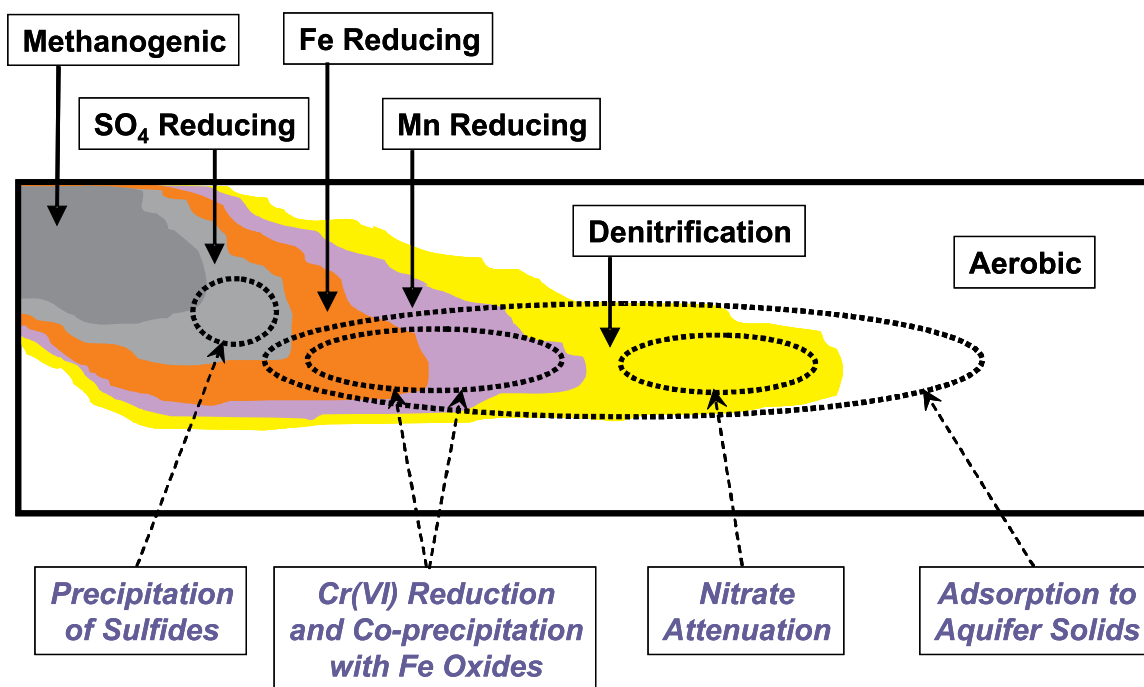


Monitored Natural Attenuation of Inorganic Contaminants in Ground Water

Volume 2

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



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Notice

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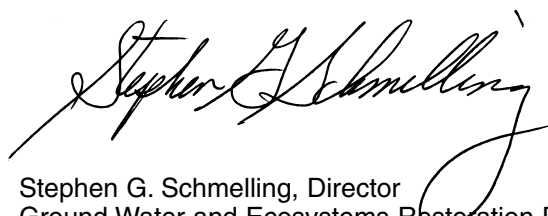
All research projects making conclusions or recommendations based on environmental data and funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project did not involve the collection or use of environmental data and, as such, did 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 (CdCO₃), greenockite (CdS), sphalerite (ZnS), smithsonite (ZnCO₃), and hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O). Soil weathering can lead to release of the Cd²⁺ 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 Cd²⁺ 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 Cd²⁺, Cd(OH)⁺, Cd(OH)₂⁰ 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).

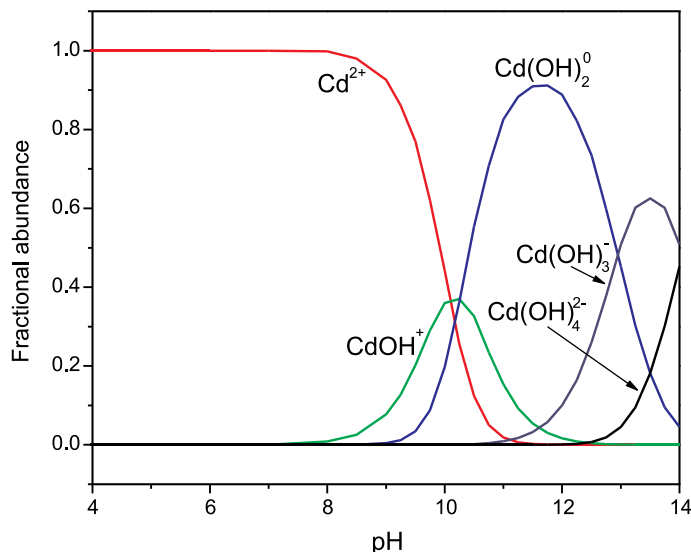


Figure 1.1 Species distribution of Cd(II) in pure water as a function of pH at 25 °C.

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 $\text{Cd}(\text{HS})_2^0$ is the dominant species at $\Sigma\text{S}(-\text{II})=10^{-5}$ 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).

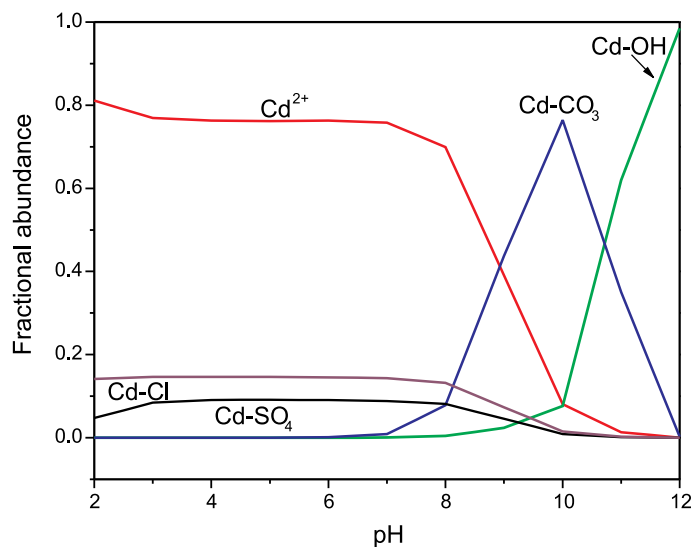


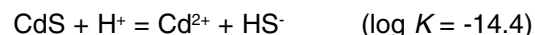
Figure 1.2 Cadmium speciation as a function of pH in solution containing chloride (100 mg L^{-1}), sulfate (100 mg L^{-1}), and inorganic carbon (100 mg L^{-1}). Cadmium chloride complexes include CdCl^+ and CdCl_2^0 . Cadmium sulfate complexes include CdSO_4^0 and $\text{Cd}(\text{SO}_4)_2^{2-}$. Cadmium complexes with inorganic carbon include CdCO_3^0 , CdHCO_3^+ , and $\text{Cd}(\text{CO}_3)_2^{2-}$. Cadmium hydroxy complexes include CdOH^+ , $\text{Cd}(\text{OH})_2^0$, and $\text{Cd}(\text{OH})_3^-$. 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:



and



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).

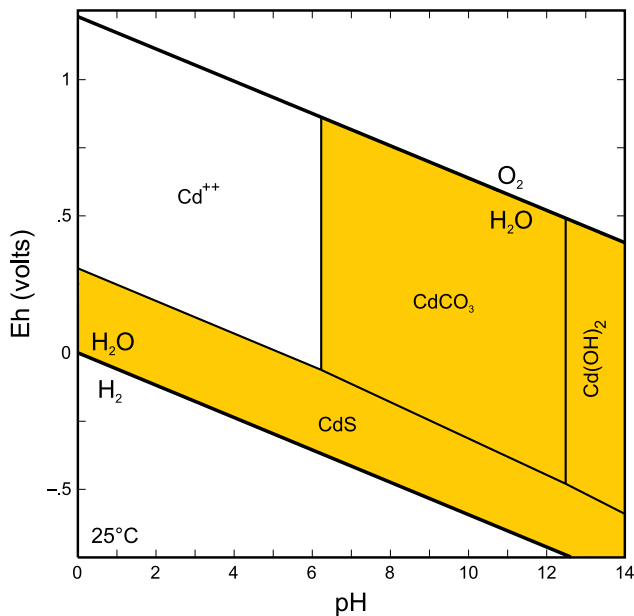


Figure 1.3 Eh-pH diagram for cadmium (total Cd = 10^{-5} molal, total C = 10^{-3} molal, total S = 10^{-3} molal; all organic cadmium complexes are suppressed; activity coefficients for all species are set equal to 1).

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 $\text{pH} < 7.5$. 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 $\text{Cd}(\text{OH})_2$. At 25°C the stable form is $\beta\text{-Cd}(\text{OH})_2$. This material is fairly soluble at circumneutral pH. Cadmium concentrations below the MCL of 0.005 mg L^{-1} would only be approached at $\text{pH} > 11$ in systems saturated with respect to $\beta\text{-Cd}(\text{OH})_2$.

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 Cd²⁺ 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 Cd²⁺ 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 primar-

ily 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 geo-

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

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

Tiered Analysis

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

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

ground-water provides justification for proceeding to Tier II characterization efforts.

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

- 1) Determination of cadmium solution speciation via direct analytical measurements in combination with speciation calculations based on characterized ground-water chemistry;
- 2) Calculation of the saturation state of ground water relative to measured aqueous chemistry complemented 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.

References

Abate, G. and J.C. Masini. Complexation of Cd(II) and Pb(II) with humic acids studied by anodic stripping voltametry using differential equilibrium functions and discrete models. *Organic Geochemistry* 33: 1171-1182 (2002).

- Ainsworth, C.C., J.L. Pilon, P.L. Gassman, and W.G. Van der Sluys. Cobalt, cadmium, and lead sorption to hydrous iron oxide: residence time effect. *Soil Science Society of America* 58: 1615-1623 (1994).
- Amacher, M.C. Nickel, cadmium, and lead. In *Methods of Soil Analysis: Chemical Methods, Part 3*. D. L. Sparks (Ed.), Soil Science Society of America, Madison, WI, pp. 739-768 (1996).
- Amonette, J.E. Methods for determination of mineralogy and environmental availability. In *Soil Mineralogy with Environmental Applications*. J.B. Dixon and D.G. Schulze (Eds.), Soil Science Society of America Book Series. Soil Science Society of America, Inc., Madison, WI, pp. 153-197 (2002).
- Baes, C.F. and R.E. Mesmer. *The Hydrolysis of Cations*. Wiley Interscience, New York, NY, 489 pp. (1976).
- Bailey, E.H., J.F.W. Mosselmans, and S.D. Young. Time-dependent surface reactivity of Cd sorbed on calcite, hydroxylapatite and humic acid. *Mineralogical Magazine*, 69: 563-575 (2005).
- Bellanca, A., S. Hauser, R. Neri, and B. Palumbo. Mineralogy and geochemistry of Terra Rossa soils, western Sicily: insights into heavy metal fractionation and mobility. *Science of the Total Environment*, 193: 57-67 (1996).
- Benjamin, M.M. and J.O. Leckie. Adsorption of metals at oxide surfaces: Effects of the concentrations of adsorbate and competing metals. In *Contaminants and Sediments, Volume 2, Analysis, Chemistry, Biology*. R.A. Baker (Ed.), Ann Arbor Science Publishers, Ann Arbor, MI (1980).
- Buanam, J., K. Tiptanasup, J. Shiwatana, M. Miro, and E.H. Hansenc. Development of a simple extraction cell with bi-directional continuous flow coupled on-line to ICP-MS for assessment of elemental associations in solid samples. *Journal of Environmental Monitoring*, 8: 1248-1254 (2006).
- Carroll, S.A., P.A. O'Day, and M. Piechowski. Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-state Mining District. 2. Geochemical interpretation. *Environmental Science and Technology* 32: 956-965 (1998).
- Carroll, S., P.A. O'Day, B. Esser, and S. Randall. Speciation and fate of trace metals in estuarine sediments under reduced and oxidized conditions, Seaplane Lagoon, Alameda Naval Air Station (USA). *Geochemical Transactions*, 3: 81-101 (2002).
- Chiarello, R.P., N.C. Sturchio, J.D. Grace, P. Geissbuhler, L.B. Sorensen, L. Cheng, and S. Xu. Otavite-calcite solid-solution formation at the calcite-water interface studied in situ by synchrotron X-ray scattering. *Geochimica et Cosmochimica Acta* 61: 1467-1474 (1997).
- Christensen, J.B. and T.H. Christensen. Complexation of Cd, Ni, and Zn by DOC in polluted groundwater: A comparison of approaches using resin exchange, aquifer material sorption, and computer speciation

- models (WHAM and MINTEQA2). *Environmental Science and Technology* 33: 3857-3863 (1999).
- Coles, C.A., S.R. Rao, and R.N. Yong. Lead and cadmium interactions with mackinawite: Retention mechanisms and the role of pH. *Environmental Science and Technology* 34: 996-1000 (2000).
- D'Amore, J.J., S.R. Al-Abed, K.G. Scheckel, and J.A. Ryan. Methods for speciation of metals in soils: A review. *Journal of Environmental Quality* 34:1707-1745 (2005).
- Cooper, C. and J.W. Morse. Biogeochemical controls on trace metal cycling in anoxic marine sediments. *Environmental Science and Technology* 32: 327-330 (1998).
- Daskalakis, K.D. and G.R. Helz. Solubility of CdS (Greenockite) in sulfidic waters at 25° C. *Environmental Science and Technology* 26: 2642-2468 (1992).
- Davis, J.A., C.C. Fuller, and A.D. Cook. A model for trace metal sorption processes at the calcite surface: Adsorption of Cd²⁺ and subsequent solid-solution formation. *Geochimica et Cosmochimica Acta* 51: 1477-1490 (1987).
- DiToro, D.M., J.D. Mahony, D.J. Hansen, J.J. Scott, M.B. Hicks, S.M. Mayr, and M.S. Redmond. Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environmental Toxicology and Chemistry* 9: 1487-1502 (1990).
- Dunnivant, F.M., P.M. Jardine, D.L. Taylor, and J.F. McCarthy. Cotransport of cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. *Environmental Science and Technology* 26:360-368 (1992).
- Ford, R.G., P.M. Bertsch, and K.J. Farley. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environmental Science and Technology* 31: 2028-2033 (1997).
- Framson, P.E. and J.O. Leckie. Limits of coprecipitation of cadmium and ferrous sulfides. *Environmental Science and Technology* 12: 465-469 (1978).
- Gibert, O., J. Pablo, J.L. Cortina, and C. Ayora. Evaluation of municipal compost/limestone/iron mixtures as filling material for permeable reactive barriers for in situ acid mine drainage treatment. *Journal of Chemical Technology and Biotechnology* 78: 489-496 (2003).
- Hickey, M.G. and J.A. Kittrick. Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. *Journal of Environmental Quality* 13: 372-376 (1984).
- Lai, C.-H., C.-Y. Chen, B.-L. Wei, and S.-H. Yeh. Cadmium adsorption on goethite-coated sand in the presence of humic acid. *Water Research* 36: 4943-4950 (2002).
- Lindsay, W.L. *Chemical Equilibria in Soils*. John Wiley and Sons, New York, NY, 449 pp. (1979).
- Martin-Garin, A., P. Van Cappellen, and L. Charlet. Aqueous cadmium uptake by calcite: A stirred flow-through reactor study. *Geochimica et Cosmochimica Acta* 67: 2763-2774 (2003).
- Martínez, C.E. and M.B. McBride. Solubility of Cd²⁺, Cu²⁺, Pb²⁺, and Zn²⁺ in aged coprecipitates with amorphous iron hydroxides. *Environmental Science and Technology* 32: 743-748 (1998).
- Martínez, C.E., M.B. McBride, M.T. Kandianis, J.M. Duxbury, S.-J. Yoon, and W.F. Bleam. Zinc-sulfur and cadmium-sulfur association in metalliferous peats: Evidence from spectroscopy, distribution coefficients, and phytoavailability. *Environmental Science and Technology* 36: 3683-3689 (2002).
- McBride, M.B. Chemisorption of Cd²⁺ on calcite surfaces. *Soil Science Society of America Journal* 44: 26-28 (1980).
- O'Day, P.A., S.A. Carroll, and G.A. Waychunas. Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-state Mining District. 1. Molecular identification using X-ray absorption spectroscopy. *Environmental Science and Technology* 32: 943-955 (1998).
- O'Day, P.A., S.A. Carroll, S. Randall, R.E. Martinelli, S.L. Anderson, J. Jelinski, and J.P. Knezovich. Metal speciation and bioavailability in contaminated estuary sediments, Alameda Naval Air Station, California. *Environmental Science and Technology* 34: 3665-3673 (2000).
- Ngiam, L.-S., and P.-E. Lim. Speciation patterns of heavy metals in tropical estuarine anoxic and oxidized sediments by different sequential extraction schemes. *Science of the Total Environment* 275: 53-61 (2001).
- Papadopoulos, P. and D.L. Rowell. The reaction of cadmium with calcium carbonate surfaces. *Journal of Soil Science* 39: 23-36 (1988).
- Parkman, R.H., J.M. Charnock, N.D. Bryan, F.R. Livens, and D.J. Vaughan. Reactions of copper and cadmium ions in aqueous solution with goethite, lepidocrocite, mackinawite, and pyrite. *American Mineralogist* 84: 407-419 (1999).
- Peltier, E., A.L. Dahl, and J.-F. Gaillard. Metal speciation in anoxic sediments: When sulfides can be construed as oxides. *Environmental Science and Technology* 39: 311-316 (2005).
- Pustišek, N., R. Milačič, and M. Veber. Use of the BCR three-step sequential extraction procedure for the study of the partitioning of Cd, Pb and Zn in various soil samples. *Journal of Soils and Sediments* 1: 25-29 (2001).
- Pye, K. Forensic examination of rocks, sediments, soils and dusts using scanning electron microscopy and X-ray chemical microanalysis. In *Forensic Geoscience: Principles, Techniques and Applications*. K. Pye and D.J. Croft (Eds.), Geological Society Special Publications, Volume 232, pp.103-122 (2004).
- Reimann, C. and P. Caritat. *Chemical Elements in the Environment*. Springer-Verlag, Berlin, 398 pp. (1998).
- Rudd, T., J.A. Campbell, and J.N. Lester. Use of model compounds to elucidate metal forms in sewage sludge. *Environmental Pollution* 50: 225-242 (1988).

-
- Saeki, K., M. Okazaki, and S. Matsumoto. The chemical phase changes in heavy metals with drying and oxidation of the lake sediments. *Water Research* 27: 1243-1251 (1993).
- Santillan-Medrano, J. and J.J. Jurinak. The chemistry of lead and cadmium in soil: solid phase formation. *Soil Science Society of America Proceedings* 39: 851-856 (1975).
- Sery, A., A. Manceau, and G.N. Greaves. Chemical state of Cd in apatite phosphate ores as determined by EXAFS spectroscopy. *American Mineralogist* 81: 864-873 (1996).
- Shannon, R.D. and J.R. White. The selectivity of a sequential extraction procedure for the determination of iron oxyhydroxides and iron sulfides in lake sediments. *Biogeochemistry* 14: 193-208 (1991).
- Simpson, S.L., S.C. Apte, and G.E. Batley. Effect of short-term resuspension events on the oxidation of cadmium, lead, and zinc sulfide phases in anoxic estuarine sediments. *Environmental Science and Technology* 34: 4533-4537 (2000).
- Stipp, S.L., J.F. Hochella, G.A. Parks, and J.O. Leckie. Cd²⁺ uptake by calcite, solid-state diffusion, and the formation of solid solution: Interface processes observed with near-surface sensitive techniques (XPS, LEED, and AES). *Geochimica et Cosmochimica Acta* 56: 1941-1954 (1992).
- Stipp, S.L., G.A. Parks, D.K. Nordstrom, and J.O. Leckie. Solubility-product constant and thermodynamic properties for synthetic otavite, CdCO₃(s), and aqueous association constants for the Cd(II)-CO₂-H₂O system. *Geochimica et Cosmochimica Acta* 57: 2699-2713 (1993).
- Tesoriero, A.J. and J.F. Pankow. Solid solution partitioning of Sr²⁺, Ba²⁺, and Cd²⁺ to calcite. *Geochimica et Cosmochimica Acta* 60: 1053-1063 (1996).
- Tessier, A., P.G.C. Campbell, and M. Biron. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844-851 (1979).
- Tonkin, J.W., L.S. Balistrieri, and J.W. Murray. Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. *Applied Geochemistry* 19: 29-53 (2004).
- USEPA. *Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb*, EPA/540/S-97/500, U.S. Environmental Protection Agency (1997).
- USEPA. *National Recommended Water Quality Criteria*, 4304T, Office of Water, Washington DC (2006).
- Wang, F. and A. Tessier. Cadmium complexation with bisulfide. *Environmental Science and Technology* 33: 4270-4277 (1999).
- Wang, Y. and E.J. Reardon. A siderite/limestone reactor to remove arsenic and cadmium from wastewaters. *Applied Geochemistry* 16: 1241-1249 (2001).
- Wolke, R.L. Cadmium. *Chemical and Engineering News* September 8, p. 120 (2003).
- Zachara, J.M., C.E. Cowan, and C.T. Resch. Sorption of divalent metals on calcite. *Geochimica et Cosmochimica Acta* 55: 1549-1562 (1991).
- Zhao, X., W.H. Höll, and G. Yun. Elimination of cadmium trace contaminations from drinking water. *Water Research* 36: 851-858 (2002).

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 (PbSO₄) and cerussite (PbCO₃).

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

Lead was ranked second on the CERCLA Priority List of Hazardous Substances in 1999 and 2001 (after arsenic - #1, and before mercury - #3, vinyl chloride - #4, and PCBs - #5). The priority list is prepared by the Agency for Toxic

Substances and Disease Registry and EPA and is based on the frequency of occurrence of particular contaminants at National Priorities List (NPL) sites and their potential threat to human health. In absolute numbers, lead is by far the most common inorganic contaminant found at Superfund sites. For example, in 1996 lead contamination was found at 460 Superfund sites, compared to 306 with chromium contamination, 235 with arsenic, 226 with zinc, 224 with cadmium, 201 with copper, and 154 with mercury (USEPA, 1996).

Plume Characteristics

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

Remedial Technologies

Technology classes potentially applicable to the remediation of lead-contaminated soils include containment, solidification/stabilization, and separation/concentration (e.g., USEPA, 1997). Containment technologies applied at metal contamination sites include caps and vertical barriers to minimize the transport of lead and co-contaminants out of source zones. Solidification/stabilization technologies are treatment processes that mix reactive agents with contaminated material to reduce solubility or otherwise limit contact between the contaminated material and potential transport fluids. Amendments such as Portland cement or phosphate-based compounds are candidates for treatment of lead contamination in soils (e.g., USEPA, 1997). Separation/concentration methods have also been used for lead treatment, including ex-situ soil washing and in-situ soil flushing to physically or chemically reduce contaminant concentrations to meet site-specific cleanup goals. Groundwater 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^+ , $\text{Pb}(\text{OH})_2^0$, and $\text{Pb}(\text{OH})_3^-$ become dominant over Pb^{2+} (Figure 2.1). Lead carbonate complexes (PbCO_3^0 , $\text{Pb}(\text{CO}_3)_2^{2-}$), lead chloride complexes (PbCl^+ , PbCl_2^0), lead sulfate complexes (PbSO_4^0 , $\text{Pb}(\text{SO}_4)_2^{2-}$), 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

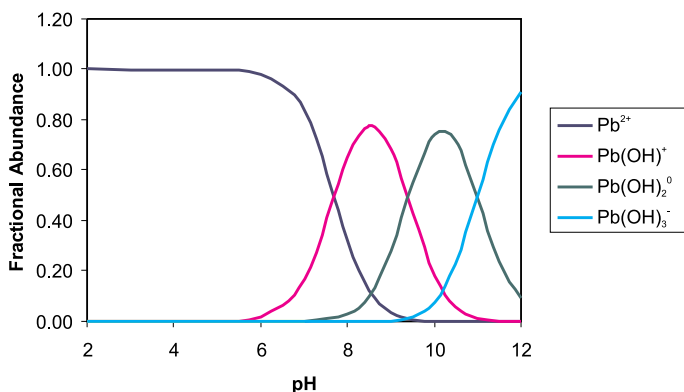


Figure 2.1 *Pb(II) species distribution in pure water at 25 °C.*

water will depend on pH, total lead concentration, and the relative and absolute abundances of the major anions: chloride, sulfate, and carbonate.

Dissolved organic carbon (DOC) may also form stable complexes with lead and play an important role in governing lead mobility in ground-water systems; however, few data are available and comparatively few attempts have been made to assess the importance of lead interactions with DOC. In a recent study of landfill leachate-polluted ground water containing up to $180 \text{ mg DOC L}^{-1}$, 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 $\text{Pb}(\text{NO}_3)_2$), PbSO_4 ($10,000 \text{ mg kg}^{-1}$), PbCO_3 ($10,000 \text{ mg kg}^{-1}$), 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.

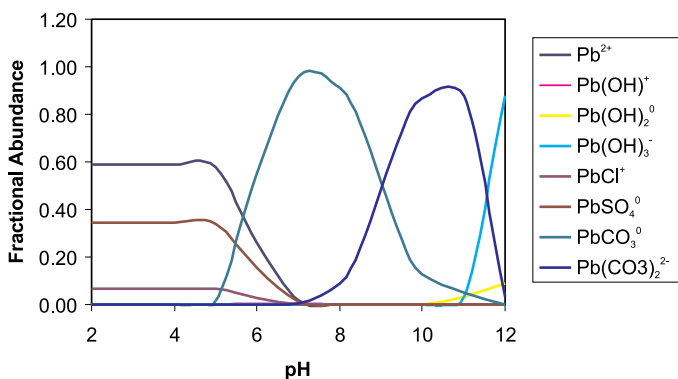


Figure 2.2 *Species distribution of lead in solution with 100 mg L^{-1} chloride, 100 mg L^{-1} sulfate, and 100 mg L^{-1} total inorganic carbon, based on thermodynamic data in MINTEQA2 (Allison et al., 1990).*

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 $\text{pH} > 12.5$ 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 $\text{pH} > 7$, the equilibrium solubility of lead was below 0.05 mg L^{-1} when $\text{Pb}(\text{OH})_2$ 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 $\text{pH} > 8$, 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).

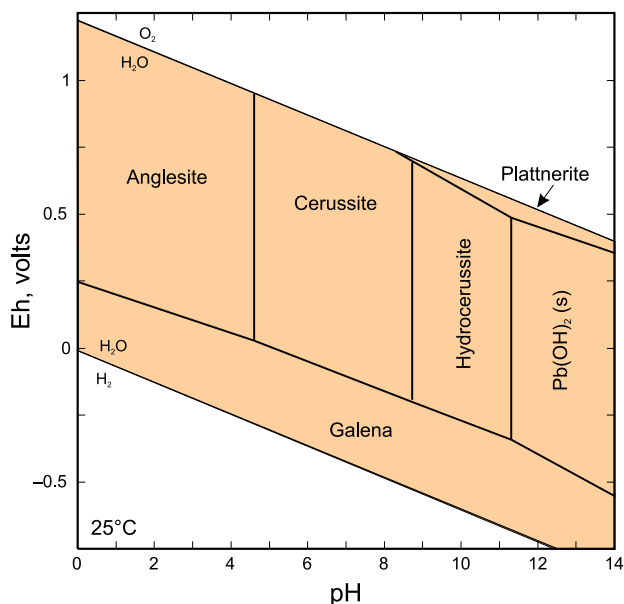


Figure 2.3 Eh-pH diagram for lead (total Pb = 10^{-5} molal, total C = 10^{-3} molal, total S = 10^{-3} molal; all organic lead complexes are suppressed; activity coefficients for all species are set equal to 1).

Important lead-bearing mineral phases include: lead hydroxide ($\text{Pb}(\text{OH})_2$), cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), anglesite (PbSO_4), galena (PbS), lead oxide (PbO), and chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) in phosphate-bearing systems. In addition, plumbojarosite

($\text{Pb}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$) has been identified as an important secondary precipitate and lead sink in weathered mine wastes (e.g., Hochella et al., 1999). Thermodynamic data for most of these phases may be found in a variety of sources (e.g., see Pierrard et al., 2002, and references therein). In carbonate and sulfate systems the most favored mineral species appear to be anglesite, cerussite, and hydrocerussite (Lindsay, 1979; Marani et al., 1995).

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

Marani et al. (1995) point out that the reliability of solubility predictions depends on the choice of the relevant solubility constants used in modeling studies. Unfortunately, such constants are wide ranging for lead. Reasonable agreement between solubility predictions from equilibrium modeling and filterable lead concentrations measured in aged soil-water systems was obtained only with a critical selection of solid phases in the modeling and by appreciating kinetic aspects of the Pb-H₂O system (Marani et al., 1995).

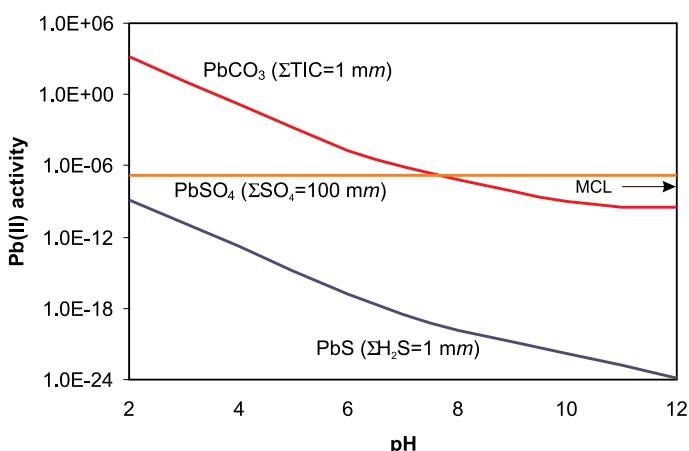


Figure 2.4 Pb(II) activity in equilibrium with PbCO_3 (at total inorganic carbon equal to 0.001 molal), PbSO_4 (at total sulfate equal to 0.1 molal), and PbS (at total sulfide equal to 0.001 molal). The solubility trend can be compared to the MCL for lead of 0.015 mg L^{-1} or an activity of $\sim 7.2 \times 10^{-8}$ 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 (FeS₂) surface was about 6.0. They suggested that the observed adsorption behavior is controlled by the hydrolysis of Pb²⁺ ions, whereby hydrolyzed species sorb directly on sulfide surface groups as a monolayer.

Lead adsorption onto or co-precipitation with amorphous FeS may be extensive in reducing systems. Experimental studies suggest that a significant fraction of the Fe in freshly precipitated FeS may be replaced rapidly by metal ions like Pb that form less soluble sulfides (Phillips and Kraus, 1965; 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 Pb²⁺ to metallic lead is expected to occur at redox potentials below the stability field of water at pH<6. The oxidized form of lead (Pb(IV)) is not expected in air-saturated solutions based on thermodynamic reasoning. However, the mineral plattnerite (PbO₂) occurs in some natural systems and is associated with other oxidation products such as cerussite and pyromorphite (e.g., Yeates and Ayres, 1892; see Figure 2.3). In general, the geochemical transport processes of lead are not directly

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; Buanam et al., 2006). As discussed in the cited reports, sequential extraction methods provide a useful tool to assist in determining the chemical speciation of trace metals in soils/sediments, but essentially all documented methods show analytical limitations in selectively extracting lead and other metals associated with specific solid components (e.g., Scheckel et al., 2003). Design and application of extraction procedures should take into account the chemical behavior of lead relative to potential analytical bias that may be introduced by the extraction chemistry. For example, due to its low solubility, lead carbonate would be anticipated to form during extractions conducted using solutions with pH buffered by an excess of dissolved bicarbonate-carbonate.

Where feasible, it is recommended that complimentary analytical techniques be employed to confirm the accuracy of lead speciation (e.g., O'Day et al., 1998; O'Day et al., 2000; Carroll et al., 2002; D'Amore et al., 2005) or the accuracy of the extraction of a targeted phase(es) for a given extractant (e.g., Shannon and White, 1991; Ngiam and Lim, 2001; Peltier et al., 2005). As an example, Peltier et al. (2005) have demonstrated that a common extraction method employed to target metals associated with easily reducible iron (hydr)oxides may also dissolve iron sulfides that may be present. The results from this analysis may lead to misidentification of a lead association with iron

(hydr)oxides, resulting in the development of a conceptual site model that misrepresents the site-specific attenuation process. Under reducing conditions, it is also critical that aquifer sediments be sampled and processed in a manner that prevents exposure to oxygen prior to extraction in order to limit oxidation of reduced minerals (e.g., iron sulfides) that may host lead. Lead associated with a sulfidic phase in sediments has been shown to repartition to more extractable phases upon oxidation (Saeki et al., 1993; Cauwenberg and Maes, 1997). Determination of the host mineral phase(es) dissolved for each extraction step is recommended, along with the use of surrogate Pb-bearing phases spiked into the sediment to confirm accuracy of the procedure (e.g., Rudd et al., 1988). The choice of appropriate lead surrogate phases would be governed by site-specific geochemical conditions or characterization of the mineralogy of the aquifer sediment.

Pb Isotopes

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

Long-term Stability and Capacity

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

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

there will be assumptions built into capacity estimations, so it is recommended that uncertainty analysis accompany capacity estimates.

Tiered Analysis

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

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

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

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

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

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

can progress to Tier IV. For cases where contaminant 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.

References

- Ainsworth, C.C., J.L. Pilon, P.L. Gassman, and W.G. Van der Sluys. Cobalt, cadmium, and lead sorption to hydrous iron oxide: residence time effect. *Soil Science Society of America* 58: 1615-1623 (1994).
- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. *MINT-EQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems, Version 3.0*, U.S. Environmental Protection Agency, Athens, GA (1990).
- Amacher, M.C. Nickel, cadmium, and lead. In *Methods of Soil Analysis: Chemical Methods, Part 3*. D.L. Sparks (Ed.), Soil Science Society of America, Madison, WI, pp. 739-768 (1996).
- Amonette, J.E. Methods for determination of mineralogy and environmental availability. In *Soil Mineralogy with Environmental Applications*. Dixon J. B. and D. G. Schulze (Eds.), Soil Science Society of America Book Series. Soil Science Society of America, Inc., Madison, WI, pp. 153-197 (2002).
- Bargar, J.R., G.E. Brown, and G.A. Parks. Surface complexation of Pb(II) at oxide-water interfaces: II. XAFS and bond-valence determination of mononuclear Pb(II) sorption products and surface functional groups on iron oxide surfaces. *Geochimica et Cosmochimica Acta* 61: 2639-2652 (1997).
- Brady P.V., B.P. Spalding, K.M. Krupka, R.D. Waters, P. Zhang, D.J. Borna, and W.D. Brady. Site screening and technical guidance for monitored natural attenuation at DOE sites. Sandia National Laboratories, Albuquerque, New Mexico. SAND99-0464 (1999).
- Buanam, J., K. Tiptanasup, J. Shiowatana, M. Miro, and E.H. Hansenc. Development of a simple extraction cell with bi-directional continuous flow coupled on-line to ICP-MS for assessment of elemental associations in solid samples. *Journal of Environmental Monitoring* 8: 1248-1254 (2006).
- Caletka, R., M. Tymple, and P. Kotas. Sorption properties of iron(II) sulphide prepared by the sol-gel method. *Journal of Chromatography* 111: 93-104 (1975).
- Cauwenberg, P. and A. Maes. Influence of oxidation on sequential chemical extraction of dredged river sludge. *International Journal of Environmental Analytical Chemistry* 68: 47-57 (1997).
- Chow, T.J. and M.S. Johnstone. Lead isotopes in gasoline and aerosols of Los Angeles basin. *Science* 147: 502-503 (1965).
- Christensen, J.B., J.J. Botma, and T.H. Christensen. Complexation of Cu and Pb by DOC in polluted groundwater: A comparison of experimental data and predictions by computer speciation models (WHAM and MINT-EQA2). *Water Research* 33: 3231-3238 (1999).
- Coles, C.A., S.R. Rao, and R.N. Yong. Lead and cadmium interactions with mackinawite: Retention mechanisms and role of pH. *Environmental Science and Technology* 34: 996-1000 (2000).
- Coston, J.A., C.C. Fuller, and J.A. Davis. Pb²⁺ and Zn²⁺ adsorption by a natural aluminum- and iron-bearing surface coating on an aquifer sand. *Geochimica et Cosmochimica Acta* 59: 3535-3547 (1995).
- Coughtrey P.J., D. Jackson, C.H. Jones, P. Kane, and M.C. Thorne. Radionuclide distribution and transport in terrestrial and aquatic systems. Vol. 6., A.A. Balkema (1986).
- D'Amore, J.J., S.R. Al-Abed, K.G. Scheckel, and J.A. Ryan. Methods for speciation of metals in soils: A review. *Journal of Environmental Quality* 34:1707-1745 (2005).
- Davis, J.A., D.B. Kent, J.A. Coston, K.M. Hess, and J.L. Joye. Multispecies reactive transport experiment in an aquifer with spatial variable chemical conditions: Experimental design and observed tracer movement. *Water Resources Research* 36: 119-134 (2000).
- Dyer, J.A., P. Trivedi, N.C. Scrivner, and D.L. Sparks. Lead sorption onto ferrihydrite. 2. Surface complexation modeling. *Environmental Science and Technology* 37: 915-922 (2003).
- Dzombak, D.A. and F.M.M. Morel. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley and Sons, New York, NY (1990).
- Emmanuel, S. and Y. Erel. Implications from concentrations and isotopic data for Pb partitioning processes in soils.

- Geochimica et Cosmochimica Acta* 66: 2517-2527 (2002).
- Ford, R.G., P.M. Bertsch, and K.J. Farley. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environmental Science and Technology* 31: 2028-2033 (1997).
- Gulson, B.L., K.G. Tiller, K.J. Mizon, and R.H. Merry, 1981. Use of lead isotopes in soils to identify the source of lead contamination near Adelaide, South Australia. *Environmental Science and Technology* 15: 691-696.
- Harrington, J.M., M.J. Laforce, W.C. Rember, S.E. Fendorf, and R.F. Rosenweig. Phase associations and mobilization of iron and trace elements in Coeur d'Alene Lake, Idaho. *Environmental Science and Technology* 32: 650-656 (1998).
- Hayes, K.F. and J.O. Leckie. Mechanism of lead ion adsorption at the goethite-water interface. In *Geochemical Processes at Mineral Surfaces*. J.A. Davis and K.F. Hayes (Eds.), American Chemical Society, Washington DC, 114-141 (1986).
- Hem, J.D. and W.H. Durum. Solubility and occurrence of lead in surface water. *Journal of the American Water Works Association* 65: 562-568 (1973).
- Hem, J.D. Geochemical controls on lead concentrations in stream water and sediments. *Geochimica et Cosmochimica Acta* 40: 599-609 (1976).
- Hochella, M.F., J.N. Moore, U. Golla, and A. Putnis. A TEM study of samples from acid mine drainage systems: Metal-mineral association with implications for transport. *Geochimica et Cosmochimica Acta* 63: 3395-3406 (1999).
- Jean, G.E. and G.M. Bancroft. Heavy metal adsorption by sulphide mineral surfaces. *Geochimica et Cosmochimica Acta* 50: 1455-1463 (1986).
- Kabata-Pendias, A. *Trace Elements in Soils and Plants*. CRC Press, Boston, MA (1984).
- Lindsay, W.L. *Chemical Equilibria in Soils*. John Wiley and Sons, New York, NY (1979).
- Manceau, A., L. Charlet, M.C. Boisset, B. Didier, and L. Spadini. Sorption and speciation of heavy metals on hydrous iron and manganese oxides: From microscopic to macroscopic. *Applied Clay Science* 7: 201-203 (1992).
- Marani, D., G. Macchi, and M. Pagano. Lead precipitation in the presence of sulphate and carbonate: Testing of thermodynamic predictions. *Water Research* 29: 1085-1092 (1995).
- Morrison, S.J. and R.R. Spangler. Chemical barriers for controlling groundwater contamination. *Environmental Progress* 12: 175-181 (1993).
- Ngiam, L.-S. and P.-E. Lim. Speciation patterns of heavy metals in tropical estuarine anoxic and oxidized sediments by different sequential extraction schemes. *Science of the Total Environment* 275: 53-61 (2001).
- Nowack, B., F.G. Kari, and F. Krueger. The remobilization of metals from iron oxides and sediments by metal-EDTA complexes. *Water, Air, and Soil Pollution* 125: 243-257 (2001).
- O'Day, P.A., S.A. Carroll, and G.A. Waychunas. Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-state Mining District. 1. Molecular identification using X-ray absorption spectroscopy. *Environmental Science and Technology* 32: 943-955 (1998).
- O'Day, P.A., S.A. Carroll, S. Randall, R.E. Martinelli, S.L. Anderson, J. Jelinski, and J.P. Knezovich. Metal speciation and bioavailability in contaminated estuary sediments, Alameda Naval Air Station, California. *Environmental Science and Technology* 34: 3665-3673 (2000).
- O'Reilly, S.E. and M.F. Hochella. Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides. *Geochimica et Cosmochimica Acta* 67: 4471-4487 (2003).
- Papini, M.P., Y.D. Kahie, B. Troia, and M. Majone. Adsorption of lead at variable pH onto a natural porous medium: Modeling of batch and column experiments. *Environmental Science and Technology* 33: 4457-4464 (1999).
- Peltier, E., A.L. Dahl, and J.-F. Gaillard. Metal speciation in anoxic sediments: When sulfides can be construed as oxides. *Environmental Science and Technology* 39: 311-316 (2005).
- Phillips, H.O. and K.A. Kraus. Adsorption on inorganic materials VI. Reaction of insoluble sulfides with metal ions in aqueous media. *Journal of Chromatography* 17: 549-557 (1965).
- Pierrard, J., J. Rimbault, and M. Aplincourt. Experimental study and modeling of lead solubility as a function of pH in mixtures of ground waters and cement waters. *Water Research* 36: 879-890 (2002).
- Pye, K. Forensic examination of rocks, sediments, soils and dusts using scanning electron microscopy and X-ray chemical microanalysis. In *Forensic Geoscience: Principles, Techniques and Applications*. K. Pye and D.J. Croft (Eds.), Geological Society Special Publications, Volume 232, pp.103-122 (2004).
- Reed, B.E., R.E. Moore, and S.R. Cline. Soil flushing of a sandy loam contaminated with Pb(II), PbSO₄ (s), PbCO₃ (s), or Pb-naphthalene: Column results. *Journal of Soil Contamination* 4: 243-267 (1995).
- Rouff, A.A., E.J. Elzinga, R.J. Reeder, and N.S. Fisher. X-ray absorption spectroscopic evidence for the formation of Pb(II) inner-sphere adsorption complexes and precipitates at the calcite-water interface. *Environmental Science and Technology* 38: 1700-1707 (2004).
- Rozan, T.F., G.W. Luther, D. Ridge, and S. Robinson. Determination of Pb complexation in oxic and sulfidic water using pseudovoltammetry. *Environmental Science and Technology* 37: 3845-3852 (2003).

- Ruby, M.V., A. Davis, and A. Nicholson. In situ formation of lead phosphates in soils as a method to immobilize lead. *Environmental Science and Technology* 28: 646-654 (1994).
- Rudd, T., J.A. Campbell, and J.N. Lester. Use of model compounds to elucidate metal forms in sewage sludge. *Environmental Pollution*, 50: 225-242 (1988).
- Saeki, K., M. Okazaki, and S. Matsumoto. The chemical phase changes in heavy metals with drying and oxidation of the lake sediments. *Water Research*, 27: 1243-1251 (1993).
- Scheckel, K.G., C.A. Impellitteri, J.A. Ryan, and T. Mcevoy. Assessment of a sequential extraction procedure for perturbed lead-contaminated samples with and without phosphorus amendments. *Environmental Science and Technology* 37: 1892-1898 (2003).
- Shannon, R.D. and J.R. White. The selectivity of a sequential extraction procedure for the determination of iron oxyhydroxides and iron sulfides in lake sediments. *Biogeochemistry*, 14: 193-208 (1991).
- Shokes, T.E. and G. Möller. Removal of dissolved heavy metals from acid rock drainage using iron metal. *Environmental Science and Technology* 33: 282-287 (1999).
- Sposito, G. *The Surface Chemistry of Soils*, Oxford University Press, Oxford, UK (1984).
- Stumm, W. and K. Morgan. *Aquatic Chemistry*, 3rd Edition. Wiley-Interscience, New York, NY (1996).
- Sutherland, R.A. Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment. *Applied Geochemistry* 17: 353-365 (2002).
- Tessier, A., P.G.C. Campbell, and M. Bison. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844-851 (1979).
- Turekian, K.K. and K.H. Wedepohl. Distribution of the elements in some major units of the Earth's crust. *Geological Society of America Bulletin* 72: 175-192 (1961).
- Trivedi, P., J.A. Dyer, and D.L. Sparks. Lead sorption onto ferrihydrite. 1. A macroscopic and spectroscopic assessment. *Environmental Science and Technology* 37: 908-914 (2003).
- Uhler, A.D. and G.R. Helz. Solubility product of galena at 298°K: A possible explanation for apparent supersaturation in nature. *Geochimica et Cosmochimica Acta* 48: 1155-1160 (1984).
- USEPA. *Selection of Control Technologies for Remediation of Lead Battery Recycling Sites*, EPA/540/2-91/014, U.S. Environmental Protection Agency (1991).
- USEPA. *Report: Recent Developments for In Situ Treatment of Metals-contaminated Soils*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response (Draft) (1996).
- USEPA. *Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb*, EPA/540/S-97/500, U.S. Environmental Protection Agency (1997).
- USEPA. *National Recommended Water Quality Criteria*, 4304T, Office of Water, Washington, DC. (2006).
- Wang E.X., F.H. Bormann, and G. Benoit. Evidence of complete retention of atmospheric lead in the soils of northern hardwood forested ecosystems. *Environmental Science and Technology* 29: 735-739 (1995).
- Xue, H., L. Sigg, and F.G. Kari. Speciation of EDTA in natural water: Exchange of FeEDTA in river water. *Environmental Science and Technology* 29: 59-68 (1995).
- Yeates, W.S. and E.F. Ayres. Plattnerite and its occurrence near Mullan, Idaho. *American Journal of Science* 43: 407-412 (1892).
- Zänker, H., H. Moll, W. Richter, V. Brendler, C. Hennig, T. Reich, A. Kluge, and G. Hüttig. The colloid chemistry of acid rock drainage solution from an abandoned Zn-Pb-Ag mine. *Applied Geochemistry* 17: 633-648 (2002).
- Zhang, P., J.A. Ryan, and L.T. Bryndzia. Pyromorphite formation from goethite adsorbed lead. *Environmental Science and Technology* 31: 2673-2678 (1997).
- Zhang, P. and J.A. Ryan. Transformation of Pb(II) from cerussite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH. *Environmental Science and Technology* 33: 625-630 (1999).

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 (Ni²⁺) 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.

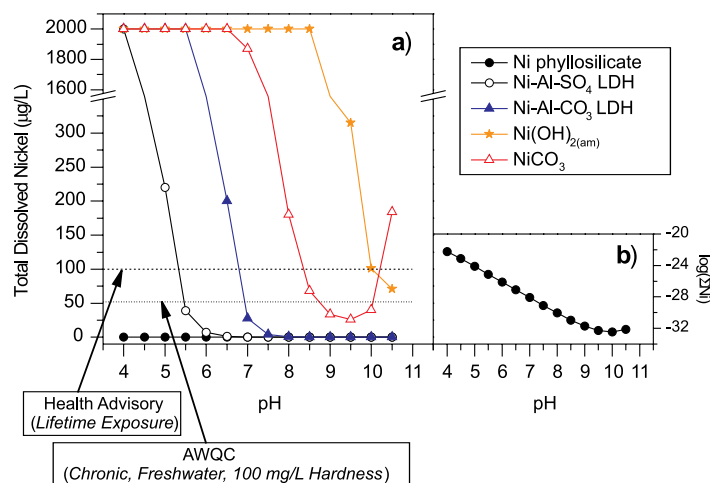


Figure 3.1 (a) Predicted solubility of various Ni precipitates that could form in aerobic ground water with concentrations of Al and Si controlled by the solubility of the clay mineral, kaolinite. (Note y-axis break to expand lower end of scale.) (b) Expansion of dissolved Ni data for equilibrium with Ni phyllosilicate; plotted on logarithmic scale. Nominal ground-water composition: 0.005 mole/L NaCl, 0.001 mole/L K₂SO₄, 0.001 mole/L MgNO₃, 0.001 mole/L CaCO₃, 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-SO₄ LDH, and Ni-Al-CO₃ LDH (Peltier et al., 2006); total dissolved Ni concentrations modeled individually for each Ni solid phase by setting kaolinite as an 'infinite' solid and the Ni solid phase as a 'possible' solid for each pH titration.

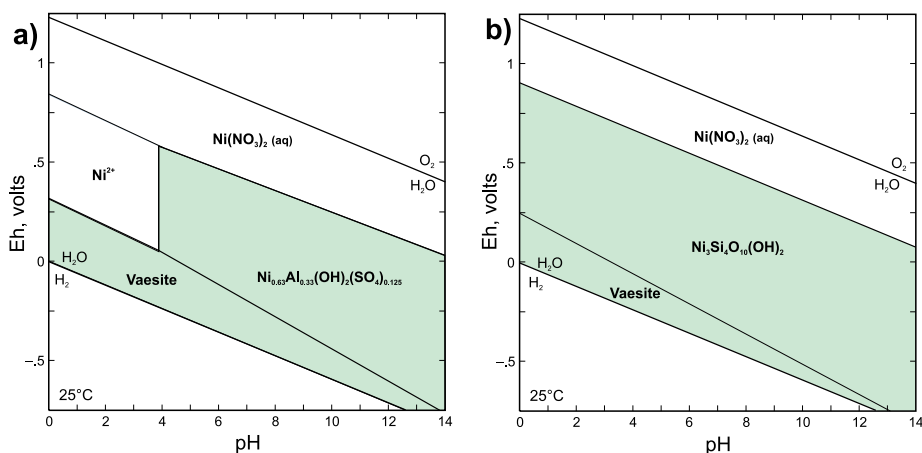


Figure 3.2 Eh-pH diagrams for nickel at 25 °C. (a) System Ni-H₂O-Ca-Al-NO₃-HCO₃-SO₄ (2 mg Ni/L; 40 mg Ca/L; 3 mg Al/L; 6 mg NO₃/L; 60 mg HCO₃/L; 100 mg SO₄/L). Stability fields for solids are shaded green (Vaesite = NiS₂). (b) Same system plus 3 mg Si /L. Thermodynamic data for Ni₃Si₄O₁₀(OH)₂ and Ni_{0.63}Al_{0.33}(OH)₂(SO₄)_{0.125} are from Peltier et al. (2006). [Note that the solubility of the Ni-Al-SO₄ LDH was adjusted to correct for charge imbalance for the chemical structure published in Peltier et al. (2006).]

Attenuation of nickel may also occur via coprecipitation during the formation of (hydr)oxides or sulfides of iron. These minerals have been observed to form at the boundaries between oxidizing and reducing zones within ground-water plumes. There are numerous laboratory and field observations that demonstrate the capacity of these precipitates for nickel uptake (Schultz et al., 1987; 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 [hydrrous 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).

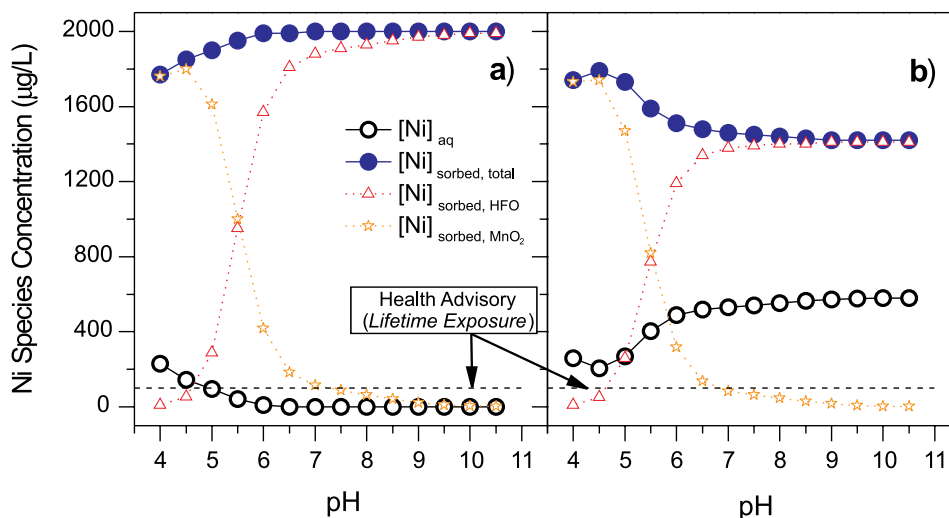


Figure 3.3 (a) Nickel sorption as a function of pH in the presence of an hypothetical aquifer sediment with iron and manganese oxides reflective of the crustal abundance of these elements (Schulze, 2002; assumed 30% porosity with 185.0 g HFO/L and 1.66 g MnO_2 /L). (b) Same conditions as in (a), but 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 $\mu\text{mole/L}$ 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., MINTQA2, 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 complemented by the possible isolation of discrete Ni mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;
- 3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Ni sorption (e.g., Amonette, 2002);
- 4) Identification of nickel association(s) with the various solid phase components of aquifer solids through combination of chemical extractions with microscopic/spectroscopic confirmation of phase associations, and;
- 5) Demonstration of concurrence between the site conceptual model and mathematical model(s) that describe nickel removal mechanism(s).

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

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

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

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

to enhance uptake capacity perpendicular to the direction of plume advance, or enhancement of natural attenuation processes within the aquifer through the injection of soluble reactive components.

References

- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. MINT-EQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. United States Environmental Protection Agency, Office of Research and Development, Washington, DC, EPA/600/3-91/021 (1991).
- Amacher, M.C. Nickel, cadmium, and lead. In *Methods of Soil Analysis: Chemical Methods, Part 3*. D.L. Sparks, (Ed.), Soil Science Society of America, Madison, WI, pp. 739-768 (1996).
- Amonette, J.E. Methods for determination of mineralogy and environmental availability. In *Soil Mineralogy with Environmental Applications*. J.B. Dixon and D.G. Schulze (Eds.), Soil Science Society of America Book Series. Soil Science Society of America, Inc., Madison, WI, pp. 153-197 (2002).
- ATSDR CERCLA Priority List of Hazardous Substances that will be the Subject of Toxicological Profiles and Support Document, Department of Health and Human Services (2005).
- Baes, C.F. and R.E. Mesmer. *The Hydrolysis of Cations*. Malabar, FL, Krieger Publishing Company (1986).
- Baeyens, B., M.H. Bradbury, and W. Hummel. Determination of aqueous nickel-carbonate and nickel-oxalate complexation constants. *Journal of Solution Chemistry* 32: 319-339 (2003).
- Basta, N.T. and M.A. Tabatabai. Ion chromatography determination of total metals in soils. *Soil Science Society of America Journal* 54: 1289-1297 (1990).
- Bedsworth, W.W. and D.L. Sedlak. Sources and environmental fate of strongly complexed nickel in estuarine waters: The role of ethylenediaminetetraacetate. *Environmental Science and Technology* 33: 926-931 (1999).
- Blowes, D.W., C.J. Ptacek, S.G. Benner, C.W.T. McRae, T.A. Bennett, and R.W. Puls. Treatment of inorganic contaminants using permeable reactive barriers. *Journal of Contaminant Hydrology* 45: 123-137 (2000).
- Boisson, J., M. Mench, J. Vangronsveld, A. Ruttens, P. Kopponen, and T. De Koe. Immobilization of trace metals and arsenic by different soil additives: Evaluation by means of chemical extractions. *Communications in Soil Science and Plant Analysis* 30: 365-387 (1999).
- Bradbury, M.H. and B. Baeyens. Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides. *Geochimica et Cosmochimica Acta* 69: 875-892 (2005).
- Bryce, A.L. and S.B. Clark. Nickel desorption kinetics from

- hydrous ferric oxide in the presence of EDTA. *Colloids and Surfaces A - Physicochemical and Engineering Aspects* 107: 123-130 (1996).
- Buanuam, J., K. Tiptanasup, J. Shiowatana, M. Miro, and E.H. Hansenc. Development of a simple extraction cell with bi-directional continuous flow coupled on-line to ICP-MS for assessment of elemental associations in solid samples. *Journal of Environmental Monitoring* 8: 1248-1254 (2006).
- Chaney, R., S. Brown, Y. M. Li, J.S. Angle, F. Homer, and C. Green. Potential use of metal hyperaccumulators. *Mining Environmental Management* September: 9-11 (1995).
- Chen, T., G. Hefter, and R. Buchner. Ion association and hydration in aqueous solutions of nickel(II) and cobalt(II) sulfate. *Journal of Solution Chemistry* 34: 1045-1066 (2005).
- Christensen, J.B. and T.H. Christensen. The effect of pH on the complexation of Cd, Ni and Zn by dissolved organic carbon from leachate-polluted groundwater. *Water Research* 34: 3743-3754 (2000).
- Christensen, J.B., D.L. Jensen, and T.H. Christensen. Effect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. *Water Research* 30: 3037-3049 (1996).
- Coughlin, B.R. and A.T. Stone. Nonreversible adsorption of divalent ions (MnII, CoII, NiII, CuII, and PbII) onto goethite: effects of acidification, FeII addition and picolinic acid addition. *Environmental Science and Technology* 29: 2445-2455 (1995).
- Dähn, R., A.M. Scheidegger, A. Manceau, M.L. Schlegel, B. Baeyens, M.H. Bradbury, and M. Morales. Neof ormation of Ni phyllosilicate upon Ni uptake on montmorillonite: A kinetics study by powder and polarized extended X-ray absorption fine structure spectroscopy. *Geochimica et Cosmochimica Acta* 66: 2335-2347 (2002).
- Dähn, R., A.M. Scheidegger, A. Manceau, M.L. Schlegel, B. Baeyens, M.H. Bradbury, and D. Chateigner. Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite clay minerals: a polarized X-ray absorption fine structure study. *Geochimica et Cosmochimica Acta* 67: 1-15 (2003).
- D'Amore, J.J., S.R. Al-Abed, K.G. Scheckel, and J.A. Ryan. Methods for speciation of metals in soils: A review. *Journal of Environmental Quality* 34:1707-1745 (2005).
- Duke, J.M. Nickel in rocks and ores. In *Nickel in the Environment*. J.O. Nriagu (Ed.), New York, NY, John Wiley & Sons, pp. 27-50 (1980).
- Dzombak, D.A. and F.M.M. Morel. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons, New York, NY (1990).
- Elzinga, E.J. and D.L. Sparks. Reaction condition effects on nickel sorption mechanisms in illite-water suspensions. *Soil Science Society of America Journal* 65: 94-101 (2001).
- Ford, R.G., P.M. Bertsch, and K.J. Farley. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environmental Science and Technology* 31: 2028-2033 (1997).
- Ford, R.G., K.M. Kemner, and P.M. Bertsch. Influence of sorbate-sorbent interactions on the crystallization kinetics of nickel- and lead-ferrihydrite coprecipitates. *Geochimica et Cosmochimica Acta* 63: 39-48 (1999a).
- Ford, R.G., A.C. Scheinost, K.G. Scheckel, and D.L. Sparks. The link between clay mineral weathering and the stabilization of Ni surface precipitates. *Environmental Science and Technology* 33: 3140-3144 (1999b).
- Friedly, J.C., D.B. Kent, and J.A. Davis. Simulation of the mobility of metal-EDTA complexes in groundwater: The influence of contaminant metals. *Environmental Science and Technology* 36 3: 355-363 (2002).
- Hewitt, A.D. Dynamic study of common well screen materials. *Ground Water Monitoring and Remediation* 9: 87-94 (1994).
- Hoffmann, U. and S.L.S. Stipp. The behavior of Ni²⁺ on calcite surfaces. *Geochimica et Cosmochimica Acta* 65: 4131-4139 (2001).
- Huerta-Diaz, M.A. and J.W. Morse. Pyritization of trace metals in anoxic marine sediments. *Geochimica et Cosmochimica Acta* 56: 2681-2702 (1992).
- Hummel, W. and E. Curti. Nickel aqueous speciation and solubility at ambient conditions: a thermodynamic elegy. *Monatshefte für Chemie* 134: 941-973 (2003).
- Jiann, K.-T. and B.J. Presley. Preservation and determination of trace metal partitioning in river water by a two-column ion exchange method. *Analytical Chemistry* 74: 4716-4724 (2002).
- Kent, D.B., J.A. Davis, L.C.D. Anderson, B.A. Rea, and J.A. Coston. Effect of adsorbed metal ions on the transport of Zn- and Ni-EDTA complexes in a sand and gravel aquifer. *Geochimica et Cosmochimica Acta* 66: 3017-3036 (2002).
- Kjoller, C., D. Postma, and F. Larsen. Groundwater acidification and the mobilization of trace metals in a sandy aquifer. *Environmental Science and Technology* 38: 2829-2835 (2004).
- Means, J.L., D.A. Crerar, and J.O. Duguid. Migration of radioactive wastes: radionuclide mobilization by complexing agents. *Science* 200: 1477-1481 (1978).
- McGregor, R., S. Benner, R. Ludwig, D. Blowes, and C. Ptacek. Sulfate reduction permeable reactive barriers to treat acidity, cadmium, copper, nickel, and zinc: Two case studies. In *Handbook of Groundwater Remediation Using Permeable Reactive Barriers*. Academic Press: New York, pp. 495-522 (2002).
- Larsen, F. and D. Postman. Nickel mobilization in a groundwater well field: release by pyrite oxidation and desorption from manganese oxides. *Environmental Science and Technology* 31: 2589-2595 (1997).

- Lindsay, W.L. *Chemical Equilibria in Soils*. New York, John Wiley and Sons, pp. 211-220 (1979).
- Lothenbach, B., G. Furrer, and R. Schulin. Immobilization of heavy metals by polynuclear aluminum and montmorillonite compounds. *Environmental Science and Technology* 31: 1452-1462 (1997).
- Ludwig, R., R.G. McGregor, D.W. Blowes, S.G. Benner, and K. Mountjoy. A permeable reactive barrier for treatment of heavy metals. *Ground Water* 40: 59-66 (2002).
- Manceau, G. and G. Calas. Nickel-bearing clay minerals: II. Intracrystalline distribution of nickel: an x-ray absorption study. *Clay Minerals* 21: 341-360 (1986).
- Manceau, G., G. Calas, and A. Decarreau. Nickel-bearing clay minerals: I. Optical spectroscopic study of nickel crystal chemistry. *Clay Minerals* 20: 367-387 (1985).
- Manceau, A., N. Tamura, M.A. Marcus, A.A. MacDowell, R.S. Celestre, R.E. Sublett, G. Sposito, and H.A. Padmore. Deciphering Ni sequestration in soil ferromanganese nodules by combining X-ray fluorescence, absorption, and diffraction at micrometer scales of resolution. *American Mineralogist* 87: 1494-1499 (2002).
- Manceau, A., M. Lanson, and N. Geoffroy. Natural speciation of Ni, Zn, Ba, and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochimica et Cosmochimica Acta* 71: 95-128 (2007).
- Mattigod, S.V., D. Rai, A.R. Felmy, and L. Rao. Solubility and solubility product of crystalline Ni(OH)₂. *Journal of Solution Chemistry* 26: 391-403 (1997).
- Merlen, E., P. Gueroult, J.-B. d'Espinose de la Caillerie, B. Rebours, C. Bobin, and O. Clause. Hydrotalcite formation at the alumina/water interface during impregnation with Ni (II) aqueous solutions at neutral pH. *Applied Clay Science* 10: 45-56 (1995).
- Nachtegaal, M. and D.L. Sparks. Nickel sequestration in a kaolinite-humic acid complex. *Environmental Science and Technology* 37: 529-534 (2003).
- Nowack, B. and L.J. Sigg. Adsorption of EDTA and metal-EDTA complexes onto goethite. *Journal of Colloid and Interface Science* 177: 106-121 (1996).
- Nowack, B., H. Xue, and L. Sigg. Influence of natural and anthropogenic ligands on metal transport during infiltration of river water to groundwater. *Environmental Science and Technology* 31: 866-872 (1997).
- Pye, K. Forensic examination of rocks, sediments, soils and dusts using scanning electron microscopy and X-ray chemical microanalysis. In *Forensic Geoscience: Principles, Techniques and Applications*. K. Pye and D.J. Croft (Eds.), Geological Society Special Publications, Volume 232, pp.103-122 (2004).
- Oakley, D. and N.E. Korte. Nickel and chromium in ground water samples as influenced by well construction and sampling methods. *Ground Water Monitoring and Remediation* 16: 93-99 (1996).
- Peltier, E., R. Allada, A. Navrotsky, and D.L. Sparks. Nickel solubility and precipitation in soils: a thermodynamic study. *Clays and Clay Minerals* 54: 153-164 (2006).
- Peltier, E., A.L. Dahl, and J.-F. Gaillard. Metal speciation in anoxic sediments: When sulfides can be construed as oxides. *Environmental Science and Technology* 39: 311-316 (2005).
- Richter, R.O. and T.L. Theis. Nickel speciation in a soil/water system. In *Nickel in the Environment*. J. O. Nriagu (Ed.), John Wiley & Sons, New York, NY, pp. 189-202 (1980).
- Ryan, P.C., A.J. Wall, S. Hillier, and L. Clark. Insights into sequential chemical extraction procedures from quantitative XRD: a study of trace metal partitioning in sediments related to frog malformities. *Chemical Geology* 184: 337-357 (2002).
- Rudd, T., J.A. Campbell, and J.N. Lester. Use of model compounds to elucidate metal forms in sewage sludge. *Environmental Pollution* 50: 225-242 (1988).
- Scheckel, K.G., C.A. Impellitteri, J.A. Ryan, and T. McEvoy. Assessment of a sequential extraction procedure for perturbed lead-contaminated samples with and without phosphorus amendments. *Environmental Science and Technology* 37: 1892-1898 (2003).
- Scheckel, K.G., A.C. Scheinost, R.G. Ford, and D.L. Sparks. Stability of layered Ni hydroxide surface precipitates - A dissolution kinetics study. *Geochimica et Cosmochimica Acta* 64: 2727-2735 (2000).
- Scheckel, K.G. and D.L. Sparks. Kinetics of the formation and dissolution of Ni precipitates in a gibbsite/amorphous silica mixture. *Journal of Colloid and Interface Science* 229: 222-229 (2000).
- Scheckel, K.G. and D.L. Sparks. Temperature effects on nickel sorption kinetics at the mineral-water interface. *Soil Science Society of America Journal* 65: 719-728 (2001).
- Scheidegger, A.M., D.G. Strawn, G.M. Lamble, and D.L. Sparks. The kinetics of mixed Ni-Al hydroxide formation on clays and aluminum oxides: A time-resolved XAFS study. *Geochimica et Cosmochimica Acta* 62: 2233-2245 (1998).
- Scheinost, A.C., R.G. Ford, and D.L. Sparks. The role of Al in the formation of secondary Ni precipitates on pyrophyllite, gibbsite, talc, and amorphous silica: A DRS study. *Geochimica et Cosmochimica Acta* 63: 3193-3203 (1999).
- Scheinost, A.C. and D.L. Sparks. Formation of layered single and double metal hydroxide precipitates at the mineral/ water interface: A multiple-scattering XAFS analysis. *Journal of Colloid and Interface Science* 223: 167-178 (2000).
- Schultz, M.F., M.M. Benjamin, and J.F. Ferguson. Adsorption and desorption of metals on ferrihydrite: reversibility of the reaction and sorption properties of the regenerated solid. *Environmental Science and Technology* 21: 863-869 (1987).

- Schulze, D.G. An introduction to soil mineralogy. In *Soil Mineralogy with Environmental Applications*. J.B. Dixon and D.G. Schulze (Eds.), Madison, Wisconsin, Soil Science Society of America, Inc., pp. 1-35 (2002).
- Seaman, J.C., J.S. Arey, and P.M. Bertsch. Immobilization of nickel and other metals in contaminated sediments by hydroxyapatite addition. *Journal of Environmental Quality* 30: 460-469 (2001).
- Shannon, R.D. and J.R. White. The selectivity of a sequential extraction procedure for the determination of iron oxyhydroxides and iron sulfides in lake sediments. *Biogeochemistry* 14: 193-208 (1991).
- Snodgrass, W.J. Distribution and behavior of nickel in the aquatic environment. In *Nickel in the Environment*. J.O. Nriagu (Ed.), New York, John Wiley & Sons, pp. 203-274 (1980).
- Stoeppler, M. Analysis of nickel in biological materials and natural waters. In *Nickel in the Environment*. J.O. Nriagu (Ed.), New York, John Wiley & Sons, pp. 661-821 (1980).
- Strathmann, T.J. and S.C.B. Myneni. Speciation of aqueous Ni(II)-carboxylate and Ni(II)-fulvic acid solutions: Combined ATR-FTIR and XAFS analysis. *Geochimica et Cosmochimica Acta* 68: 3441-3458 (2004).
- Tessier, A., P.G.C. Campbell, and M. Bisson. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844-851 (1979).
- Thoenen, T. Pitfalls in the use of solubility limits for radioactive waste disposal: The case of nickel in sulfidic groundwaters. *Nuclear Technology* 126: 75-87 (1999).
- Tonkin, J.W., L.S. Balistreri, and J. W. Murray. Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. *Applied Geochemistry* 19: 29-53 (2004).
- USEPA. *Health Assessment Document for Nickel and Nickel Compounds*, Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, Research Triangle Park, NC, EPA-600/8-83-012F (1986).
- USEPA. *Toxic Release Inventory*. Washington, DC (2003). <http://www.epa.gov/tri/>.
- USEPA. *2006 Edition of the Drinking Water Standards and Health Advisories*, EPA 822-R-06-013, Office of Water, Washington, DC, (2006a).
- USEPA. *National Recommended Water Quality Criteria*, 4304T, Office of Water, Washington, DC, (2006b).
- Van den Berg, C.M.G. and M. Nimmo. Determination of interactions of nickel with dissolved organic material in seawater using cathodic stripping voltammetry. *Science of the Total Environment* 60: 185-195 (1987).
- Warwick, P., A. Hall, J. Zhu, P.W. Dimmock, R. Robbins, L. Carlsen, and P. Lassen. Effect of temperature on the nickel humic acid equilibrium reaction. *Chemosphere* 35: 2471-2477 (1997).
- Wilkin, R.T. and M.S. McNeil. Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage. *Chemosphere* 53: 715-725 (2003).
- Zachara, J.M., J.K. Fredrickson, S.C. Smith, and P.L. Gassman. Solubilization of Fe(III) oxide-bound trace metals by a dissimilatory Fe(III) reducing bacterium. *Geochimica et Cosmochimica Acta* 65: 75-93 (2001).

Copper

Richard T. Wilkin

Occurrence and Distribution

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

It is believed that the ancient civilizations of Mesopotamia (region of modern Iraq) made use of native copper and gold, possibly as far back as ca. 8700 BC. Indeed the exploitation of natural deposits of copper and gold, which are soft metals that can be hammered into shape without heat, marked the transition from the Stone Age to more modern ways of life (Diamond, 1997). Typical copper-bearing minerals include native copper, sulfides (chalcopyrite, CuFeS₂; bornite, Cu₅FeS₄; chalcocite, Cu₂S; covellite, CuS; digenite, Cu₉S₅), sulfosalts (tetrahedrite, Cu₁₂Sb₄S₁₃), carbonates (malachite, Cu₂(OH)₂CO₃; azurite, Cu₃(OH)₂(CO₃)₂), and oxides (tenorite, CuO). In the US, the principal copper mining states are Arizona, Utah, and New Mexico. In 2004, domestic mine production of copper was about 1.16 million tons, or about 8% of world mine production. While the US is the world's second-largest producer of copper, it is the world's largest copper-consumer. The principal modern use of copper is as an electrical conductor. Alloys of copper (e.g., brass and bronze) are used in jewelry, sculptures and for minting coins. Copper also has broad uses as an agricultural poison and as an algicide in water purification.

Plume Characteristics

Copper has five possible oxidation states (0, +1, +2, +3, and +4). Under most conditions, copper is present in aqueous solution as the divalent cation, Cu²⁺, or as Cu(II) hydroxide or carbonate complexes. However, copper is

not especially mobile in aquatic environments due to the relatively low solubility of Cu(II)-bearing solids and high affinity of copper for mineral and organic surfaces. Certain organic compounds are able to keep copper soluble by ligand complexation. Hence, copper does not typically enter ground water except under conditions of low pH or high ligand concentrations. Where present, copper contamination in soils and ground water stems primarily from mining activities, metal production, wood production, fertilizer production, and combustion of fossil fuels and wastes (e.g., 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^- 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 $\text{pH} > 6$.

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 $<40 \text{ mg C L}^{-1}$.

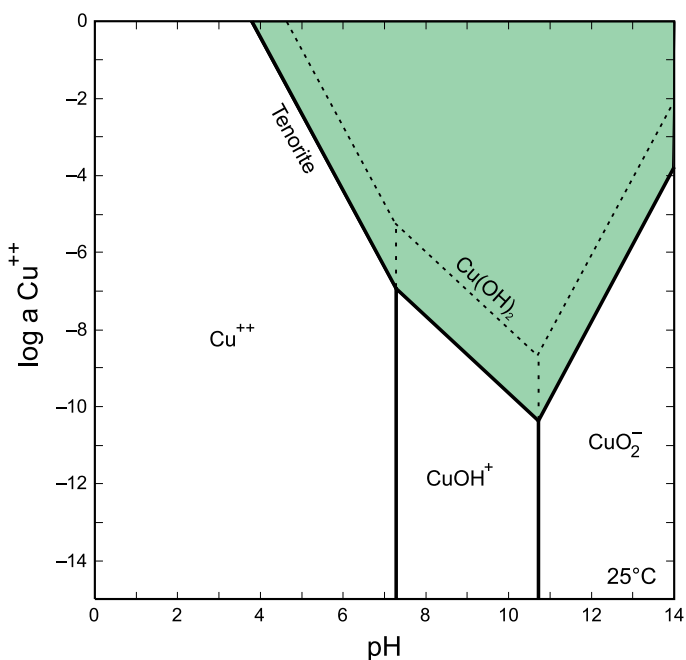


Figure 4.1 Solubility of copper oxide and copper hydroxide as a function of pH in the system Cu-O-H at 25 °C.

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 $\text{pH} < 6$ 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.

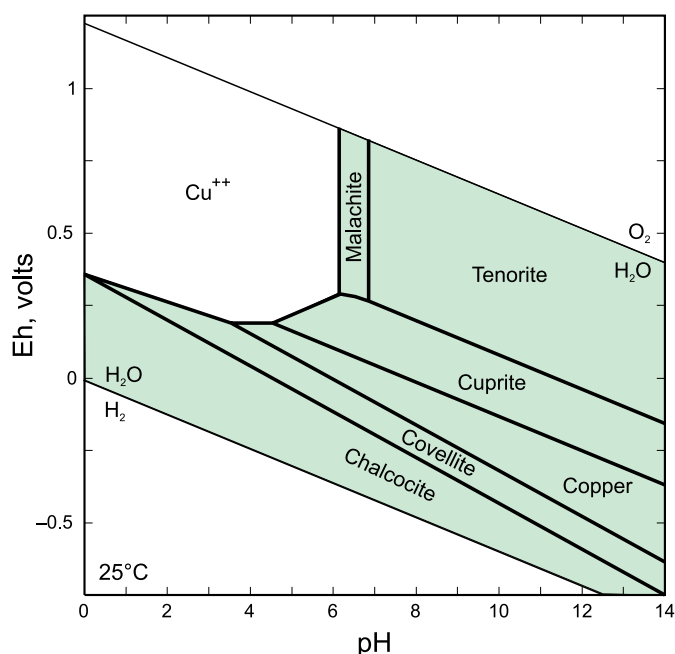


Figure 4.2 Eh-pH diagram for copper at 25 °C (total inorganic carbon = 10^{-2} molal; total sulfur = 10^{-3} molal; total copper = 10^{-5} molal).

Cavallaro and McBride (1980) found that in alkaline soils copper was present as $\text{Cu}(\text{OH})_2$ and with progressive aging, copper solubility decreased consistent with the formation of $\text{Cu}_2(\text{OH})_2\text{CO}_3$. 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 impor-

tant copper-bearing phases, with $\text{Cu}(\text{OH})_2$ 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 $f \text{CO}_2$ 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.

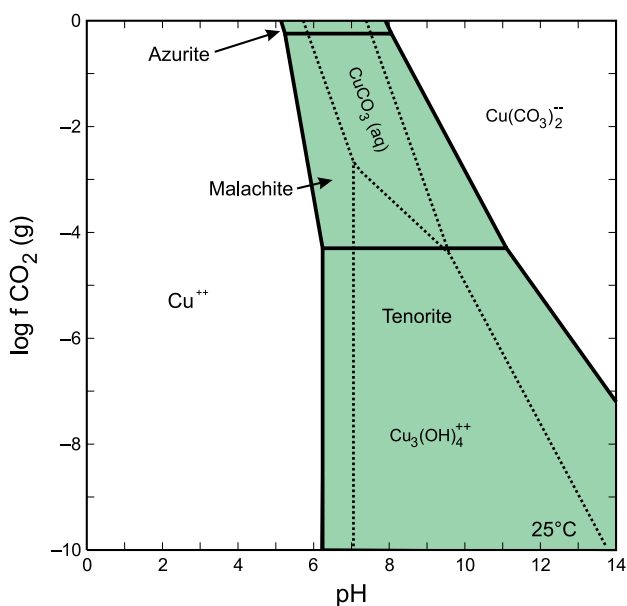


Figure 4.3 Solubility and speciation of copper as a function of pH and log fugacity of $\text{CO}_2(\text{gas})$ at 25 °C. Solid lines separate stable phases and dotted lines separate aqueous species (total copper = 10^{-5} molal). Diagram drawn using thermodynamic data from MINTQA2.

Based on the solubility and sorption behavior of copper, it is expected that over a wide range of geochemical conditions copper will be effectively stable in the solid phase of soils and sediment materials. Copper has a strong affinity for the surfaces of iron oxides and hydroxides (e.g., Benjamin and Leckie, 1981; Robertson and Leckie, 1998; Martínez and McBride, 1998), clays (e.g., Pickering, 1980; Farqhar et al., 1997; Morton et al., 2001), sulfides (e.g., Patrick et al., 1997; Parkman et al., 1999), and organic matter (e.g., Sauv e 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 $\text{Pb} < \text{Cu} < \text{Zn} < \text{Cd}$. 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 $\text{pH} > 6$, 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. Mart nez 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 $\text{pH } 5.5 \pm 0.2$ 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:



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 (Sa nudo-Wilhelmy et al., 2002; Jensen et al., 1999; Freedman et al., 1996; Pauwels et al., 2002). The association between metals and ground water colloids is evident both in uncontaminated ground-water (e.g., Sa nudo-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 $0.45 \mu\text{m}$ had been used, since only negligible amounts of metal were found with colloids $> 0.40 \mu\text{m}$. 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 Sa nudo-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 $0.45 \mu\text{m}$ 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 $0.45 \mu\text{m}$ filter papers. The use of filter papers with pore sizes less than $0.1 \mu\text{m}$ 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 1 - 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 complemented by the possible isolation of discrete Cu mineral phases via density separations (or other schemes) in regions of the aquifer with highest solid phase concentrations;
- 3) Determination of aquifer mineralogy to determine the relative abundance of components with documented capacity for Cu sorption (e.g., Amonette, 2002; Burton et al., 2005); and
- 4) Determination of Cu-sediment associations via chemical extractions designed to target specific components within the aquifer sediment (e.g., Lee et al., 2005).

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

Tier III - Once the partitioning mechanism(s) have been identified for the site, the subsequent characterization effort under Tier III will involve determination of the stability of immobilized Cu and the capacity of the aquifer to sustain continued uptake. It is recommended that the stability of immobilized Cu be tested based on the anticipated evolution of ground-water chemistry concurrent with plume shrinkage. For example, changes in ground-water pH can exert a significant influence on Cu adsorption or precipitate solubility. Therefore, it is recommended that sediment leach tests be conducted to characterize the magnitude of Cu mobilization as a function of pH for a ground-water chemistry representative of site conditions. It is recommended that the capacity for Cu uptake onto aquifer solids be determined relative to the specific mechanism(s) identified in Tier II. For example, if site characterization under Tier II indicated that precipita-

tion of Cu sulfide due to microbial degradation of organic compounds coupled with sulfate reduction occurs within the aquifer, then it is recommended that the mass distribution of organic carbon and sulfate to support this reaction within the aquifer be determined. This site-specific capacity can then be compared to Cu mass loading within the plume in order to assess the longevity of the natural attenuation process. If site-specific tests demonstrate the stability of immobilized Cu and sufficient capacity within the aquifer to sustain Cu attenuation, then the site characterization effort can progress to Tier IV. For cases where contaminant stability is sufficient but aquifer capacity is insufficient for capture of the entire plume, then a determination of the benefits of contaminant source reduction may be necessary.

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

References

- Amonette, J.E. Methods for determination of mineralogy and environmental availability. In *Soil Mineralogy with Environmental Applications*. J.B. Dixon and D.G. Schulze (Eds.), Soil Science Society of America Book Series. Soil Science Society of America, Inc., Madison, WI, pp. 153-197 (2002).
- Baes, C.F., and R.E. Mesmer. *The Hydrolysis of Cations*. Wiley Interscience, New York, NY, 489 pp. (1976).
- Benjamin, M.M., and J.O. Leckie. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron hydroxide. *Journal of Colloid and Interface Science* 79: 209-221 (1981).

- Bocheńska, T., J. Fiszler, and M. Kalisz. Prediction of groundwater flow into copper mines of the Lubin Głogów Copper District. *Environmental Geology* 39: 587-594 (2000).
- Boyle, E.A. Copper in natural waters. In *Copper in the Environment*. J.O. Nriagu (Ed.), Wiley, New York, NY pp. 77-88 (1979).
- Burton, E.D., I.R. Phillips, and D.W. Hawker. Geochemical partitioning of copper, lead, and zinc in benthic, estuarine sediment profiles. *Journal of Environmental Quality* 34: 263-273 (2005).
- Cavallaro, N. and M.B. McBride. Activities of Cu^{2+} in soil solutions as affected by pH. *Soil Science Society of America Journal* 44: 729-732 (1980).
- Cavallaro, N. and M.B. McBride. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. *Soil Science Society of America Journal* 42: 550-556 (1978).
- Christensen, J.B., J.J. Botma, and T.H. Christensen. Complexation of Cu and Pb by DOC in polluted groundwater: A comparison of experimental data and predictions by computer speciation models (WHAM and MINTEQA2). *Water Research* 33: 3231-3238 (1999).
- Diamond, J. *Guns, Germs, and Steel: The Fate of Human Societies*. W.W. Norton, New York, NY (1997).
- Dudley, L.M., J.E. McLean, T.H. Furst, and J.J. Jurinak. Sorption of cadmium and copper from an acid mine waste extract by two calcareous soils: Column studies. *Soil Science* 151: 121-135 (1991).
- Dvorak, D.H., R.S. Hedin, H.J. Edenborn, and P.E. McIntire. Treatment of metal-contaminated water using bacterial sulfate reduction: Results from pilot scale reactors. *Biotechnology and Bioengineering* 40: 609-616 (1992).
- Farquhar, M.L., D.J. Vaughan, C.R. Hughes, J.M. Charnock, and K.E.R. England. Experimental studies of the interaction of aqueous metal cations with mineral substrates: Lead, cadmium, and copper with perthitic feldspar, muscovite, and biotite. *Geochimica et Cosmochimica Acta* 61: 3051-3064 (1997).
- Freedman, Y.E., D. Ronen, and G.L. Long. Determination of Cu and Cd content of groundwater colloids by sampling graphite furnace atomic absorption spectrometry. *Environmental Science and Technology* 30: 2270-2277 (1996).
- Guilbert, J.M. and C.F. Park. *The Geology of Ore Deposits*. W. H. Freeman and Company, New York, NY 985 pp. (1986).
- Han, N. and M.L. Thompson. Impact of dissolved organic matter on copper mobility in aquifer material. *Journal of Environmental Quality* 32: 1829-1836 (2003).
- Hickey, M.G. and J.A. Kittrick. Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. *Journal of Environmental Quality* 13: 372-376 (1984).
- Hidmi, L. and M. Edwards. Role of temperature and pH in $\text{Cu}(\text{OH})_2$ solubility. *Environmental Science and Technology* 33: 2607-2610 (1999).
- Inglezakis, V.J., M.D. Loizidou, and H.P. Grigoropoulou. Ion exchange of Pb^{2+} , Fe^{3+} , and Cr^{3+} on natural clinoptilolite: Selectivity determination and influence of acidity on metal uptake. *Journal of Colloid and Interface Science* 261: 49-54 (2003).
- Jensen, D.L., A. Ledin, and T.H. Christensen. Speciation of heavy metals in landfill-leachate polluted groundwater. *Water Research* 33: 2642-2650 (1999).
- Khaodhiar, S., M.F. Azizian, K. Osathaphan, and P.O. Nelson. Copper, chromium, and arsenic adsorption and equilibrium modeling in an iron-oxide-coated sand, background electrolyte system. *Water, Air, and Soil Pollution* 119: 105-120 (2000).
- Leckie, J.O. and J.A. Davis. Aqueous environmental chemistry of copper. In *Copper in the Environment*. J.O. Nriagu, (Ed.), Wiley, New York, NY pp. 89-121 (1979).
- Lee, P.-K., Y.-H. Yu, S.-T. Yun, and B. Mayer. Metal contamination and solid phase partitioning of metals in urban roadside sediments. *Chemosphere* 60: 672-689 (2005).
- Luther, G.W., S.M. Theberge, T.F. Rozan, D. Rickard, C.C. Rowlands, and A. Oldroyd. Aqueous copper sulfide clusters as intermediates during copper sulfide formation. *Environmental Science and Technology* 36: 394-402 (2002).
- Martinez, C.E. and M.B. McBride. Solubility of Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} in aged coprecipitates with amorphous iron hydroxides. *Environmental Science and Technology* 32: 743-748 (1998).
- Martinez, C.E. and H.L. Motto. Solubility of lead, zinc, and copper added to mineral soils. *Environmental Pollution* 107: 153-158 (2000).
- Martinez, C.E., A. Jacobson, and M.B. McBride. Thermally induced changes in metal solubility of contaminated soils is linked to mineral recrystallization and organic matter transformations. *Environmental Science and Technology* 35: 908-916 (2001).
- McBride, M.B. and D.R. Bouldin. Long-term reactions of copper(II) in a contaminated soil. *Soil Science Society of America Journal* 48: 56-59 (1984).
- Morton, J.D., J.D. Semrau, and K.F. Hayes. An X-ray absorption spectroscopy study of the structure and reversibility of copper adsorbed to montmorillonite clay. *Geochimica et Cosmochimica Acta* 65: 2709-2722 (2001).
- Mosselmans, J.F.W., R.A.D. Patrick, J.M. Charnock, and V.A. Sole. EXAFS of copper in hydrosulfide solutions at very low concentrations: Implications for speciation of copper in natural waters. *Mineralogical Magazine* 63: 769-772 (1999).
- Mountain, B.W. and T.M. Seward. The hydrosulphide/sulphide complexes of copper(I): Experimental deter-

- mination of stoichiometry and stability at 22° C and reassessment of high temperature data. *Geochimica et Cosmochimica Acta* 63:11-29 (1999).
- Mountain, B.W. and T.M. Seward. Hydrosulphide/sulphide complexes of copper(I): Experimental confirmation of the stoichiometry and stability of $\text{Cu}(\text{HS})_2^-$ to elevated temperatures. *Geochimica et Cosmochimica Acta* 67: 3005-3014 (2003).
- Park, J.-B., S.-H. Lee, J.-W. Lee, and C.-Y. Lee. Lab scale experiments for permeable reactive barriers against contaminated groundwater with ammonium and heavy metals using clinoptilolite. *Journal of Hazardous Materials* B95: 65-79 (2002).
- Parkman, R.H., J. M. Charnock, N.D. Bryan, F.R. Livens, and D.J. Vaughan. Reactions of copper and cadmium ions in aqueous solution with goethite, lepidocrocite, mackinawite, and pyrite. *American Mineralogist* 84: 407-419 (1999).
- Patrick, R.A.D., J.F.W. Mosselmans, J.M. Charnock, K.E.R. England, G.R. Helz, C.D. Garner, and D.J. Vaughan. The structure of amorphous copper sulfide precipitates: An X-ray absorption study. *Geochimica et Cosmochimica Acta* 61: 2023-2036 (1997).
- Paulson, A.J. and L. Balistreri. Modeling removal of Cd, Cu, Pb, and Zn in acidic groundwater during neutralization by ambient surface waters and groundwaters. *Environmental Science and Technology* 33: 3850-3856 (1999).
- Pauwels, H., M. Tercier-Waeber, M. Arenas, R. Castroviejo, Y. Deschamps, A. Lassin, F. Graziottin, and F. Elorza. Chemical characteristics of groundwater around two massive sulphide deposits in an area of previous mining contamination, Iberian Pyrite Belt, Spain. *Journal of Geochemical Exploration* 75: 17-41 (2002).
- Pickering, W.F. Copper retention by soil/sediment components. In *Copper in the Environment*. J.O. Nriagu (Ed.), Wiley, New York, NY pp. 217-253 (1980).
- Reimann, C. and P. Caritat. *Chemical Elements in the Environment*. Springer-Verlag, Berlin, 398 pp. (1998).
- Robertson, A.P. and J.O. Leckie. Acid/base, copper binding, and $\text{Cu}^{2+}/\text{H}^+$ exchange properties of goethite, an experimental and modeling study. *Environmental Science and Technology* 32: 2519-2530 (1998).
- Rose, A.W. Mobility of copper and other heavy metals in sedimentary environments. In *Sediment-hosted Stratiform Copper Deposits*. R.W. Boyle, A.C. Brown, C.W. Jefferson, E.C. Jowett, and R.V. Kirkham (Eds.), Geological Association of Canada, Special Paper 36, pp. 97-110 (1989).
- Sañudo-Wilhelmy, S.A., F.K. Rossi, H. Bokuniewicz, and R.J. Paulsen. Trace metal levels in uncontaminated groundwater of a coastal watershed: Importance of colloidal forms. *Environmental Science and Technology* 36: 1435-1441 (2002).
- Sauve, S., M.B. McBride, W.A. Norvell, and W.H. Hendershot. Copper solubility and speciation of in situ contaminated soils: Effects of copper level, pH and organic matter. *Water, Air, and Soil Pollution* 100: 133-149 (1997).
- Schilling, M. and W.T. Cooper. Identification of copper binding sites in soil organic matter through chemical modifications and ^{13}C CP-MAS NMR spectroscopy. *Environmental Science and Technology* 38: 5059-5063 (2004).
- Smolyakov, B.S., M.V. Zhigula, A.P. Ryzhikh, E.V. Sinitsyna, N.I. Ermolaeva, and A.A. Fedotova. Copper(II) speciation in a freshwater ecosystem. *Water Resources* 31: 55-63 (2004).
- Steed, V.S., M.T. Suidan, M. Gupta, T. Miyahara, C.M. Acheson, and G.D. Sayles. Development of a sulfate-reducing biological process to remove heavy metals from acid mine drainage. *Water Environment Research* 72: 530-535 (2000).
- Stumm, W. and K. Morgan. *Aquatic Chemistry*, 3rd Edition. Wiley-Interscience, New York, NY (1996).
- Tabak, H.H., R. Scharp, J. Burckle, F.K. Kawahara, and R. Govind. Advances in biotreatment of acid mine drainage and biorecovery of metals: 1. Metal precipitation for recovery and recycle. *Biodegradation* 14: 423-436 (2003).
- Tessier, A., P.G.C. Campbell, and M. Bison. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844-851 (1979).
- Thompson, R.A. and G.R. Helz. Copper speciation in sulfidic solutions at low sulfur activity: Further evidence for cluster complexes? *Geochimica et Cosmochimica Acta* 58: 2971-2983 (1994).
- USEPA. *2006 Edition of the Drinking Water Standards and Health Advisories*, EPA 822-R-06-013, Office of Water, Washington DC, (2006a).
- USEPA. *National Recommended Water Quality Criteria*, 4304T, Office of Water, Washington DC, (2006b).
- Waybrandt, K.R., D.W. Blowes, and C.J. Ptacek. Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. *Environmental Science and Technology* 32: 1972-1979 (1998).
- Wedepohl, K.H. The composition of continental crust. *Geochimica et Cosmochimica Acta* 59: 1217-1232 (1995).
- Wilkin, R.T. and M.S. McNeil. Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage. *Chemosphere* 53: 715-725 (2003).
- Woinarski, A.Z., I. Snape, G. W. Stevens, and S.C. Stark. The effects of cold temperature on copper ion exchange by nature zeolite for use in a permeable reactive barrier in Antarctica. *Cold Regions Science and Technology* 37: 159-168 (2003).

-
- Xiao, Z., C.H. Gammons, and A.E. Williams-Jones. Experimental study of copper(I) chloride complexing in hydrothermal solutions at 40 to 300° C and saturated water vapor pressure. *Geochimica et Cosmochimica Acta* 62: 2949-2964 (1998).
- Zagury, G.J., R. Samson, and L. Deschênes. Occurrence of metals in soil and ground water near chromated copper arsenate-treated poles. *Journal of Environmental Quality* 32: 507-514 (2003).

