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A Site-Specific Approach for the Evaluation of Natural Attenuation at Metals-Impacted Sites

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Consideration of monitored natural attenuation (MNA) as a remedy component for metals-contaminated sites can be achieved using a site-specific screening approach, followed by application of one or a series of sequential extraction measurements. Hazardous waste sites contaminated with metals can be screened for the implementation of monitored natural attenuation on the basis of contaminant-specific soil chemical characteristics (i.e., K_d's, solubilities, and nonexchangeable sorbed fraction). Field cases are used to demonstrate the screening approach and to outline the primary considerations involved in accurately applying sequential extraction procedures to support the of MNA for site remediation.

The results of these case studies provide strong evidence that site-specific screening and the use of sequential extraction procedures are effective methods for evaluating natural attenuation for metals impacted sites.

KEY WORDS: *natural attenuation, metals, sequential extraction, bioavailability.*

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INTRODUCTION

NATURAL attenuation includes "naturally occurring processes in soils and groundwaters that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media" (U.S. Environmental Protection Agency, 1997). These processes include biodegradation, dispersion, dilution, sorption, precipitation, volatilization, and/or chemical and biochemical stabilization of contaminants. Metals are not lost through degradation processes; consequently, ignoring dilution, natural attenuation involves sorption of soluble metals to solid phases or the formation through precipitation of insoluble contaminant-containing phases. Precipitation is a three-dimensional solid phase arrangement of molecules from the solution, while adsorption is the net accumulation of matter in a two-dimensional molecular arrangement at a solid/aqueous interface.

The biogeochemical parameters that govern metal partitioning include the concentration and type of metal, oxidation/reduction potential (Eh), ionic strength, pH, concentration of complexing ligands, and biological reactions. Metals are generally found in one of the following soil or sediment fractions (e.g., Shuman, 1991): dissolved; occupying exchange sites of inorganic and organic soil constituents; specifically adsorbed on inorganic soil constituents; complexed with insoluble soil organics; precipitated or coprecipitated as solids; and occluded within the structure of primary and/or secondary minerals. The dissolved fraction represents the portion of the total metal concentration that all approaches assume is bioavailable. The remaining fractions represent immobilized metals that are progressively more difficult to leach.

The interaction of metal contaminants with soil solids typically prevents complete clean up of anthropogenic and nonanthropogenic metals-contaminated sites. At the same time, the decreased bioavailability resulting from solid-solution interaction provides a strong rationale for some reliance on natural attenuation (NA) as a site remedy for applicable sites. Despite this, NA has only been applied sporadically. This may be due to the lack of a common protocol for screening candidate metals-impacted sites for MNA, and the absence of a generally accepted analytical technique for demonstrating attenuation mechanisms sorption, sequestration, and metal valence changes.

For metals MNA site-screening, minimal site-specific data are generally available to identify specific attenuation mechanisms. Instead, the results tend to be only semiquantitative and provide little more than an indication whether MNA should be examined more closely. The implementation of MNA at a site requires expanded site-specific analyses. A more complete knowledge of metal immobilization processes at specific sites is needed for full MNA implementation because an understanding of mechanism(s) is a prerequisite to: selecting the site remedy, developing site closure pathways, and implementing any long-term monitoring (USEPA, 1997). Below a series of case studies are used to demonstrate an approach to evaluating natural attenuation at impacted sites. The initial screening effort uses a web-based screening tool, MNAtoolbox (http://www.sandia.gov/eesector/gs/gc/na/mnahome.html), developed by Sandia National Laboratories for the US Dept. of Energy (Brady *et al.,* 1998) and existing site data. The second step involves using sequential extractions for collecting baseline data to identify site-specific attenuation mechanisms for metals.

Metal Attenuation and Bioavailability

Solids-associated metals can be separated into two groups, both of which must be addressed by soil and groundwater remediation efforts. The easily leached solids-associated fraction is assumed to be 'potentially bioavailable', whereas a nonleachable fraction is assumed to be 'nonbioavailable'. In this context, the definition of bioavailability is operative and depends on the nature of the leaching procedure. Metal extraction techniques that mimic natural biologic processes might in theory provide accurate estimates of bioavailability.

Different exposure pathways (ingestion vs. drinking water uptake vs. dermal exposure) and the likely receptors (plants, animals, humans) will be important at different sites, and these exposure pathways and receptors may change over time with land use changes. For example, the exposure pathway for metal-impacted surface sediment may be ingestion by human receptors. Consequently, risk assessment would address the bioavailability of metals through the ingestion pathway. Over time as deposition isolates the sediments from surface receptors, sediment ingestion may no longer prevail as an exposure pathway, and the concern may shift to metals leaching to groundwater. All of these factors must be kept in mind when assessing the fate of metals in soils.

All measures of bioavailability depend on the biogeochemical processes controlling metal mobility in the soil and that ultimately define its resistance to solubilization and transport to groundwater, solubility in digestive fluids, or potential to be dermally transported. Potentially bioavailable forms require considerably more attention than nonbioavailable ones. Consequently, some differentiation between the two should be made before active remediation is prescribed. This is accomplished by toxicity or tissue tests on benthic organisms, plants, or microorganisms, for acute and/or chronic effects, or by soluble metal analyses that define the fraction of metals available for reactions with organisms.

METHODS

Sequential Extraction Procedures

Sequential extraction procedures (SEPs) are chemical extractions used to remove metals from specific solid-associated phases. SEPs progressively use stronger reagents to solubilize metals from increasingly recalcitrant phases. Although these procedures do not identify the specific metal phases in a soil, they do provide a means to evaluate metal release in relation to redox and pH fluctuations (Tessier *et al.,* 1979; Sposito *et al.,* 1984; Hickey and Kittrick, 1984; Gruebel *et al.,* 1988; Kuo *et al.,* 1983). Typically, metals can be grouped into the following geochemical fractions or "sinks" (Tessier *et al.,* 1979).

1. Exchangeable Phase — This extraction includes metals that are reversibly sorbed to soil minerals, amorphous solids, and/or organic material by electrostatic forces. These forces may be overcome by exposing the soil to a concentrated electrolyte solution, such as 1 *M* $MgCl_2$ that displaces the metal ions from solid surfaces.
2. Carbonate Phase — This extraction targets metals that are irreversibly sorbed or otherwise bound in carbonate minerals. This phase is soluble in a mild acid solution (1 *M* NaOAc solution in 25% HOAc at pH 5).
3. Metal Hydroxide Phase — Metals bound to hydroxides of iron, manganese, and/or aluminum are extracted during this phase. Metals associated with this phase may be extracted using a solution of 0.1 *M* hydroxylamine hydrochloride in pH 2 nitric acid.
4. Organic Phase — This extraction targets metals strongly bound via chemisorption to organic material. The oxidation of soil organic matter (using pH 8.5; at 5% NaOCl), will bring into solution metals irreversibly bound to organic functional groups.
5. Acid/Sulfide Fraction — The extraction is used to identify metals precipitated as sulfide minerals. Metals associated with sulfide minerals will be removed by leaching with 4 *M* HNO_3 at 95°C.
6. Residual Fraction — Metals remaining in the soil after the previous extractions are distributed between silicates, phosphates, and refractory oxides. These residual metals can be removed from the soil through total dissolution with Aqua Regia.

There are a number of SEP methods that have been developed with different extracting solutions, different extraction orders, and metal-specific SEPs. The SEP approach outlined above is a modification of the SEP currently being calibrated by the NIST (Schultz *et al.,* 1996). The SEP provides several important pieces of evidence. First, analysis of the exchangeable leachate represents the fraction of metal reversibly sorbed, that is, the fraction that can rapidly (seconds to hours) equilibrate with soil solution. Additionally, this is the metal fraction available for exchange with organic and inorganic soil phases. The remaining steps perform two functions: (1) quantify the amount of metal that is either irreversibly sorbed under ambient conditions or exists as a separate mineral phase, and (2) quantifies the concentration of metal and characterizes the type of immobilization complexes.

Sequential extractions have been used for a number of applications. Song and Breslin (1998) used SEP data combined with amphipod toxicity testing data to characterize metal bioavailability in lake sediments. Perin *et al.* (1997) performed a 5-year study of metals in sediments at a site in Rio De Janeiro, Brazil, using a five extraction SEP to characterize metal bioavailability. The authors segregated the SEP extractions into two groups: the (1) bioavailable phase (BAP) and (2) the nonbioavailable phase (NBAP). The BAP consisted of the exchangeable, carbonate, and metal hydroxide extractions. The NBAP was comprised of the organic matter, sulfide, and residual extractions. These studies and others (Vangronsveld *et al.,* 2000; Grzebisz, 1997; Keller and Vedy, 1994; Peters *et al.,* 1997; Ramos *et al.,* 1999) have used SEPs to quantitatively evaluate metal bioavailability. Total metals analysis provides limited information with regard to bioavailability (Basta and Gradwohl, 2000; Davis *et al.,* 1994); therefore, sequential extractions combined with toxicity testing provide a powerful tool for identifying contaminant metal bioavailability based on the state of the metal in soil or sediment and the observed response of less complex organisms (earthworms, water fleas, mussels, etc.) at the base of the food chain.

The SEP may also be used to estimate the fraction of metal expected to accumulate in the human body under an ingestion and/or inhalation risk scenario. The solution used in metal hydroxide extractions (pH = 2) is near the reported pH range used by several researchers performing *in vitro* testing to evaluate the degree of metals dissolution in a simulated gastrointestinal tract environment (Williams *et al.,* 1998 and Ruby *et al.,* 1996). The use of SEPs for this type of correlation should be limited to screening applications as *in vitro* tests use organic acids representative of the gastrointestinal tract and the SEP uses inorganic extracting solutions.

The SEP analysis can also be used to effectively evaluate remedial alternatives for metal-impacted sites. For example, SEPs can be used to determine the optimum flushing solution (pH, oxidant, reductant, acid, base, chelating agent) to use for metal recovery by soil flushing (Hammick *et al.,* 1998; Grasso *et al.,* 1997). The SEP can also be used to verify reduced metal solubility and characterize metal immobilization mechanisms following soil stabilization treatments (Chlopeka and Adriano, 1997; Xenidis *et al.,* 1999; Vangronsveld *et al.,* 2000). The SEP has also been used to evaluate the potential effectiveness of phytoremediation in extracting soluble and labile metals from soil (Barbafieri, 2000).

As with most analytical methods, limitations and potential caveats are associated with the use of SEPs. Tessier *et al.* (1979) and Martin *et al.* (1987) list reagent specificity, sample preparation and storage, kinetics, readsorption, and varying element suitability as the major issues that must be addressed when using SEPs. Despite these considerations, the SEP analysis provides an increased understanding of metal solubility that is useful for all phases of site restoration (investigation, risk assessment, and remedial technology selection) and provides more critical data than the total and/or soluble metals analysis currently performed at most sites.

Step 1. Site Screening

Site screening for MNA is focused on determining if MNA should be examined further at a particular site. This screening can be answered rapidly if some combination of preliminary site data, prior experiences from other sites, laboratory measurements, and/or simple soil chemical process knowledge is used. In many cases standard site characterization data, collected during routine site assessment, may provide information that natural attenuation may be feasible. The behavior of many metals in soils tends to be contaminant specific and somewhat predictable for order of magnitude estimates. Order of magnitude estimates of metal partitioning (K_d's) can often be made for a specific contaminant given some knowledge of the soil solution chemistry (in particular pH). Nonetheless, the types and kinetics of these reactions will be site specific. The partitioning of metals to solid phases is controlled by the biogeochemical processes (i.e., concentration, pH, redox, etc.) discussed in the introduction. Special caution should be exercised to avoid extrapolating K_d estimates in varying biogeochemical environments.

Estimates of the extent to which formation of contaminant-bearing solids can limit the dissolved levels of the contaminant can also be estimated using geochemical modeling programs (ex. Geochemists Workbench, MINTEQ, and AQUESOLV). At the same time, extensive compilations of SEP results from impacted sites (especially those with similar mineralogy) can be used to provide an estimate of the fraction of a contaminant that might be irreversibly sorbed.

One rapid means for assessing whether chemical and hydrologic conditions favor MNA to meet remediation goals is the MNAtoolbox, a web-based MNA screening tool maintained by DOE at **www.sandia.gov/eesector/gs/gc/na/mnahome.html** (Brady *et al.,* 1998). The MNAtoolbox provides tabulated K_d's, standard soil chemical data (e.g., solubilities, phase associations), and nonexchangeable sorption fractions taken from field-measured compilations for most metals. The MNAtoolbox uses these data as inputs for a modification of the EPA soil screening guideline calculations (USEPA, 1996) to roughly estimate the probability of NA being an important control on the fate of the particular metal at a given site. Also, likely attenuation pathways (e.g., sorption to iron hydroxides, ion exchange on clays, mineral precipitation, etc.) have been taken from the literature and are provided for each metal. Table 1 provides a sample of MNA pathways and contraindicators for natural attenuation of a number of metals.

The pH-dependent K_d's for most of the metals in MNAtoolbox were taken from EPA soil screening guidelines and are used as defaults in the estimate when site-specific measurements are not available. Default nonexchangeable fractions have been compiled from field studies found in the technical literature. Obviously, site-

TABLE 1
Natural Attenuation Pathways and Contraindicators for Various Inorganic Contaminants (Modified after Brady *et al.*, 1998)

Chemical	Natural Attenuation Pathways	Contraindicators and pathways
Pb	Sorption to iron hydroxides, organic matter, noncrystalline aluminosilicates, carbonate minerals; formation of sparingly soluble carbonates, sulfides, sulfates, phosphates.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates (e.g., EDTA) may decrease sorption. Low E_H dissolves iron hydroxides but favors sulfide formation.
Cr(III)	Sorption to Fe/Al/Mn hydroxides, organic matter, noncrystalline aluminosilicates; formation of sparingly soluble hydroxides	Low pH destabilizes hydroxides. Commingled organic acids and chelates (e.g., EDTA) may decrease sorption. Low E_H dissolves iron hydroxides. Sorption to Mn-oxides and oxidation to Cr(VI) at low pH.
Cr(VI) as CrO_4^{2-}	Reduction, sorption to Fe/Mn/Al hydroxides, noncrystalline aluminosilicates; formation of $BaCrO_4$	Low pH destabilizes iron hydroxides. Low E_H dissolves iron hydroxides but favors reduction.
As(III or V)	Sorption to iron and aluminum hydroxides, noncrystalline aluminosilicates, Fe and Ca precipitates; formation of sulfides	Low pH destabilizes iron hydroxides. Low E_H dissolves iron hydroxides.
Zn	Sorption to Fe/Mn/Al hydroxides, noncrystalline aluminosilicates and carbonate minerals; formation of sulfides; ion exchange.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E_H dissolves iron hydroxides but favors formation of sulfides.
Cu	Sorption to Al/Fe/Mn oxides, noncrystalline aluminosilicates, organic matter and silicate clays; sparingly soluble carbonate, hydroxide, and sulfides.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E_H dissolves iron hydroxides but favors formation of sulfides.
Cd	Sorption to Fe/Mn/Al hydroxides and carbonate minerals; formation of sparingly soluble carbonates, phosphates, and sulfides.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E_H dissolves iron hydroxides, but favors formation of sulfides.
Ba	Formation of sparingly soluble sulfate and carbonate minerals; ion exchange.	Low E_H may destabilize sulfates.
Co	Sorption to Al/Mn/Fe hydroxides and organic matter, carbonate minerals.	Low pH destabilizes carbonates. Low E_H dissolves iron hydroxides. Stable complexes form with chelators.
Ni	Sorption to Fe/Mn/Al hydroxides and noncrystalline aluminosilicates; ion exchange; formation of sulfides.	Commingled organic acids and chelates may decrease sorption. Low E_H dissolves iron hydroxides but favors sulfide formation.
Hg	Formation of sparingly soluble sulfides; sorption to organic matter.	Is methylated by organisms

specific K_d's and nonexchangeable fractions are clearly preferable — even at the site-screening stage.

The phase diagrams in the MNAtoolbox were generated using the Geochemist's Workbench (Bethke, 1984), a standard speciation code that relies on the thermodynamic database from EQ3/6 (Wolery, 1983). The phase diagrams are presented as pH and either (1) total concentration (mol/L) or (2) redox potential (E_H) for those metals or radionuclides that are greatly influenced by E_H as a function of pH (e.g., Cr, Tc). The likely solid and aqueous species are indicated on the phase diagram as well as being listed separately. Much of the latter are taken from standard reference sources (McBride, 1994; Rai and Zachara, 1984).

The MNAtoolbox identifies the likely attenuation pathways for a given metal and estimates the potential for natural attenuation. The MNAtoolbox is not intended to define clean up levels for metals but rather as an 'expert system' to provide a first-pass assessment of whether MNA should be considered in depth and, if so, as a means for focusing subsequent characterization efforts.

Before proceeding to the details of second step of the MNA evaluation, existing site characterization data may be used as indirect evidence of natural attenuation. Total metal analysis is generally performed during the delineation phase of site characterization. Other metal analysis performed as part of this investigation may include toxicity characteristic leaching procedure (TCLP) analysis, deionized (DI) water leaches, and/or the Synthetic Precipitation and Leaching Procedure (SPLP). The TCLP generally is used to determine whether an excavated metal-bearing soil is defined as hazardous for disposal at a landfill and typically gives an overly conservative estimate of the soluble fraction (Dragun *et al.,* 1990). Unlike the TCLP analysis, the DI water leach is prone to underestimate metal immobilization by working purely on concentration gradients between the soil and DI water and is also susceptible to improperly estimating metal mobility due to pH changes. The SPLP analysis is used to estimate the fraction of metal that may be soluble under acid rain conditions. A pH 4.2 extracting solution of sulfuric and nitric acid is used to extract soluble metals from sites east of the Mississippi River, and a pH 5.0 solution is used to extract soluble metals from sites on the west side of the Mississippi River. When TCLP (or other soluble metals analyses) and total metals analyses are available, a high total to low-soluble ratio indicates metal immobilization and implies the influences of some attenuation processes.

Table 2 provides a summary of the attenuation mechanism(s) and scorecards for three example sites with different metal concentrations, followed by the management decision resulting from the preliminary screening. As shown in Table 2, the MNAtoolbox screening results were useful in identifying the likely attenuation mechanism for the contaminant of concern and identifying when the conditions would be conducive for natural attenuation or where immobilization processes were not likely to be sufficient to meet site restoration goals. Table 3 provides a comparison of total metal analysis to soluble metal analysis results from several sites. These comparisons are provided to demonstrate how the combination of soluble and total data can be used to ascertain if immobilization processes may be sufficient to investigate natural attenuation further. For these sites identified in Table 3, there are several orders of magnitude differences in soluble and total metal concentrations indicating significant attenuation for some metals. A comparison of total to soluble metal concentrations should only be performed to determine the extent of rNA process affecting the solubility of metals at a site.

TABLE 2
MNAtoolbox Screening Results and Decision Framework for Further MNA Investigation Using Three Impacted Sites (From Brady *et al.,* 2000)

Impacted Media	**Scorecard attenuation pathways**	**Scorecard result**	**Management Decision**
Cu/Cr/Zn-in soil with areas of low pH and reducing conditions	Sorption, reduction (Cr), ion exchange, and mineral formation	Low at low pH; high at neutral pH	MNA was evaluated in areas of neutral pH (6 to 8)
Hg-in surface soils with low organic matter	Sorption to organic matter, mineral formation	Moderate	MNA was not evaluated since attenuation is unlikely with site conditions.
Ni, Cu, Pb, and Zn in Sediments	Sorption, ion exchange, and mineral formation	High	MNA was evaluated indirect site data also provided evidence for metal immobilization.

TABLE 3

Comparison of Total and Soluble Metal Concentrations in Soil Samples (After Brady *et al.,* 2000)

Metal	Number of Samples	Range of Total Metal Concentrations (mg/kg)	Range of Soluble Metal Concentrations (mg/L)	Soluble Metals Analysis Method
Lead	45	29,000 - 300	450 - 0.046	TCLP
Copper	14	750 - 1	4.0 – ND	DI Water
Nickel	14	35 - ND	0.5 – ND	DI Water
Zinc	10	200 - 52	2.0 – ND	DI Water
Chromium	20	5920 - 7.8	1.343 - 0.096	SPLP
Lead	20	10.5 – 2.5	<0.005	SPLP
Barium	20	106 – 21.7	<0.005	SPLP
Lead	35	2500 - 130	0.092-ND	SPLP

Although such comparisons are useful in providing indirect evidence of natural attenuation, these techniques do not define the specific immobilization mechanism(s) and therefore provide only qualitative evidence for attenuation. For sites where the preliminary analysis indicates the potential for natural attenuation, site-specific characterization is required to more effectively estimate the behavior of trace elements at specific locations.

Step 2. Site-Specific Assessment of MNA

The design of remedial engineering approaches is a complicated process requiring the explicit consideration of a number of factors, including achievable extraction efficiencies (for *in situ* treatments), long-term performance of semipassive treatment approaches (such as landfill caps), environmentally acceptable end points for in situ approaches, remedial action objectives, applicable or relevant and appropriate requirements (ARARs), cost, regulatory acceptance, and long-term monitoring requirements. For sites where MNA is applicable, the potential for metals to be resolubilized and, for surficial soils, potential bioavailablity is of key importance. Various extractions will provide different answers at a particular site and, often, at various places within a site. Therefore, the intended application and likely results of the SEP must be determined to answer the relevant site management questions in regards to risk and fate and transport.

The following case studies provide examples of effective SEPs used for evaluating natural attenuation in addition to estimating risk and screening other remedial technologies. These case studies are provided to demonstrate the following uses of SEPs:

- Enhanced site characterization and metal fate and transport determination in support of natural attenuation
- Natural attenuation evaluation and bioavailability estimation
- Remedial technology screening (e.g., phytoremediation)

Site 1. Site Characterization and Natural Attenuation

A former Chlor Alkali facility impacted by Cu, Cr, and Zn was evaluated using SEP. The site contained two surface impoundments previously used to store on-site process water. Impoundment 1 was used for storage of ammoniacal copper solutions, alum sediments, copper sulfate solutions, as well as copper and chromium solutions. Sediment samples collected in the impoundments indicate elevated levels of Cr, Cu, and Zn (Brady *et al.,* 2000). This site was screened using the

MNA toolbox (First site in Table 2). Based on this screening, additional data were collected to further characterize metal immobilization mechanisms.

The SEP was used to characterize the immobilization of site metals, as described in Figure 1. The SEP method used to characterize the immobilization pathways of site metals was derived from Schultz *et al.,* 1996 (Figure 2).

Chromium and zinc accumulated in the sulfide and residual soil extractions. The presence of chromium in the sulfide extraction further demonstrates the complexity of using SEP analysis. Chromium is not likely to precipitate as a sulfide. Nonetheless, the harshness of the extraction indicates that chromium is very stable and has a limited potential for remobilization. The chromium found in the sulfide extraction is likely associated with chromium forming sparingly soluble complexes. Copper was distributed between the carbonate, organic, sulfide, and residual fractions. Metals that are irreversibly sorbed, precipitated, or coprecipitated in these phases are stable and very insoluble under current conditions. Metals were not detectable in the exchangeable fraction at this site, indicating a low potential for metals to solubilize. The low concentration of leachable metals and the relative stability of the binding forms modeled by the SEP indicate that this site may be suitable for natural attenuation. Further assessment identified similar areas where MNA is currently being implemented. Areas where metals were present in more soluble forms underwent active remediation.

Site 2. Bioavailability and Natural Attenuation

Sequential extractions were performed to assist in ecological assessment for wetland soils impacted by metals from a former manufacturing facility. Previous testing in the area consisted of total metals analysis and toxicity testing using a freshwater amphipod (*Hyallella azteca)* as an indicator organism. Percent survival was reduced but not significantly different from the control treatment; however, mean weight and mean length of the organism was significantly affected by exposure. Total metal analysis of the sample used for toxicity testing suggested Cr, Cu, Pb, and Ag could cause toxicity. Based on the total metal results, chromium and copper were implicated as the two most important metals contributing to toxicity.

During the early assessments, SEPs were performed to more quantitatively target the metal(s), resulting in the observed toxicity using the SEP method derived from Schultz *et al.,* 1996 (Figure 2). It is important to note that during the initial risk evaluation, Cr was assumed to be in the +6 state to remain conservative in estimating toxic effects. The SEP does not speciate between the +3 and +6 chromium forms. Nonetheless, the type(s) of Cr binding identified by the SEP can be used to qualitatively identify the likely chromium form, which in this case is likely +3 and would have a low toxicity.

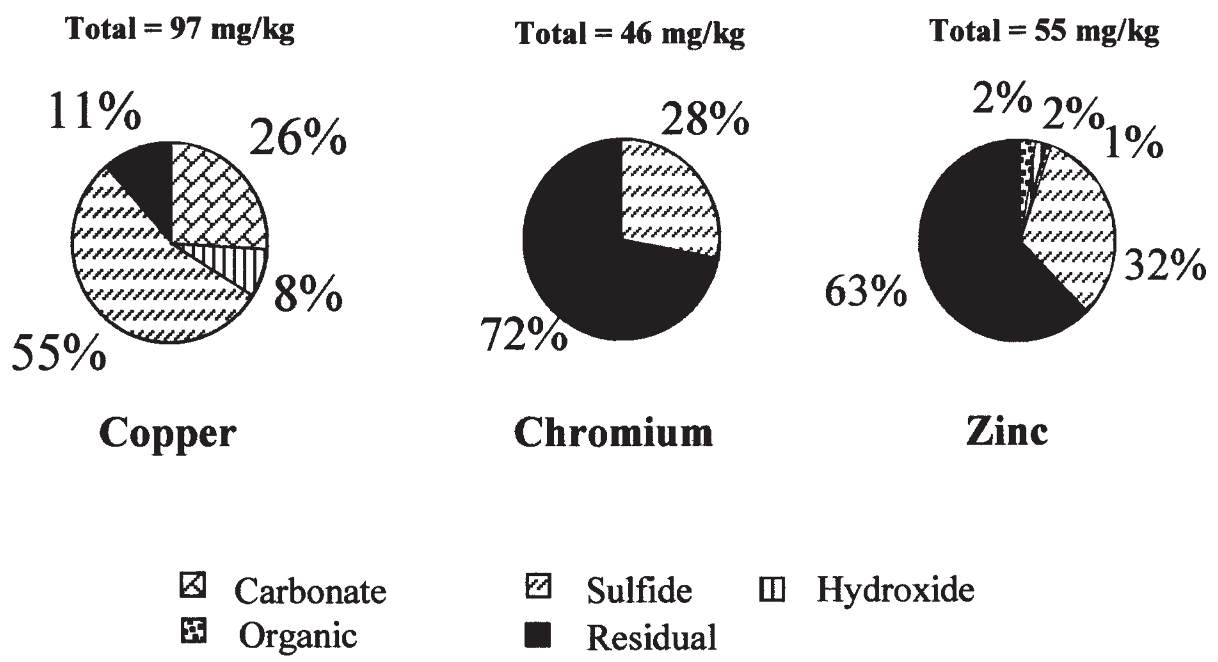

FIGURE 1

Sequential extraction results for copper, chromium, and zinc. (From Brady et al., 2000.)

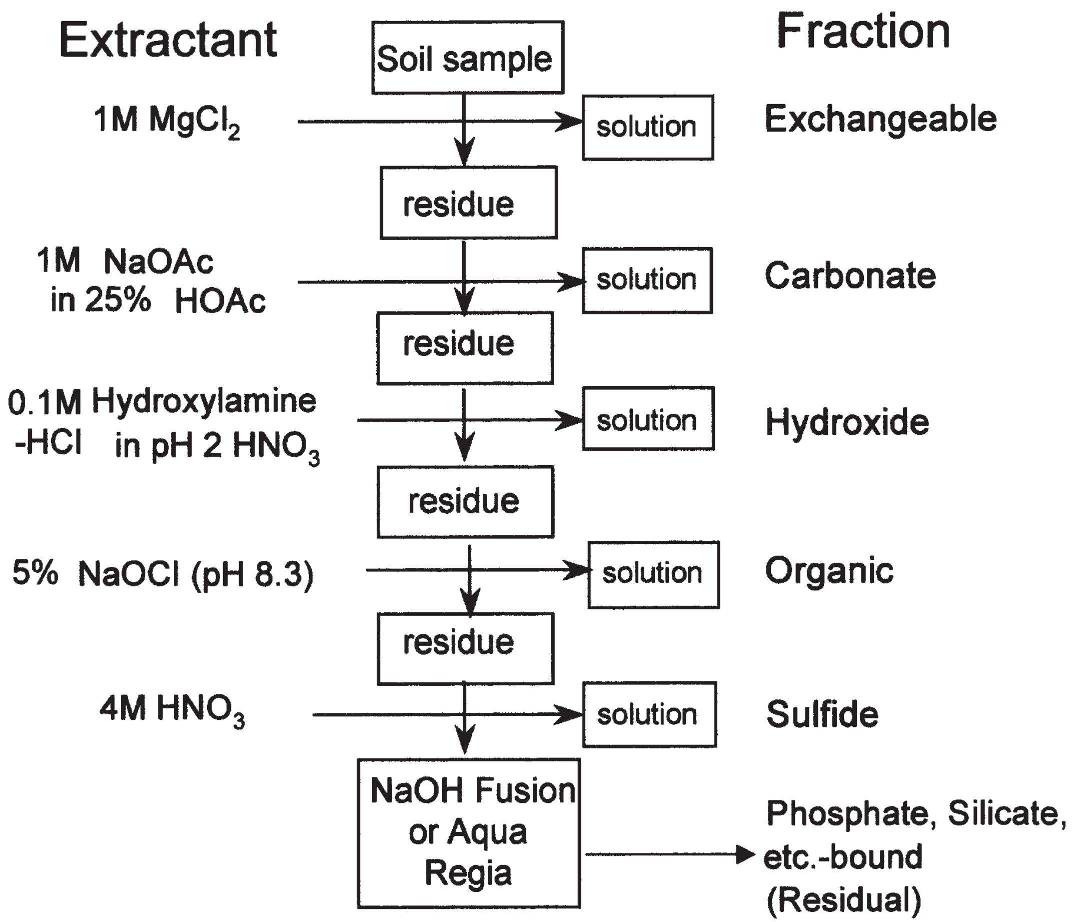

FIGURE 2

Sequential extraction procedure (Schultz et al., 1996).

Figure 3 provides the fractionation results determined by the SEP analysis. The fractions of the SEP were combined (Figure 4) based on their likely mobility and potential bioavailability using a method similar to Perin *et al.* (1997). The environmentaly mobile and potentially bioavailable fraction consists of the exchangeable, carbonate, and oxyhydroxide extractions. Metals are loosely bound in these fractions and were modeled to have a higher potential for toxicity or bioaccumulation. The oxyhydroxide extraction was included in this group because metals associated with the oxyhydroxide fraction have less stability in reduced environments. The second group was modeled as the immobile, but potentially macrobiologically reactive fraction and includes the organic extraction of the SEP. Although metals in the organic extraction were not viewed as environmentally mobile, the bioavailability of metals likely vary depending on the type(s) of organic matter complexation; this cannot be differentiated with the SEP. The remaining fraction consists of metals present in the sulfide and residual extractions. Metals in these fractions were modeled as immobile with a limited potential for bioaccumulation or toxic response. Consistent with published applications of SEP data, the immobile, unavailable, and potentially bioavailable fractions were modeled to have no ecological toxicity (Perin *et al.,* 1997).

Total analysis indicated that silver was present at a lower concentration than the other metals. SEP results modeled most of the detected Ag was immobile and not ecologically bioavailable. Most of the Cr was immobile and not ecologically bioavailable although nearly 3 mg/kg were present in the oxyhydroxide fraction. The majority (95%) of the Cu was immobile and not ecologically bioavailable. However, nearly 50 mg/kg was considered environmentally mobile and bioavailable. A large portion of lead (50 mg/kg) was environmentally mobile and bioavailable. The remaining Pb, approximately 30 mg/kg, was immobile and not ecologically bioavailable. Based on the total metal results, Cr and Cu would likely be implicated as the two most important toxic metals. The SEP results indicate that Cr probably had no effect on toxicity because Cr is partitioned into essentially inert fractions. The SEP results also demonstrated that Pb, although reported at a lower total concentration than Cu and Cr, may have a higher bioavailable concentration than the other metals. This case study demonstrated a novel application of SEP that greatly aided the risk evaluation process. This site screening was used to more effectively identify metals driving risk at the site and focus active remediation to areas and metals that were clearly causing toxic effects.

Site 3. Phytoremediation

In the third study, a modified SEP was performed on a serpentine soil, derived from the weathering of ultramafic rocks containing high levels of trace metals such as Nickel (Ni), Cr, and Co. This silt loam soil, collected from the foothills of the Sierra Nevada Mountains in California, had a pH of 6.8 and contained 2.28%

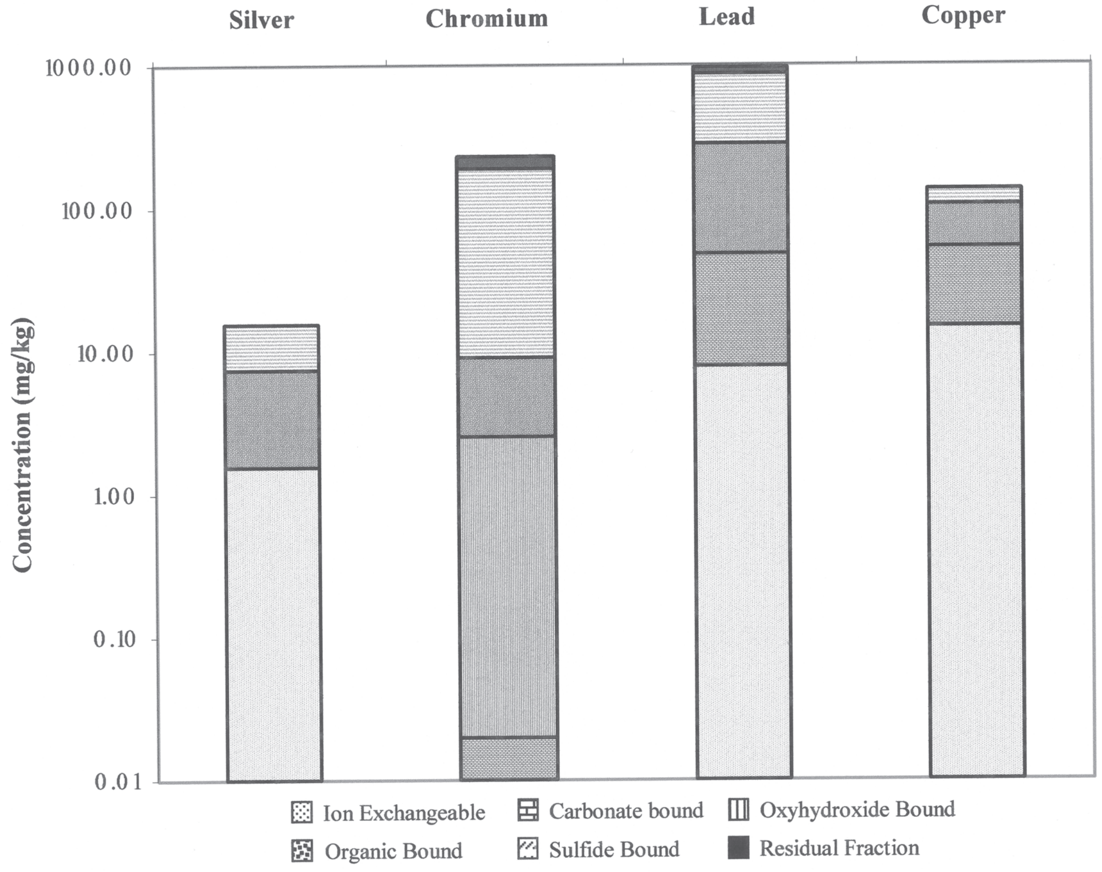

FIGURE 3

Sequential extraction results for silver, chromium, copper, and lead.

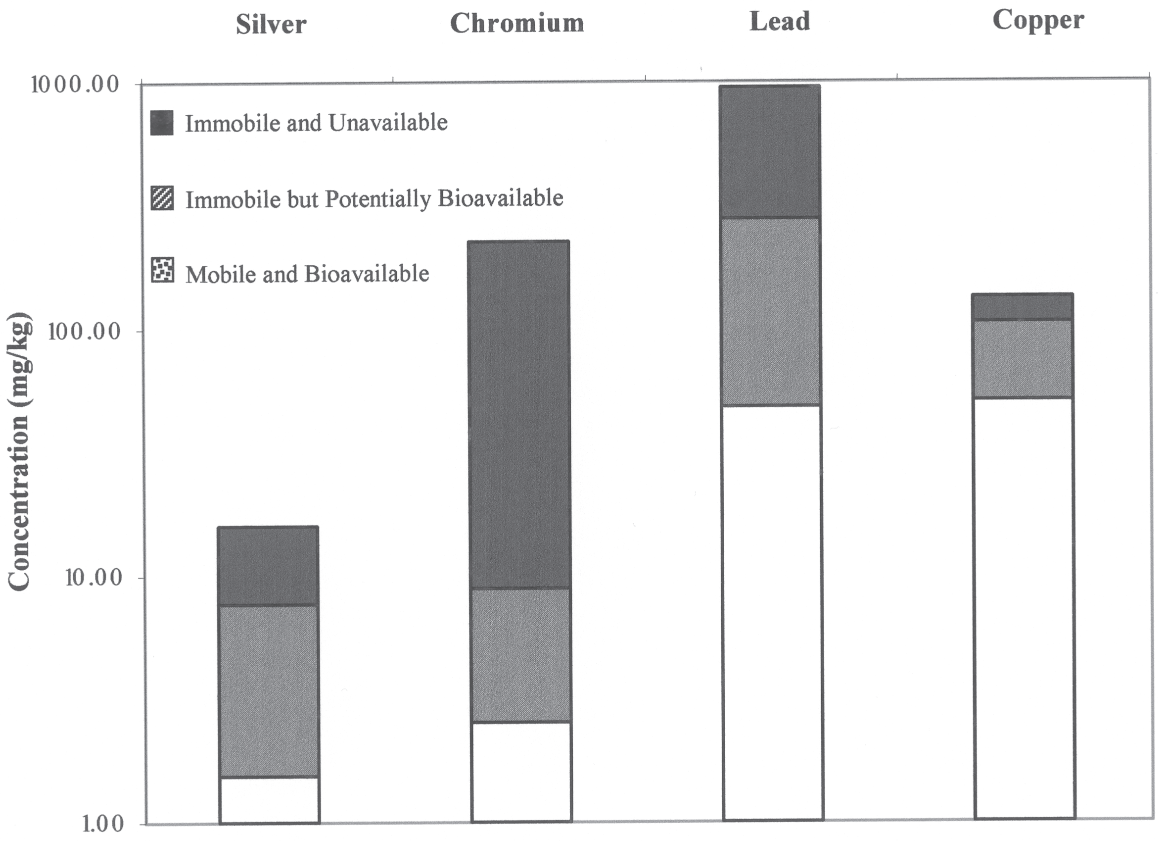

FIGURE 4

Bioavailability indices for silver, chromium, copper, and lead.

organic matter. Total metal concentrations of the soil were 150 mg/kg Co; 8120 mg/kg Cr; 6.2% Fe; 970 mg/kg Mn; 3000 mg/kg Ni; and 110 mg/kg Zn, while DTPA extract (an index of bioavailable metal levels) concentration values were 9 mg/kg Fe; 4 mg/kg Mn; 37 mg/kg Ni; and 1.3 mg/kg Zn. No Cr or Co was detected in the DTPA extracts. The relatively high level of bioavailable Ni was of concern due to its toxicity to many plant species, which was apparent from the few tolerant species that grew on the serpentine soil. One species that did thrive on this soil was *Streptanthus polygaloides*.

The SEP was performed to determine the fractions regulating nickel (Ni) bioavailability to the Ni hyperaccumulator *Streptanthus polygaloides* present on this soil (Cramer, 1997). *S. polygaloides* was evaluated as a potential tool in the phytoremediation (extraction or stabilization) and bio-mining of Ni contaminated sites (Nicks and Chambers, 1995). Phytoextraction uses metal hyperaccumulating plants that by definition can accumulate over 100 mg kg^{-1} Cd, and 1000 mg kg^{-1} Co, Cu, Cr, Pb, Ni, and 1% Mn and Zn per dry weight of plant shoot, thus concentrating metals into a form that facilitates disposal (Baker and Brooks, 1989). This technology maintains the biological and physical integrity of the soil and allows recovery of metals that have economic value (bio-mining) (Baker *et al.,* 1994; Cunningham *et al.,* 1995a, 1995b). A description of the SEP method used, obtained from Amacher (1999), is provided in Figure 5. This SEP targets different fractions than the SEP described previously from Schultz *et al.,* 1998. As stated previously, the SEP should be designed based on the metal of concern and application during the remediation, investigation, or risk process. The SEP can be easily modified to take into account specific sinks for specific metals, which was the intent during this study.

The harshness of the extractants increases with each step, with steps 1 to 5 addressing adsorbed Ni, whereas step 6 extracts Ni that is incorporated into either mineral or organic matrices, which was modeled as unavailable. Of the total Ni content of the serpentine soil, about two-thirds was unavailable and most likely incorporated into insoluble solid phases (Figure 6). Nickel adsorbed onto Fe and Mn oxides represents the greatest portion of the adsorbed Ni. About 5% of the Ni was associated with the carbonate fraction. However, carbonate testing revealed the absence of carbonates in this soil, suggesting that the Ni measured in step 2 was probably weakly bound or exchangeable Ni. This demonstrates that caution must be exercised when interpreting SEP data, and that supplemental chemical characterization (i.e., carbonate equivalent, clay mineral analysis) may be required to aid in interpretation. From the SEP, we surmized that when solid phases containing Ni weathered, dissolved Ni was adsorded onto secondary metal oxide (predominately Fe oxide) surfaces that is the labile pool of Ni available to *S. polygaloides.* The labile pool provides enough bioavailable Ni to make hyperaccumulation possible though the rate of Ni release and subsequent attenuation may adversely affect the rate of hyperaccumulation. Thus, information gleaned from the SEP can assess if

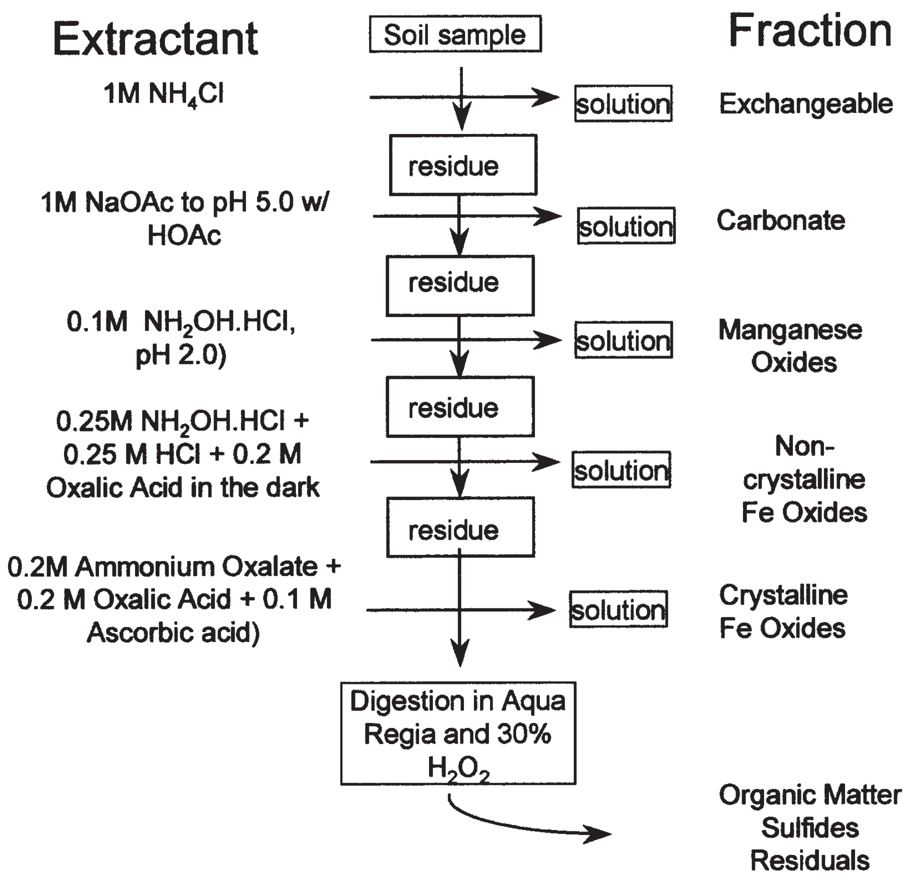

FIGURE 5

Sequential extraction procedure (Amacher, 1999).

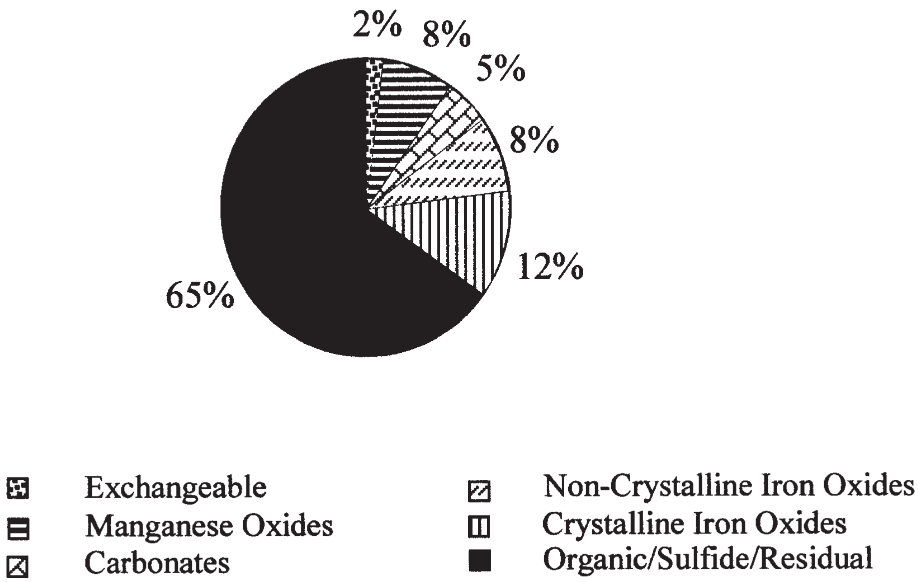

FIGURE 6

Sequential extraction results for nickel.

enough bioavailable metal is present in a soil to warrant phytoremediation of metal-contaminated sites.

The site screening in this example effectively determined the fraction of Ni that could be hyperaccumulated or is bioaccessible and also identified the limitations of phytoremediation. This example also provides important information on metal bioavailability to plants. The SEP results indicated that approximately 65% of the soil Ni was modeled as inaccessible to the plant. At a starting Ni concentration of 3000 mg/kg, at best phytoremediation would only effectively address 1000 mg/kg, leaving a substantial amount of Ni in the soil.

Residence Time Effects

The fate and transport of immobilized metals is greatly influenced by the residence time of the metal as a sorbed or precipitated complex. If a substantial fraction of total metal is to remain in the subsurface due to implementation of MNA, an estimate must be made of the potential for remobilization or long-term transport. The majority of transport codes model and predict the transport of metals in soils and sediments by assuming reversible sorption through a K_d approach. This approach obscured important issues associated with MNA, as it presumes that metal initially sorbed from contaminant-rich solutions will instantaneously desorb when, for example, fresh recharge causes metal levels in solution to drop.

Recent research has demonstrated that desorption of many trace element cations becomes more recalcitrant with time (McLaren *et al.,* 1986; Ainsworth *et al.,* 1994; Backes *et al.,* 1995; McLaren *et al*., 1998; Eick *et al.,* 1999). Several explanations have been proposed for these observed residence time effects, including solid-state diffusion within oxide particles (Bruemmer *et al.,* 1988), diffusion into micropores and intraparticle spaces (Backes *et al.,* 1995), change in the type of surface complex (McBride, 1994), incorporation into the mineral structure via recrystallization (Ainsworth *et al*.,1994), surface-catalyzed oxidation and incorporation into the crystal matrix (McKenzie, 1970; Backes *et al.,* 1995), and surface-catalyzed hydrolysis and precipitation (Backes *et al.,* 1995). Thus, irreversible sorption results in a net decrease in bioavailable metals in the subsurface. Soil solids have a substantial capacity to sorb trace metals, and these sorption processes can become more important with time. This is important from a remediation standpoint because most metal-contaminated sites have existed for long periods of time, and residence time effects will be more pronounced. The strong sequestration of metals resulting from these processes inhibits remedial technologies that attempt to aggressively remove metals from the soil.

SUMMARY

The approach outlined above might be usefully applied in the earliest stages of site investigation, even at those sites where monitored natural attenuation will only follow more active efforts. Specifically, it provides a rapid means for focusing efforts to develop a conceptual model describing the chemical state of the contaminant in the subsurface — a critical input for both active and passive remediation. The approach also lends itself to use in a tiered approach to implementation of monitored natural attenuation.

REFERENCES

Ainsworth, C.C., Pilon, J.L., Gassman, P.L., and Van Der Sluys,W.G. 1994. Cobalt, cadmium, and lead sorption to hydrous iron oxide: Residence time effects. *Soil Sci. Soc. Am. J*. **58,** 1615–1623.

Amacher, M.C. 1999. *Manual of Methods*. Open File Report 1999 Edition. USDA Forest Service Intermountain Research Station, Forestry Sciences Laboratory, Logan, Utah.

Backes, C.A., McLaren, R.G., Rate, A.W., and Swift, R.S. 1995. Kinetics of cadmium and cobalt desorption from iron and manganese dioxides. *Soil Sci. Soc. Am. J*. **59,** 778–785.

Baker, A.J.M. and Brooks, R.R. 1989. Terrestrial higher plants which hyperaccumulate metal elements — a review of their distribution, ecology, and phytochemistry. *Biorecovery* **1**, 81–126.

Baker, A.J.M., McGrath, S.P., Sidoli, C.M.D., and Reeves, R.D. 1994. The possibility of in-situ heavy metal decontamination of polluted soils using crops of metal-accumulating crops. *Resour. Cons. Recyc.* **11**, 41–49.

Barbafieri, M. 2000. The importance of Nickel Phytoavailable Chemical Species Characterization in Soil for Phytoremediation Applicability. *Int. J. Phytoremedi* **2(2),** 105–115.

Basta, N. and Gradwohl, R. 2000. Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure. *J. Soil Contamin.* **9(2)**, 149–164.

Bethke C. 1984. *The Geochemist's Workbench: Version 2.*

Bruemmer, G.W., Gerth, J., and Tiller, K.G. 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc, and cadmium by goethite. I. Adsorption and diffusion of metals. *J. Soil Sci.* **39**, 37–52.

Brady P. V., Spalding, B.P., Krupka, K.M., Waters, B.D., Zhang, P., Borns, D.J., and Brady, W.D. 1998. *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites.* Sandia National Laboratories Report SAND99-0464.

Brady, W.D., Graves, D., Klens, J., and Eick, M. 2000. Evaluation and implementation of natural attenuation at metals impacted sites. In: Wickramanayake, G.B., Gavaskar, A.R., and Kelley, M.E. (Eds.) *Natural Attenuation Considerations and Case Studies.* Battelle Press, Columbus, OH, 209–215.

Chopleka, A. and Adriano, D.C. 1997. Influence of zeolite, apatite, and Fe-oxide on Cd and Pb uptake by crops. *Sci. Total Environ.* **207,** 195–206.

Cramer, J.L. 1997. Phytoremediation of nickel contaminated soils by the hyperaccumulator *S. polygaloides.* M.S. Thesis. Utah State University.

Cunningham, S.D., Berti, W.R., and Huang, J.A. 1995a. Phytoremediation of contaminated soils. *Biotechnology* **13(9),** 393–397.

Cunningham, S.D., Berti,W.R., and Huang, J.A. 1995b. Remediation of contaminated soils and sludges by green plants. In: Hinchee, R.E. Means, J.L., and Burris, D.L. (Eds.). *Bioremed. Inorgan.* Battelle Press, Columbus, OH, 33–53.

Davis, A., Ruby, M.V., and Bergstrom, P.D.,1994. Factors controlling lead bioavailability in the Butte mining district, Montana, USA. *Environ. Geochem. Health,* **(3/4),** 147–157.

Dragun, J., Barkach, J., and Mason, S.A. 1990. Misapplication of the EP-TOX, TCLP, and CAM-WET tests to derive data on migration potential of metals in soil tests to derive data on migration potential of metals in soil systems. In: Kostecki, P.T. and Calabrese, E.J. (Eds.). *Petroleum-Contaminated Soils.* Lewis Publishers, Chelsea, MI. pp. 368.

Eick, M.J., Peak, J.D., Brady, P.V., and Pesek, J.D. 1999. Kinetics of lead adsorption/desorption on goethite: residence time effects. *Soil Sci.* **164**, 28–39.

Grasso, G., Butkus, M.A., O'Sullivan, D., and Nikolaidis, N. 1997. Soil washing design methodology for a lead-contaminated sandy soil. *Water Res.* **31(12),** 3045–3056.

Gruebel, K.A., Davies, J.A., and Leckie, J.O. 1988. The feasibility of using sequential extraction techniques for arsenic and selenium in soils and sediments. *Soil Sci. Soc. Am. J.* **52,** 390–397.

Grzebisz, W., Kocialkowski, W.Z., and Chudzinski, B. 1997. Copper geochemistry and availability in cultivated soils contaminated by a copper smelter. *J. Geochem. Explor.* **58,** 301–307.

Hammick, E.N., Nikolaidis, and Brookman, G. 1998. Enhanced mobilization of heavy metals using sequential extraction. In: Kostecki, P.T., Calabrese, E.J., and Bonazountas, M. (Eds.). *Contaminated Soils.* ASP Press, New York.

Hickey, M.G. and Kittrick, J.A. 1984. Chemical partitioning of cadmium, copper, nickel, and zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.* **13**, 372–376.

Keller, C. and Vedy, J.C. 1994. Distribution of copper and cadmium fractions in two forest soils. *J. Environ. Qual.* **23**, 987–999.

Kuo, S., Heilman, P.E., and Baker, A.S. 1983. Distribution and forms of copper, zinc, cadmium, iron, and manganese in soils near a copper smelter. *Soil Sci*. **135,** 101–109.

Martin, J.M., Nirel, P., and Thomas, A.J. 1987. Sequential extraction techniques: promises and problems. *Marine Chem*. **22**, 313–341.

McBride, M. 1994. *Environmental Chemistry of Soils*, Oxford University Press, New York, 406 pp.

McLaren, R.G., Backes, C.A., Rate, A.W., and Swift, R.S. 1998. Cadium and cobalt desorption kinetics from soil clays: effect of sorption period. *Soil Sci. Soc. Am. J*. **62**, 332–337.

Nicks, L.J. and Chambers, M.F. 1995. Farming for metals. *Mining Environ. Methods* **3**, 15–18.

Perin G., Fabris, R., Manente, S., Wagener, A.R., Hamacher, C., and Scotto, S. 1997. A five-year study on the heavy metal pollution of Guanaro Bay sediments and evaluation of the metal bioavailability by means of geochemical speciation. *Wat. Res*. **31(12),** 3017–3028.

Peters, G.M., Mather, W.A., Barford, J.P., and Gomes, V.G. 1997. Selenium associations in estuarine sediments: redox effects. *Water Air Soil Pollut*. **99**, 275–282.

Rai D. and Zachara J. M. .1984. Chemical attenuation rates, coefficients, and constants in leachate migration. *Electric Power Res. Inst*. EA-3356.

Ramos L, Gonzales, M.J., and Hernandez, L.M. 1999. Sequential extraction of copper, lead, cadmium, and zinc in sediments from Ebro River (Spain): relationship with levels detected in earthworms. *Bull. Environ. Contam. Toxicol*. **62**, 301–308.

Ruby, M.W., Davis, A., Schoof, R., Eberle, S., and Sellstone, C.M. 1996. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environ. Sci. Technol*. **30(2),** 422–430.

Schultz, M.K., Burnett, W.C., Inn, K.G.W., Thomas, J.W.L., and Lin, Z. 1996. Conference Report by the NIST Speciation Workshop. *J. Res. Natl. Inst. Stand. Technol*. **101(5),** 707–715.

Schultz, M.K., Burnett, W.C., Inn, K.G.W., Smith, G., Biegalski, S.R., and Filliben, J. 1998. Identification of radionuclide partitioning in soils and sediments: determination of optimum conditions for the exchangeable fraction of the NIST standard sequential extraction protocol. *Appl. Radiat. Isot*. **49(9–11),** 1289–1293.

Shuman, L.M. 1991. Chemical forms of micronutrients in soils. In: Mortvedt, J.J. (Ed.). Micronutrients in agriculture. *Soil Sci. Soc. Am. Book Series #4*. Soil Sci. Soc. of America Inc., Madison, WI.

Song, K.H. and Breslin, V.T. 1998. Accumulation of contaminant metals in the amphipod Diporeia spp. in western Lake Ontario. *J. Great Lakes Res*. **24**, 949–961.

Sposito, G., LeVesque, C.S., LeClaire, J.P., and Senesi, N. 1984. Methodologies to predict the mobility and availability of hazardous metals in sludge-amended soils. California Water Resource Center, University of California, Davis, CA.

Tessier, A., Campbell, P.G.C., and Bisson, M. 1979. Sequential extraction procedures for the speciation of particulate trace metals. *Anal. Chem*. **51**, 844–851.

U.S. Environmental Protection Agency. 1996. *Soil Screening Guidance: Technical Background Document*, USEPA-OSWER, EPA/540/R95/128.

U.S. Environmental Protection Agency. 1997. *Use of Monitored Natural* Attenuation at Superfund, RCRA Corrective Action, and Underground Storage *Tank Sites*, Office of Solid Waste and Emergency Response.

Vangronsveld, J., Spemans, N., Clijsters, H., Adriansens, E., Carleer, R., and Van Poucke, L. 2000. Phico Chemical and Biological Evaluation of the Efficacy of In Situ Metals Inactivation in Contaminated Soils. *Proceedings of the International Conference on Heavy Metals in the Environment*, University of Michigan. August 2000.

Williams, T.M., Rawlins, B.G., Smith, B., and Breward, N. 1998. *In vitro* determination of arsenic bioavailability in contaminated soil and mineral beneficiation waste from Ron Phibun, southern Thailand: a basis for improved human risk assessment. *Environ. Geochem. Health* **20(4),** 169–177.

Wolery T.J. 1983. A computer program for geochemical aqueous speciation-solubility calculations: user's guide and documentation. *Lawence Livermore National Labratory Report* **UCRL-53414**.

Xenidis, A., Stouratti, C., and Paspaliaris, I. 1999. Stabilization of oxidic tailings and contaminated soils by calcium oxyphosphate addition: the case of Montevecchio (Sardinia, Italy). *J. Soil Contamin.* **8(6),** 681–697.