

Trace Element Chemistry in Residual-Treated Soil: Key Concepts and Metal Bioavailability

N. T. Basta,* J. A. Ryan, and R. L. Chaney

ABSTRACT

Trace element solubility and availability in land-applied residuals is governed by fundamental chemical reactions between metal constituents, soil, and residual components. Iron, aluminum, and manganese oxides; organic matter; and phosphates, carbonates, and sulfides are important sinks for trace elements in soil-residual systems. The pH of the soil-residual system is often the most important chemical property governing trace element sorption, precipitation, solubility, and availability. Trace element phytoavailability in residual-treated soils is often estimated using soil extraction methods. However, spectroscopic studies show that sequential extraction methods may not be accurate in perturbed soil-residual systems. Plant bioassay is the best method to measure the effect of residuals on phytoavailability. Key concepts used to describe phytoavailability are (i) the salt effect, (ii) the plateau effect, and (iii) the soil-plant barrier. Metal availability in soil from metal-salt addition is greater than availability in soil from addition of metal-containing residuals. Plant metal content displays plateaus at high residual loadings corresponding to the residual's metal concentration and sorption capacity. The soil-plant barrier limits transmission of many trace elements through the food chain, although Cd (an important human health concern) can bypass the soil-plant barrier. Results from many studies that support these key concepts provide a basis of our understanding of the relationship between trace element chemistry and phytoavailability in residual-treated soils. Research is needed to (i) determine mechanisms for trace element retention of soil-residual systems, (ii) determine the effect of residuals on ecological receptors and the ability of residuals to reduce ecotoxicity in metal-contaminated soil, and (iii) predict the long-term bioavailability of trace elements in soil-residual systems.

ELEMENTS PRESENT IN natural materials at concentrations of $<1000 \text{ mg kg}^{-1}$ have been defined as trace elements (Kabata-Pendias and Pendias, 1992). Most elements of the periodic table are trace elements. Although some trace elements are essential to life, many are toxic in high concentrations. Further, awareness is growing of the extent and severity of trace element contamination of soils and water resulting from the industrial and commercial use of metals. Contamination occurs from metal mine tailings; disposal of high metal wastes in improperly protected landfills; leaded gasoline and lead-

based paints (The Conservation Foundation, 1987; Pirbazari et al., 1989); land application of fertilizer, animal manures, biosolids, composts, pesticides, coal combustion residues; and atmospheric deposition (Adriano, 2001). These anthropogenic additions of trace elements to the soil environment can adversely affect human, crop, and wildlife health (Adriano, 2001). A great deal of research has focused on anthropogenic activities, including land application of trace elements associated with numerous residuals (e.g., biosolids, livestock manures, composts). Trace elements that occur in some residuals of environmental concern include As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, and others. This manuscript presents important concepts and issues regarding trace elements in residuals-treated soil but is not meant to provide a comprehensive review.

The objectives of this paper are to (i) present fundamental chemical reactions common to soils, residuals, and soils amended with residuals; (ii) highlight important research findings on solubility and availability of trace elements in residual-amended soils; and (iii) identify future research needed to answer important questions regarding environmental fate of trace elements.

FUNDAMENTAL CHEMICAL REACTIONS OF TRACE ELEMENTS WITH COMMON SOIL AND RESIDUAL COMPONENTS

Trace elements undergo a wide variety of chemical reactions in soil and soil-residual systems. Reviewing all fundamental chemical reactions of trace elements in soil or soil-residual systems is beyond the scope of this manuscript. Only fundamental reactions that greatly affect trace element availability in aerobic terrestrial systems are presented.

Trace Element Reaction with Iron and Manganese Oxides

Sorption is an important chemical process that regulates partitioning of trace elements between solution and solid phases in soils. Iron, aluminum, and manganese oxide soil minerals are important sinks for trace elements in soil (McBride, 1994; Sposito, 1986) and residual-amended soils (Essington and Mattigod, 1991; Hettiarachchi et al., 2003; Lake et al., 1984; Lombi et al., 2002; Scheckel and Ryan, 2004). Trace element sorption by the oxide surface is a highly pH-dependent process described by the following chemical reactions:

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Abbreviations: Eco-SSL, ecological soil screening levels; ERA, ecological risk assessment; NOM, natural organic matter; SOM, soil organic matter.

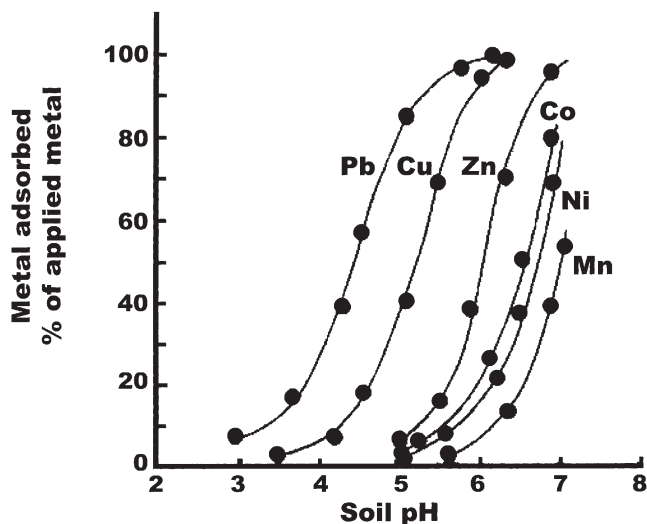


Fig. 1. Adsorption of heavy metal cations on goethite. Metal hydrolysis pK_a values for each metal, in parentheses, are Pb (7.7), Cu (8), Zn (9.0), Co (9.7), Ni (9.9), and Mn (10.6) (extracted from McKenzie, 1980).

cation adsorption: $\text{Fe-OH} + M^+ = \text{Fe-OM} + \text{H}^+$

oxyanion adsorption: $\text{Fe-OH} + \text{H}_2\text{L} = \text{FeH}^{(i-i)}\text{L}^{(1-i)} + (i-1)\text{H}^+ + \text{H}_2\text{O}$

where Fe-OH is an iron oxide surface, M is a trace element cation, and L is an oxyanion ligand. Cationic trace element adsorption by oxide surfaces increases to almost 100% with increasing pH (Fig. 1). The pH region where metal adsorption increases is known as the adsorption edge (Kinniburgh and Jackson, 1981; Sparks, 2003). The adsorption edge is inversely related to the pK_a of the metal ion hydrolysis reaction but also varies with the soil or residual mineral sorbent. Oxyanion adsorption is also pH dependent and is related to the pK_a of the anion's conjugate acid (Fig. 2) (Karmarkar and Tabatabai, 1993). Differences in adsorption and desorption isotherms typically show significant hysteresis and evidence that this process is not simply a competitive ion-exchange reaction between metal ions and protons or hydroxyls. Some adsorbed metal is strongly bonded and not readily desorbed from these oxide surfaces.

A recent review of trace element sorption by oxides (Brown and Parks, 2001) shows that Fe and Mn oxides

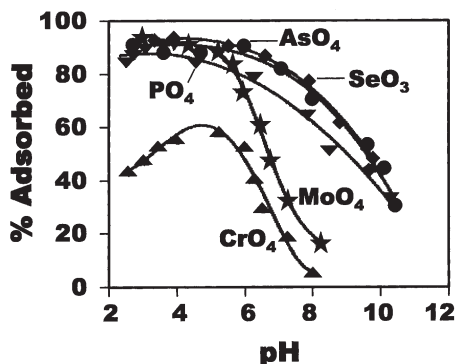


Fig. 2. Adsorption of oxyanions from goethite suspension (extracted from Okazaki et al., 1989).

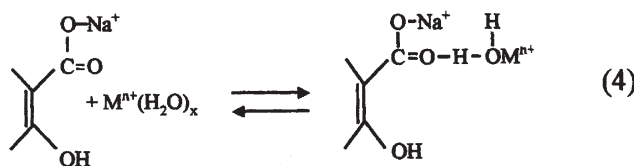
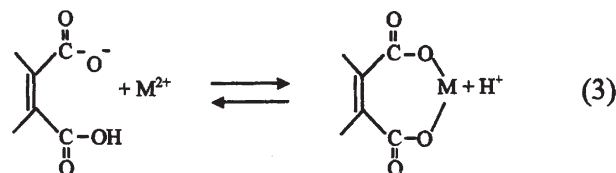
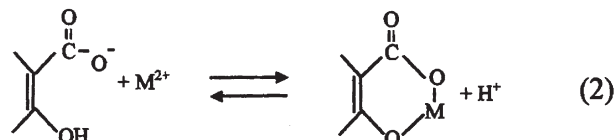
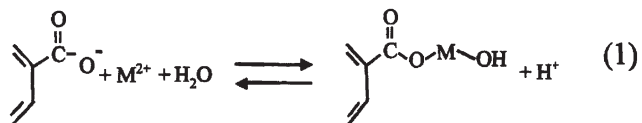


Fig. 3. Mechanisms of complexation of heavy metal cations with natural organic matter (NOM) (extracted from Senesi, 1992).

have a much greater adsorption capacity (e.g., high capacity scavengers) compared with Al oxides and other clay minerals. Molecular-scale X-ray spectroscopic studies show that the strong bonding of Pb, Cu, Co, Cr, Mn, Ni, and Zn to these oxide surfaces is due to formation of inner-sphere metal surface complexes and formation of metal hydroxide precipitate phases (Brown and Parks, 2001; Sparks, 2001). New solids found after metal ion reactions with soil materials, including metal silicates and mixed double hydroxides with Al, can substantially reduce metal solubility and availability (Scheckel and Sparks, 2001). Sorption by metal oxides is a major mechanism for removal of trace element cations (i.e., Pb, Cu, Zn, Cd, Cr, Cu, Pb, Hg, Ni, and Zn) and trace element oxyanions (i.e., AsO_4^{3-} , AsO_2^- , SeO_4^{2-} , SeO_3^- , MoO_4^{2-} , WO_4^{2-} , VO_4^{3-} , CrO_4^{2-}) from aqueous solution (e.g., soil solution) (Sparks, 2003; Stumm, 1992).

Trace Element Reaction with Organic Matter

Trace element cations also sorb to soil organic matter (SOM) and other forms of humified natural organic matter (NOM) (Fig. 3). Strong adsorption by NOM in residuals by formation of metal chelates reduces solubility of several metals in soil (Adriano, 2001). Molecular-scale Fourier transform infrared spectroscopic studies show that trace elements form bonds with specific functional groups of SOM, including COOH, phenolic, and thiol-SH functional groups. Soft acid metals (Cd^{2+} , Hg^{2+}) prefer soft base ligands (thiol); hard acid metals (Fe^{3+} , Mn^{2+}) prefer hard base ligands (OH^- , COO^-); borderline acids (Cu^{2+} , Zn^{2+} , Pb^{2+}) will form complexes with a weak or strong base (Essington, 2004; Pearson, 1968). The electronic properties of Cu and Pb result in

a very strong affinity for SOM and formation of strong inner-sphere metal surface complexes. Sorption of trace elements by SOM or NOM increases with pH because metals preferentially bind with ionized functional groups formed with increasing pH. Metal sorption by NOM is reduced less at lower pH than metal sorption on oxides.

Trace Element Precipitation with Specific Anions

Trace element cations form sparingly soluble precipitates with phosphate, sulfides, and other anions (Lindsay, 2001). Trace element precipitation is highly pH dependent and increases with pH for many trace element cations. Arsenate and other trace element oxyanions can form insoluble precipitates with multivalent cations including Fe, Al, and Ca. The trace element mineral (i.e., precipitate) formed may control the amount of trace elements in solution (i.e., availability and mobility).

Trace Element Reactions with Select Residuals

Residuals typically contain components (organic matter; Fe, Mn, Al oxides; and anions) that can adsorb or precipitate trace elements. Many types of residuals (biosolids, manure, municipal solid waste compost, coal combustion products, etc.) with a wide range of properties have been applied to agricultural land and have modified the adsorption properties of soils (Power and Dick, 2000). Some residuals have greater amounts of these sorbents than soil and can increase the sorption capacity of soils for trace elements. Added to soil in sufficient amounts, residual can dominate the metal-binding chemistry of the soil-residual mixture.

Biosolids often contain significant amounts of sorbents (e.g., oxides, organic matter, phosphates) or have favorable properties (e.g., pH) that reduce trace element solubility and phytoavailability. For example, biosolids often contain up to 50% NOM and 50% inorganic mineral forms (Fe, Mn, and Al oxides; silicates; phosphates; and carbonates) (McCalla et al., 1977; Sommers et al., 1976). The sorbent phase responsible for reduction in metal bioavailability in biosolids has been a matter of debate. Some suggest trace elements are sequestered in biosolids mainly by chelation with organic matter (Beckett et al., 1979; McBride, 1995), whereas others point out the importance of the inorganic surfaces in biosolids on sequestering trace elements (Chaney et al., 1999a, 1999b; Li et al., 2001; Hettiarachchi et al., 2003).

Trace elements in livestock and poultry manure by-products have recently been reviewed by Bolan et al. (2004). Trace elements including As, Co, Cu, Fe, Mn, Se, and Zn are added as feed supplements to prevent diseases and to improve weight gain and feed conversion (Bolan et al., 2004). In general, the largest enrichment of manure occurs for As, Cu, and Zn (Bolan et al., 2004). Organic matter is the main adsorptive phase to sequester cationic metals in manure by-products. Sequential extraction results suggest that most (>60%) Cu and Zn is organically complexed in dairy cattle and poultry manure (Bolan et al., 2003, 2004). However, more than 90% of As in poultry litter remains water soluble (Jackson and Bertsch, 2001). The arsenic species

in poultry litter were the original chemical in the feed (Roxarsone, *p*-arsanilic acid) and the metabolites (arsenate, arsenite, dimethyl arsenic acid, and monomethyl arsenic acid) (Jackson and Bertsch, 2001). These compounds are not sequestered by the manure solids. Residual addition to contaminated soil can reduce trace element solubility and bioavailability. Alternate in situ remediation techniques, involving the addition of inexpensive residuals (e.g., biosolids, Fe-oxide-containing industrial waste) to contaminated soil, can reduce the solubility and environmental risk of trace element contaminants. Organic residuals used to immobilize Pb, Cd, and Zn in contaminated soil include municipal biosolids (sewage biosolids), composts, and manures (Brown et al., 2003; Chaney et al., 1999a). Oxide-containing residuals can immobilize cationic (Pb, Cd, Zn) and anionic (As) forms of trace elements (Hettiarachchi and Pierzynski, 2002; Lombi et al., 2002; Mench et al., 1994). These residuals contain trace element sorbents (i.e., Fe, Al, or Mn oxides, NOM) or components (i.e., phosphate) that reduce trace element solubility, thereby “immobilizing” trace elements in contaminated soils (Basta et al., 2001; Hettiarachchi and Pierzynski, 2002). “Tailor-made” products that feature large amounts of Fe oxide, alkalinity, and NOM (alkaline biosolids) can reduce Zn phytotoxicity and help revegetate Zn smelter sites (Chaney et al., 1999a). Addition of high Fe biosolids compost (114 g kg⁻¹ reactive Fe) to urban home garden soils contaminated with Pb (2135 mg kg⁻¹ Pb) decreased Pb bioavailability (Brown et al., 2003). High Fe biosolids compost reduced in vivo Pb bioavailability, measured by using Sprague-Dawley weaning male rats (*Rattus* spp.), by 37%. Decreased bioavailability of Pb was attributed to increased amorphous Fe content and was not correlated to the total Pb content of the biosolids compost-soil system.

Li et al. (2001) found that Cd adsorption was increased by biosolids application in long-term field studies. For each study site, the increase was related to rate of biosolids application (Fig. 4). Removal of organic C reduced adsorption for both the control and biosolids-amended samples; however, the increased adsorption attributed to biosolids application was still present and the adsorption provided by the inorganic fraction of the biosolids-amended soil was greater than that of the intact control soil. Li et al. (2001) concluded that the inorganic fraction of the biosolids application provided a persistent, important adsorption surface. Removal of both the organic C and Fe and Mn fractions was required to remove the increased adsorption associated with biosolids application (Hettiarachchi et al., 2003), thus supporting the hypothesis that Fe and Mn fractions of biosolids are important sources of metal sequestration. Direct observation of the importance of the inorganic phases of biosolids in sorption, using advanced molecular spectroscopic techniques, showed that trace elements were sorbed to oxide phases of biosolids (Hettiarachchi et al., 2002; Scheckel and Ryan, 2004).

Trace element adsorption capacity varies with the amount of sorptive phase (i.e., reactive oxide content, organic matter content) and chemical property (i.e., pH)

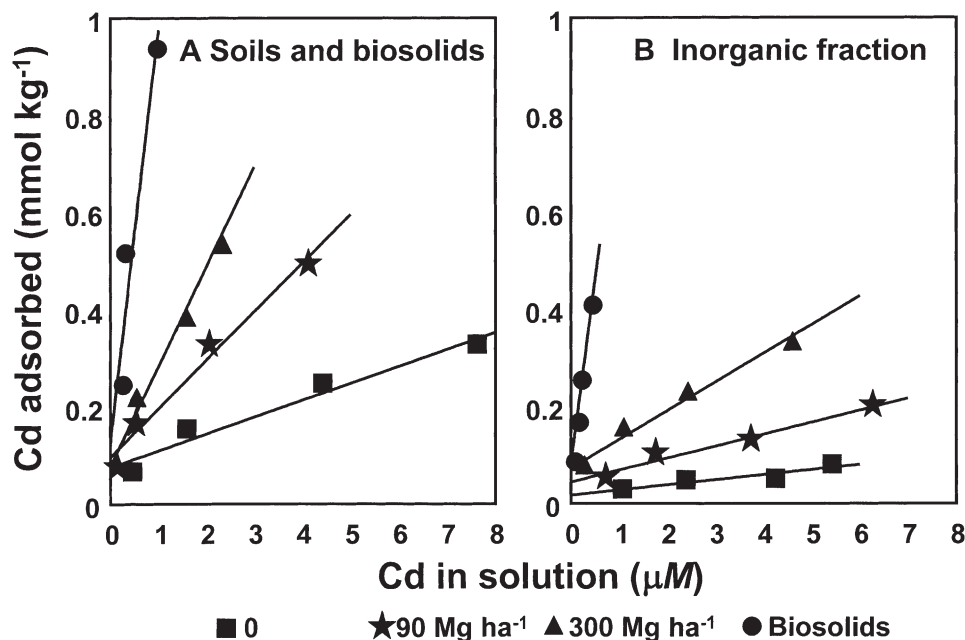


Fig. 4. Effect of biosolids and organic carbon removal on Cd adsorption isotherms on Miamian silt loam (fine, mixed, active, mesic Oxyaquic Hapludalfs) at pH 5.5 in 0.01 M $\text{Ca}(\text{NO}_3)_2$ solution for (A) soils treated with 0, 90, or 300 Mg ha^{-1} , or pure biosolids, and (B) inorganic fraction of soils treated with 0, 90, or 300 Mg ha^{-1} , or pure biosolids.

of the residual. For example, different processing of biosolids can produce material with different sorption capacities. Solubility of several cationic trace elements (e.g., Cd, Pb, Zn) in nonalkaline biosolids is greater than in alkaline biosolids (Sloan and Basta, 1995), and low metal solubility in high Fe oxide biosolids (Chaney et al., 1999a) showed the expected effect of soil pH and/or sorbent Fe oxide on solubility. However, solubility of select oxyanion trace elements (e.g., Mo) may be greater in alkaline biosolids than nonalkaline biosolids. Iron oxide residuals can adsorb or “immobilize” anionic trace elements, including As, and can dramatically reduce As solubility (Lombi et al., 2002). Brinton and O’Connor (2000) reported that addition of Largo, FL, biosolids (60 mg kg^{-1} Mo) to uncontaminated soil (0.1 mg kg^{-1} Mo) increased total Mo content but decreased Mo solubility. The decrease in Mo solubility was attributed to the much higher amorphous $\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$ in the Largo biosolids (11.2 g kg^{-1}) than the receiving Immokalee (sandy, siliceous, hyperthermic Arenic Alaquods) soil (0.12 g kg^{-1}).

Trace element availability is affected by the sorption capacity and properties (e.g., pH, salinity) of both the soil and the residual. Sandy soils with low oxide content and low NOM have low sorption capacities and will have greater metal availabilities than loamy or clayey soils with greater amounts of sorbents (i.e., reactive oxides, SOM), provided the soils have similar pH values. Similarly, residuals with low oxide content and low NOM have low metal sorption capacities and high metal availabilities as compared with residuals with high oxide and NOM. Soil-residual mixtures would have intermediate sorption properties between that of the soil and residual and, perhaps, intermediate availabilities if other properties (i.e., pH) were similar. As the loading rate of the

residual increases, the soil-residual mixture would assume the sorption properties of the residual.

TRACE ELEMENT PHYTOAVAILABILITY IN RESIDUAL-TREATED SOILS

Trace Element Phytoavailability Estimated by Soil Extraction Methods

Availability of trace elements in soils has been measured using single extractions of soil or residual-treated soils. Chemical extractants cannot extract plant nutrients in the same manner as a living plant. However, good correlation between soil extractants and plant uptake has allowed use of the extractant to make reasonable predictions of plant-available nutrients in soil and fertilizer recommendations (Amacher, 1996). One of the requirements of a good soil extractant (one where plant response is correlated with nutrient extracted by the soil test) is that the soil test measures “some or all of the (phyto)available pool” (Bray, 1948). Soil extraction methods correlated with plant uptake of trace elements include those based on solutions containing chelates, such as diethylenetriaminepentaacetic acid (DTPA), or neutral salt solutions (CaCl_2). The extensive use of such methods to estimate trace element availability in residual-treated soils has been reviewed by McLaughlin (2002) and Pierzynski (1998).

Caution is recommended when using soil extractants because they only measure metal availability (i.e., soil and residual factors). Plant physiology and rhizosphere biochemistry can alter the relationship between the extractant and plant tissue concentration. For example, rape (*Brassica napus* L.) had a concentration ratio of plant to soil of 1.7 for Cd, about 10 times greater than

corn (*Zea mays* L.) (CF = 0.18) grown on the same soil treated with biosolids (McBride, 2003).

Application of residuals to soil can affect phytoavailability by introducing trace elements into the soil and/or adsorptive phases causing redistribution of trace elements into different chemical pools or "chemical species" that vary in phytoavailability (Alloway and Jackson, 1991). Chemical speciation methods involving sequential extraction are used to determine the amount of contaminant in specific but operationally defined chemical pools. These chemical pools range from water soluble to recalcitrant forms trapped in mineral lattices. Trace elements in soluble or weakly adsorbed pools are regarded as more available than trace elements in strongly adsorbed and occluded forms (Kennedy et al., 1997). Most chemical speciation methods are variants of Tessier et al. (1979). In Tessier et al. (1979), sequential extraction was used to divide trace elements into five operationally defined fractions: (i) exchangeable, (ii) bound to carbonates, (iii) bound to Fe and Mn oxides, (iv) bound to organic matter, and (v) residual. Currently used standardized extraction methods, such as the Community Bureau of Reference (BCR) sequential extraction method of the Standard Methods Testing Programme of the European Commission (Rauret et al., 1999), fractionate trace elements in soils and residual-treated soils into four operationally defined pools: (i) easily desorbed or dissolved, (ii) bound to Mn and Fe oxides, (iii) bound to organic matter, and (iv) residual. A major limitation of sequential extraction methods is that trace element fractionation into chemical pools is "operationally defined" and extraction is not perfectly selective. For example, ZnS is extracted by the acidic $\text{NH}_2\text{OH}(\text{HCl})$ used to determine trace elements associated with Fe and Mn oxides, but ZnS is not sorbed to Fe or Mn oxide. Zinc in the operationally defined Fe oxide fraction may not be in the Fe oxide fraction. Acidic $\text{NH}_2\text{OH}(\text{HCl})$ will desorb Zn and other metals from numerous soil solid phases, including organic matter. Metal desorbed or dissolved during extraction may be reabsorbed by another solid phase. Although these and other operational problems result in error assigning metal to specific solid phases, sequential extractions can be useful in determining potential bioavailability of metal contaminants. Nirel and Morel (1990) discussed some limitations of these procedures. Despite the limitations of sequential extraction methods, Ahnstrom and Parker (1999) reported that reagent specificity and selectivity were good, suggesting the dissolution of major components at targeted phases, for a five-step sequential extraction method applied to soil. They found redistribution was minimal ($\leq 3\%$), but reached 12% for the organic matter fraction of biosolids-amended soil.

Basta and Gradwohl (2000) described a four-step sequential extraction derived from Tessier et al. (1979). The strength of the extracting solutions increased from 0.5 M $\text{Ca}(\text{NO}_3)_2$ solution (Step 1) to hot, 4 M HNO_3 (Step 4). Metals measured in various fractions corresponded to extractability and relative potential bioavailability in soils, not the exact metal geochemical association (i.e., Fe oxide) in soil or residual-treated soil.

Scheckel et al. (2003) showed that the extracting solutions used in sequential extraction methods may create reaction artifacts that do not occur in situ (e.g., field state). An eloquent comparison of sequential extraction and X-ray adsorption spectroscopies showed that Pb pyromorphite was formed during the sequential extraction process. Thus, sequential extraction methods may not be suitable for Pb speciation in perturbed environmental systems (i.e., treated contaminated soils). Sequential extraction methods should be used in conjunction with plant bioassays to determine residual effects on phytoavailability.

Plant bioassay is the best method to measure the effect of land application on phytoavailability. Plant uptake studies have reported that metals added to soils as a constituent of biosolids are less phytoavailable than metal salt added to soil, and metal salt added to soils with biosolids are intermediate in phytoavailability (Bell et al., 1991; Brown et al., 1998; Cunningham et al., 1975a, 1975b, 1975c; Mahler et al., 1987). From the body of work on plant response in biosolids-amended soils, several important concepts have evolved. Three of these concepts are (i) the salt effect, (ii) the plateau effect, and (iii) the soil-plant barrier.

The Salt Effect

The salt effect occurs when trace element salts are added to soils (metal-spiking studies) to simulate the effect of addition of heavy-metal-containing residuals. Greater bioavailability of metal applied as salts than as biosolids has been demonstrated in greenhouse pot studies (Cunningham et al., 1975a, 1975b, 1975c; Korcak and Fanning, 1985; Logan and Chaney, 1983). Cunningham et al. (1975a, 1975b, 1975c) showed that metal toxicity and phytoavailability in metal-salt-spiked soil was greater than the same amount of metal in biosolids-treated soil and that metal salts spiked into biosolids before addition to the soil were intermediate. Others have reported similar findings (Bell et al., 1991; Korcak and Fanning, 1985). Similarly, in a field experiment, Giordano and Mays (1977) illustrated that plant tissue concentration from salts was greater than from equivalent metal application in biosolids or compost (Fig. 5). The salt effect has been demonstrated under field conditions in long-term, biosolids-amended soils as well (Brown et al., 1998). Brown et al. (1998) reported that the Cd content of lettuce (*Lactuca sativa* L.) was 30.4 mg kg^{-1} for Cd salt-treated soil, 9.78 mg kg^{-1} for Nu Earth-biosolids treated soil, and 0.50 mg kg^{-1} for heat-treated biosolids (high Fe biosolids).

Residuals may contain significant amounts of sorbents (e.g., oxides, NOM) or have favorable properties that reduce trace element solubility and phytoavailability. For example, biosolids often contain up to 50% NOM by weight and up to 50% by weight inorganic constituents (Al, Mn, and Fe oxides, silicates, and carbonates) that act as sorption materials.

The Plateau Effect

Corey et al. (1981, 1987) proposed that at high residual (e.g., biosolids) application to soil, the metal avail-

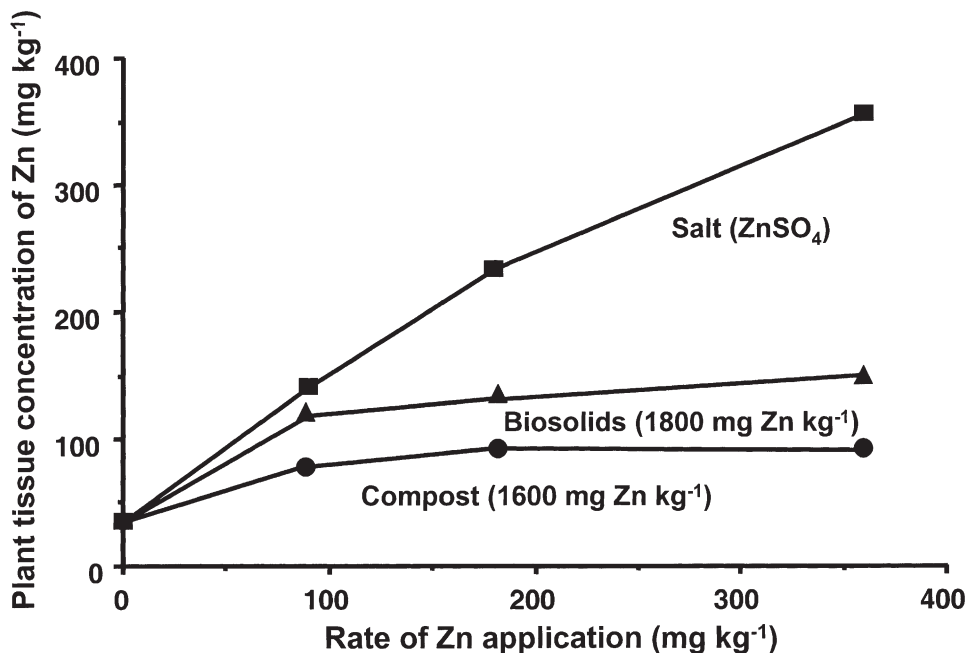


Fig. 5. Effect of source of Zn addition on plant tissue concentration during a 4-yr field experiment (modified from Giordano and Mays, 1977).

ability would be a function of the sorption capacity of the residual. Metal availability in residual-treated soils would show a “plateau” at high residual loadings corresponding to the trace element content and sorption capacity of the residual (Fig. 6). That is, as the amount of biosolids added to a soil increases, either from increased loading rate or continuous application of a rate over time, the soil would become the residual and thus whatever phytoavailability the residual supported would be the plateau. This phenomenon is clearly apparent in the results of Giordano and Mays (1977) in which the plant response from the biosolids and compost amendments exhibited a plateau, while that from equivalent salt additions was linear (Fig. 5). The concentration of trace elements and sorption capacity of the residual affects metal availability. Jing and Logan (1992) tested Corey’s hypothesis by conducting a greenhouse pot study where

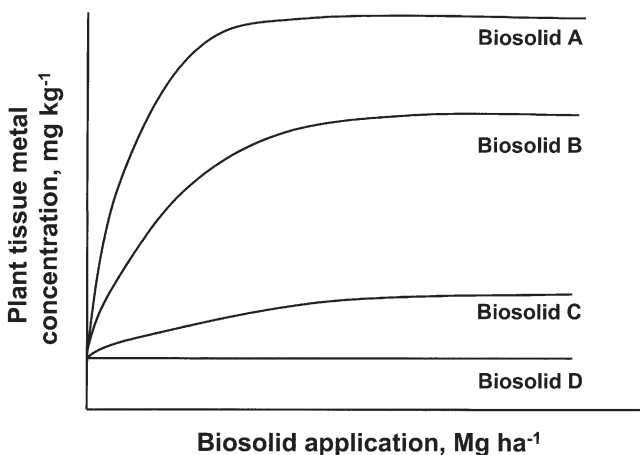


Fig. 6. The effect of heavy metal adsorption capacity on heavy metal phytoavailability. Heavy metal adsorption capacity follows the trend $D > C > B > A$ (modified from Corey et al., 1987).

equal amounts of Cd but unequal amounts of biosolids were added. One soil was treated with 17 different biosolids with Cd contents ranging from 8 to 226 mg kg⁻¹. Uptake of Cd by sudax [*Sorghum bicolor* (L.) Moench] was positively correlated with total Cd in biosolids ($r^2 = 0.33$) and available Cd in biosolids ($r^2 = 0.91$). These results show that trace element phytoavailability was a function of the Cd concentration in biosolids. Biosolids with higher Cd concentrations had higher plant uptake slopes. This is consistent with Freundlich-type sorption processes in soil where solubility and availability increase with loading of sorption sites. This work underscores the importance not only of the residual’s sorption capacity but also of the concentration of the metal and thus the relative saturation of this sorption capacity with trace elements and strongly supports the hypothesis of Corey et al. (1981, 1987). The plateau has been observed in field studies. Analysis of data from multiyear field plots in Maryland using orthogonal contrast ANOVA and covariance adjustment for pH among treatments found that the rate² term was significant in uptake of Cd, Zn, and Cu by lettuce, tobacco (*Nicotiana tabacum* L.), and soybean [*Glycine max* (L.) Merr.], respectively (Bell et al., 1988; Chaney et al., 1982; Heckman et al., 1987). This indicates that simple linear regression is not appropriate for interpretation of biosolids-applied Zn, Cd, and Cu. When plateau regression was tested on the data, the plateau models converged. The prediction of crop elements from added elements is remarkably different for linear regression vs. plateau regression (Fig. 7). Chang et al. (1987) showed a plateau for Cd in Swiss chard (*Beta vulgaris* L. var. *cicla* L.). Barbarick et al. (1995) showed a plateau response for Cu and Zn but not Ni or Mo for winter wheat (*Triticum aestivum* L.). Much greater concentrations of Zn and Cu were in biosolids-treated soils than Ni or Mo following the abun-

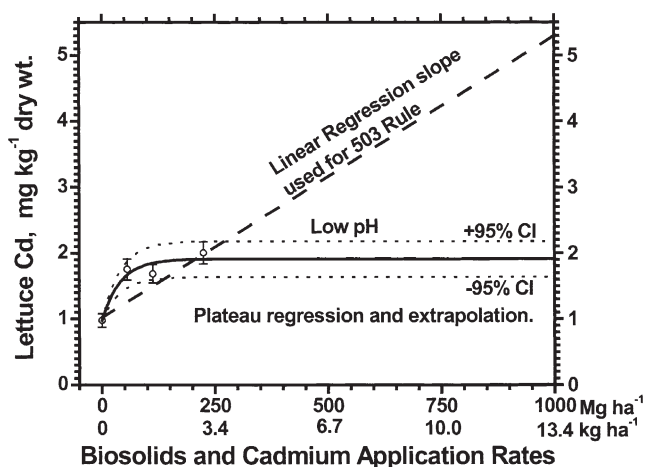


Fig. 7. Cadmium concentration in leaves of romaine lettuce grown on unlimed (pH 5.6) Christiana fine sandy loam (fine, kaolinitic, mesic Typic Paleudults) amended with 0, 56, 112, and 224 Mg ha^{-1} of heat-treated biosolids in 1976 (mean for six crop years) analyzed by linear regression standard error, or plateau regression 95% confidence intervals. Biosolids contained 13.4 mg Cd kg^{-1} , 1330 mg Zn kg^{-1} , and 83 g Fe kg^{-1} dry weight.

dance of these metals in biosolids of $\text{Zn, Cu} > \text{Ni, Mo}$. Smaller amounts of Ni and Mo added to soil may have been below the soil concentration required to observe a plateau.

A recent review (McBride, 2003) summarized biosolids studies where an approximate linear relationship, not a plateau, between metal phytoavailability and soil metal concentration for land-applied biosolids was found. The plateau requires large cumulative application of residuals if the metal concentrations are high relative to sorption capacity. The Soon et al. (1980) manuscript to which McBride (2003) refers added < 500 Mg of biosolids that had Zn concentrations of 730 to 10 000 mg kg^{-1} . In the Soon et al. (1980) study (three biosolids were applied during the 4 yr of application), the average concentration of Zn in mg kg^{-1} was 1400 for the Ca biosolids, 5500 for the Al biosolids, and 2900 for the Fe biosolids. Thus, the high metal concentrations in these biosolids relative to their adsorption would require high application rates before the plateau becomes apparent.

One possible explanation offered by McBride (2003) for the observed plateau is that the plateau may be due to plant physiology, not residual properties (i.e., metal content, sorption capacity, pH). A plateau-like response of plant Cd and Zn vs. soil solution Cd and Zn was obtained for radish (*Raphanus sativus* L.) grown on soils with various loading rates of biosolids (Hamon et al., 1999). The authors concluded that plant physiology and not metal bioavailability in soils may be responsible for the observed plateau. However, a study with multiple sources of Cd and Zn (illustrating that the plant tissue concentration observed at the plateau is not related to source) is required to test this hypothesis. Furthermore, numerous studies have reported higher plant tissue concentrations from metal salt than biosolids, suggesting that the plant is not responsible for the plateau.

The Soil-Plant Barrier

Transmission of trace elements through the food chain is affected by the soil-plant barrier described by Chaney and Giordano (1977); details for several elements are summarized in Logan and Chaney (1983). Processes of soils and plants may limit risk from trace elements in residuals applied to soil. The soil or plant barriers can limit transmission of many metals through the food chain either by soil chemical processes that limit solubility (e.g., soil barrier) or by plant senescence from phytotoxicity (e.g., plant barrier). The soil barrier limits transmission of trace elements, including Ti, Si, Zr, Au, Ag, V, and Hg, that are very insoluble and/or strongly adsorbed to soil or in roots. These elements are less likely to be bioaccumulated in plant shoots to levels that constitute risk to consumers than metals not affected by the soil barrier. The plant barrier limits transmission of trace elements, including Zn, Cu, Ni, Mn, Cr, As, and F, that result in plant phytotoxicity before they reach levels in the edible parts of plants often considered harmful to consumers. The soil-plant barrier limits transmission of many trace elements through the soil-crop-animal food chain, except Cd, Mo, Se, and possibly Co for ruminant livestock.

The degree of protection offered by the soil-plant barrier may depend on the plant species. For example, rape had a concentration ratio of plant to soil of 1.7 for Cd, about 10 times greater than corn ($\text{CF} = 0.18$) grown on the same soil treated with biosolids (McBride, 2003). Lettuce has higher Cd uptake slope than rape, but many plants are harmed by about 500 mg kg^{-1} Zn. Therefore, the degree of protection provided by the plant barrier for Cd will depend on the plant's tolerance of Zn. If the plant species has a Cd to Zn ratio of 1:100, the maximum Cd before toxicity would be similar for different crop species regardless of their Cd uptake slope. Differences in plant physiology and rhizosphere biochemistry between different plant species may result in large differences in trace element phytotoxicity. Hence, species-specific effects on metal phytotoxicity should be considered when using the soil-plant barrier concept.

It is beyond the scope of this manuscript to discuss the phytoavailability of all trace elements. However, further discussion on a cationic metal (Cd) and an anionic metal (Mo) in soil-residual systems that may accumulate to levels of concern in plant tissue (e.g., escape the soil-plant barrier) follows.

Cadmium Phytoavailability

Cadmium has lower affinity for metal-sorbing phases (e.g., oxides, NOM) and is readily translocated to shoots at high levels before phytotoxicity is observed. Cadmium has great potential to escape the "soil-plant" barrier, resulting in transmission through the food chain in levels that have the potential to present risk to consumers (Chaney and Ryan, 1994; Chaney et al., 1987, 1999a, 1999b). Cadmium has been the subject of concern and extensive research for more than 30 yr.

Factors affecting Cd phytoavailability have been recently reviewed (Adriano, 2001; Chaney et al., 1999b;

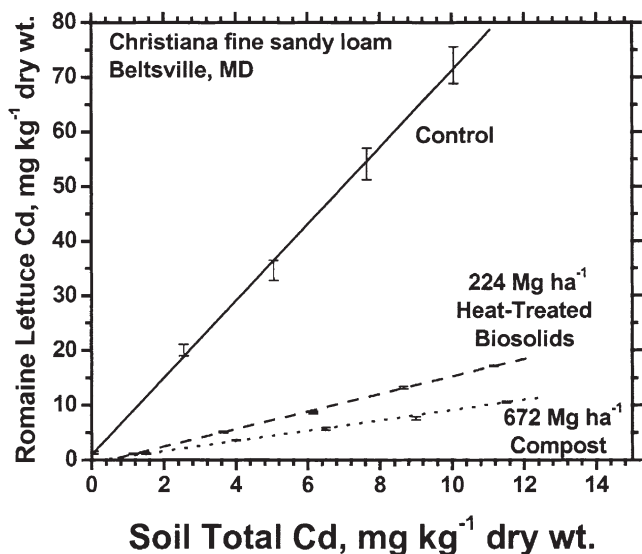


Fig. 8. Effect of historic biosolids applications on the phytoavailability of applied Cd salt to romaine lettuce; soils from long-term, biosolids-amended, and control soils from plots established in 1976 on Christina fine sandy loam (fine, kaolinitic, mesic Typic Paleudults). Soils with all treatments and Cd rates were adjusted to pH 6.5 in 0.01 M $\text{Ca}(\text{NO}_3)_2$ before growing 'Paris Island' romaine lettuce to maturity. The Cd concentration in heat-treated biosolids was 13.4 mg kg^{-1} , and the Cd concentration in compost was 7.2 mg kg^{-1} .

Kabata-Pendias, 2000; McLaughlin, 2002). Soil properties that affect Cd solubility and soil solution speciation affect Cd phytoavailability. Soil pH is often inversely related to Cd uptake by plants (Kabata-Pendias, 2000). Other factors that increase Cd phytoavailability include soil salinity from chloride salts (Smolders et al., 1998). Chloride additions to biosolids-treated soil increased Cd phytoavailability to wheat and Swiss chard (Weggler-Beaton et al., 2000; Weggler et al., 2004). The effect of land application of residuals on soil pH and soluble chloride can clearly affect Cd phytoavailability.

In addition to the Cd content, the Zn content of land-applied residuals will affect Cd phytoavailability (Chaney and Ryan, 1994). The usual co-contamination of Cd and Zn of geological origin (Adriano, 2001) in many residuals is very important because Zn competes with Cd uptake by most plants. For most biosolids, manures, and by-products, Zn is present at 100-fold the level of Cd or greater; co-contaminating Zn can inhibit plant Cd uptake, reduce plant yield with low plant Cd levels, and reduce the bioavailability of crop Cd to animals. If soil amendments contain Cd without Zn, they constitute risk through most crops; such unusual Cd-rich amendments should not be applied to cropland. Because of effective pretreatment (Stehouwer et al., 2000), many U.S. biosolids are low in Cd and Cd to Zn ratio and may not constitute Cd risk. For example, the 95th percentile Cd content of Pennsylvanian biosolids was only 4 mg kg^{-1} (Stehouwer et al., 2000). Further, high Cd adsorption by biosolids-amended soils, especially biosolids rich in Fe and Mn, can strongly reduce the phytoavailability of amended soil Cd. Recently completed pot tests of lettuce uptake of Cd from long-term, biosolids-amended, and control field plot soils showed much lower

Cd uptake slopes with increasing cumulative applied rates of Fe-rich biosolids (Kukier et al., 2003) (Fig. 8). Such strong metal sorption by biosolids-amended soils substantially reduces potential Cd uptake and allows metal remediation.

Molybdenum Phytoavailability

Molybdenum has a natural abundance of 3 mg kg^{-1} in soil and occurs as the molybdate oxyanion in aerobic environments. Residuals that may contain elevated (e.g., above background) Mo include biosolids, coal ash, and some steel wastes. Excessive land application of Mo that results in forage or feed enriched with Mo may increase the risk of molybdenosis, an induced Cu deficiency in ruminants. Some plants, particularly leguminous species, can accumulate large amounts of Mo (as much as 500 mg kg^{-1}) showing phytotoxicity symptoms (Kabata-Pendias, 2000). Using Mo-rich forage for ruminant feed increases the risk of molybdenosis.

Molybdenum solubility and phytoavailability increases with pH (Adriano, 2001). Molybdate is strongly specifically adsorbed by Fe oxides (Brown and Parks, 2001) and mainly associated with Fe oxides in soil (Kabata-Pendias, 2000). Soils and/or residuals with high Fe oxide will adsorb molybdate and decrease Mo phytoavailability. Conversely, soil-residual systems with high pH and/or low Fe oxide content will promote Mo phytoavailability. Britton and O'Connor (2003) determined the effects of biosolids on Mo sorption in two sandy Florida soils field-equilibrated with various biosolids applied up to 4 yr. Biosolids application had only a small effect on Mo sorption as a result of added Fe and Al oxides but Mo sorption was strongly related to soil pH and was maximized at soil pH values of <4 to 5. Britton and O'Connor (2003) concluded that although biosolids additions had only a small effect on Mo sorption as a result of added Fe and Al oxides, biosolids (and other amendments) can change the pH of the soil environment, which can dramatically affect Mo retention and release.

Alkaline-stabilized biosolids have been shown to increase Mo availability, resulting in increased tissue Mo and low tissue Cu to Mo ratios in red clover (*Trifolium pratense* L.) (McBride et al., 2000). Similarly, a study conducted using soybean showed high Mo accumulation ($>10 \text{ mg kg}^{-1}$) in soybean grain grown on biosolids-amended soils (O'Connor et al., 2001b) on 29 field soils with soil pH > 6.8 . Conversely, corn grown in a biosolids-amended soil showed little to no increase in stover Mo concentration on soils with pH 7.0 to 7.3, even at high soil Mo loading rates ($>18 \text{ kg ha}^{-1}$) (O'Connor et al., 2001c).

In examining potential risk to ruminant livestock that consumed crops grown on soils amended with high Mo alkaline biosolids, O'Connor et al. (2001a) evaluated the many factors that increase or decrease risk from biosolids Mo. In particular, they argued that it was inappropriate to model the case in which cattle were fed only red clover for the whole year because cattle are

fed a mixture of legume and grass forages and grains. In addition, if the worst-case alkaline condition occurs, Mo will leach from the root zone. Application at low fertilizer rates reduces the probability that high crop Mo would be attained and livestock producers know about and manage to prevent Cu deficiency. Interestingly, the bioavailability of Cu in forages is strongly increased by drying to make hay rather than feeding fresh forages. By balancing the many factors involved, O'Connor et al. (2001a) recommended that a revised limit of 40 mg Mo kg⁻¹ be set by the USEPA.

TRACE ELEMENT BIOAVAILABILITY AND ECOLOGICAL RISK IN RESIDUAL-TREATED SOIL

Healthy soil systems are essential for crop production and proper functioning of natural resource ecosystems. Land application of biosolids (Basta, 2000) and other residuals (Power and Dick, 2000) may be beneficial to crop production and silviculture and to improvement of soil quality. However, many municipal by-products, including biosolids, contain trace elements that may have the potential to degrade the soil environment and its productivity.

Ecological risk assessment is an evolving approach to protect and/or restore natural resource ecosystems. In the 1980s, the emergence of risk assessment as a regulatory paradigm and the first widespread use of potential ecological impacts to influence regulatory and policy decisions occurred in the United States. *Standards for the Use or Disposal of Sewage Sludge*, Part 503, was one of the regulatory products of this paradigm shift promulgated by USEPA to govern all aspects of biosolids disposal, including land application (USEPA, 1993a, 1993b). Part 503 is a risk-based regulation designed to protect the public health and the environment from reasonable worst-case scenarios. Fourteen potential exposure pathways for pollutants from land-applied biosolids were considered in the Part 503 rule. Of the 14 pathways, five of the receptor targets were ecological receptors (e.g., crops, soil organisms, predators of soil organisms, and livestock or wildlife).

To help improve the quality and consistency of USEPA's Ecological Risk Assessment (ERA), the USEPA published *Guidelines for Ecological Risk Assessment* (USEPA, 1998) and the *Ecological Risk Assessment Guidance for Superfund* (ERAGS) (USEPA, 1997). In these documents, ecological risk assessment is defined as "a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors" (USEPA, 1992). The primary audience for USEPA ERA documentation is risk assessors and managers conducting an ecological risk assessment at contaminated sites (i.e., Superfund sites). The USEPA ERA is an eight-step, tiered process: screening levels (Steps 1 and 2), problem formulation (Step 3), study design and data quality objectives (Step 4), verification field sampling design (Step 5), site investigation and data analysis (Step 6), risk

Table 1. Comparison of total heavy metal soil concentrations for land application of biosolids (USEPA Part 503) or screening of contaminated sites (ecological soil screening levels [Eco-SSL]).

Metal	Eco-SSL [†]		Cumulative pollutant levels, CFR Part 503 [‡]
	Plant	Soil invertebrate	
	mg kg ⁻¹		
Cu	pending	pending (61) [§]	670
Zn	pending (190) [§]	pending (120) [§]	1250
As	pending (41) [§]	pending	18
Pb	110	1700	134

[†] USEPA (2003b).

[‡] USEPA (1993a, 1993b).

[§] Values in parentheses are Eco-SSL values of earlier drafts still under consideration.

characterization (Step 7), and risk management (Step 8) (USEPA, 1997).

As part of USEPA ERA, the USEPA recently published *Guidance for Developing Ecological Soil Screening Levels* (Eco-SSL) (USEPA, 2003a). Eco-SSL should be used in Step 2 (screening level) of ERAGS. The Eco-SSL are concentrations of contaminants in soil that are protective of ecological receptors that commonly come in contact with soil or ingest biota that live in or on soil. The Eco-SSL are defined as soil concentrations of chemicals that, when not exceeded, will theoretically protect terrestrial ecosystems from unacceptable harmful effects. Eco-SSL are not cleanup guidelines but serve only as a conservative screening value for prioritizing elements that would warrant further consideration in a baseline ecological risk assessment. If the soil trace element concentration exceeds an Eco-SSL guideline, further investigation of the "contaminated" soil under the USEPA ERA framework is required. Further investigation could include making adjustments to ecological risk due to modifying factors from variation in soil pH, soil organic matter, and mineral oxide contents. One modifying factor is the adjustment because of metal bioavailability in soil. The limits indicated in Table 1 are for the worst case of strongly acidic, low organic matter, low clay content soils; higher levels would be expected to be nontoxic for soils with higher ability to adsorb the element in question.

The USEPA prepared a list of 24 contaminants to be initially addressed by Eco-SSL guidance from a review of contaminants of concern reported in recent Record of Decisions at Superfund National Priority sites. The list of 24 Eco-SSL contaminants contains 17 metals (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, V, and Zn). Recently, the USEPA listed Eco-SSL values for nine contaminants (Al, Sb, Ba, Be, Cd, Co, Fe, Pb, dieldrin) (USEPA, 2003b) frequently found in soil at hazardous waste sites. Eco-SSL values were derived for four ecological receptors of concern: mammals, birds, plants, and soil invertebrates. Eco-SSL values were not derived for reptiles, amphibians, soil microbes, or soil microbial processes (USEPA, 2003a). Thus, Eco-SSL values may not be protective for these ecological receptors. Two external peer reviews were conducted on the Eco-SSL document.

Based on Table 1, it appears that there is great variation in the values for metal levels in soils provided by

the USEPA for the protection of human and ecological receptors exposed to metals in soils. The USEPA regulations governing land-application biosolids cumulative pollutant levels exceed USEPA Eco-SSL values for several metals in Table 1. The USEPA Eco-SSL guidelines do not apply to soils treated with biosolids. The USEPA ERA guidelines (USEPA, 1998, 2003a, 2003b) are used to investigate ecological risk at contaminated sites (e.g., Superfund sites) and are not applicable to land treated with biosolids. If they were, soils that contain contaminant levels above the Eco-SSL levels but below the Part 503 cumulative pollutant level (Cu, Zn, Pb, As) would require further investigation to determine the level of ecological risk on biosolids-treated soil.

In part, the difference between Part 503 and Eco-SSL regulatory approaches is that the very conservative Eco-SSL values were derived from studies where soil chemistry conditions (e.g., low soil pH and low organic matter content) produced relatively high bioavailability of metals, including data from studies where metal salts were used to spike exposure media. Part 503 regulatory metal limits were derived from field experiments where the metal source was biosolids and thus includes bioavailability. It is well known that bioavailability of metal applied as salts in greenhouse pot studies are much greater than metals applied with biosolids (Cunningham et al., 1975a, 1975b, 1975c; Korcak and Fanning, 1985; Logan and Chaney, 1983).

Soil chemical processes that control trace element adsorption in soil and residual-treated soil, discussed earlier, will control solubility and availability of contaminants to soil organisms. Most ecosystem risk is associated with trace elements that are biologically available for absorption to the ecological receptors (e.g., plants, soil invertebrates, etc.). Several cationic trace elements, in water soluble and ion exchangeable forms, are available to plants (Basta and Gradwohl, 2000; McLaughlin, 2002) and soil invertebrates (Conder et al., 2001; Lanno, 2003; Peijnenburg, 2002). Sorption to oxide and organic matter in soil was found to greatly affect metal (Pb, As, Cd, Zn) bioavailability to lettuce (Dayton, 2003) and earthworms (*Eisenia fetida*) (Bradham, 2002). Residuals have been used to remediate contaminated soil and restore ecosystem function (Chaney et al., 1999a). The effect of residual treatments on soil contaminated by Zn, Cd, and Pb was evaluated by bioassay using the earthworm (Conder et al., 2001). Residual treatments included lime-stabilized municipal biosolids, rock phosphate, and anaerobically digested municipal biosolids. Biosolids containing lime were the only remediation treatment to successfully immobilize lethal levels of Zn in the smelter soil, although rock phosphate amendment did reduce toxicity slightly. Trace elements extracted from soil using 0.1 M Ca(NO₃)₂ were strongly correlated with ecotoxicity (Conder et al., 2001).

The effect of residual application on organism health and important biological processes (organic residue recycling, nitrogen fixation, respiration) is a concern. A recent review of toxicity of trace elements to microorganisms and microbial processes in agricultural soil concludes that microorganisms are “far more sensitive

to trace element stress than soil animals or plants growing in the same soils” (Giller et al., 1998). Additional research noted that rhizobia are inherently sensitive to soil acidity factors, that high-quality biosolids may stimulate growth of these species (Ibekwe et al., 1997a, 1997b), and that white clover was more sensitive to Cd and Zn than was the rhizobium for white clover (Ibekwe et al., 1998). Additional information on the toxicity of biosolids-borne metals to soil microbes is needed. McGrath (2002) provided an excellent review of bioavailability of trace elements to soil microbes. Further research is needed on the effect of metal addition to soils via land application of residuals.

LONG-TERM REACTIONS AND ENVIRONMENTAL FATE OF TRACE ELEMENTS IN RESIDUAL-AMENDED SOILS

Trace elements do not degrade in soil, and many are considered persistent toxins. The risk to human and ecosystem health from land application of persistent toxins in residuals depends on solubility and bioavailability of these contaminants in the residual-treated soil. Chemical reactions between the trace element and the soil and residual matrices determine their solubility and bioavailability. Chemical reactions are temporal—some reactions occur in seconds to days, while much slower reactions occur over a timescale of months to years (Sparks, 2003).

Most studies have reported the short-term (<5 yr) effects of residuals to soil. Few studies have reported the long-term effects of residuals on trace element additions to soil. Most of these studies have focused on the long-term fate of trace elements land-applied with biosolids. The trace element content of biosolids is greater than background soil, and USEPA regulations allow accumulation of several metals to 100 times their background concentration in soil. Although USEPA limits are risk-based, scientific concerns regarding long-term chemical reactions and risks posed by trace elements have been raised (McBride, 1995). Uncertainties exist in the effect of decomposition of soil organic matter complexes that bind metal and in the effect of slower, long-term reactions between metals adsorbed to inorganic oxide surfaces in soil on metal solubility and bioavailability.

The ability to predict long-term changes in metal bioavailability depends on the fate of the sequestered metal's solid phase. If the trace element is sequestered by biosolids NOM, slow organic mineralization reactions of biosolids NOM could release adsorbed metal into soil solution, thereby increasing metal bioavailability (McBride, 1995). Other research findings suggest that trace elements are not predominately sequestered by biosolids NOM (Brown et al., 1998; Chaney et al., 1999a; Mahler et al., 1987). Recent research findings showed the importance of the oxide phases of biosolids on the adsorption of trace elements (Hettiarachchi et al., 2002, 2003; Li et al., 2001). Trace elements sequestered to oxide surfaces will probably remain sequestered longer than

metal complexed by biosolids NOM. Long-term studies where the organic matter of the biosolids-amended soils has declined to a level equivalent to the control soils illustrate that the changes in chemistry and phytoavailability of metals caused by biosolids application are unaltered by decomposition of the added organic matter (Brown et al., 1998; Mahler et al., 1987). This result implies that an inorganic or a very recalcitrant organic phase is responsible for the biosolids-induced reductions in phytoavailability.

Zinc fertilizer additions to soil show maximum availability immediately after application to soil followed by decreases in Zn availability (Logan and Chaney, 1983). This phenomenon is referred to as “metal reversion.” Several studies have documented long-term changes (>10 yr) in metal availability after termination of biosolids application (Basta, 2000; Bell et al., 1991; Brown et al., 1998; Chang et al., 1987; McBride, 1995; McGrath and Cegarra, 1992; Sloan et al., 1997; Stuckenberg et al., 1993). In general, results from these studies showed that trace element availability remains constant, neither increasing nor decreasing after application of biosolids ceased, as long as the soil pH remains relatively constant. Phytotoxicity has been noted on old sites that received biosolids approximately 50 yr ago, but these toxicities may be due to high metal content of land-applied biosolids (Marks et al., 1980). Improvements in pretreatment processes over the last two decades have dramatically decreased the trace element content of biosolids. Research on the long-term fate of trace elements land-applied with residuals is still needed.

Changes in land management over time can affect metal availability. For example, changes in cropping system or crop rotation can affect soil properties (i.e., pH) that have a great influence on trace element availability. Cropping systems can affect soil properties that affect trace element availability. Long-term (>30 yr) crop rotations affected the metal adsorption maxima of two soils at different experimental stations in Iowa (Basta and Tabatabai, 1992a). Soil under continuous corn rotation had lower (approximately 15 to 20% lower) Cd, Cu, and Pb adsorption maxima than the same soil type under corn-soybean or corn-oat (*Avena sativa* L.)-alfalfa (*Medicago sativa* L.)-alfalfa crop rotations (Basta and Tabatabai, 1992a). In part, differences in metal adsorption were attributed to differences in pH of soil under different crop rotations (Basta and Tabatabai, 1992a, 1992b). Thus, changing land management (i.e., cropping rotation, residential development) can affect the long-term availability of trace elements in soil-residual systems.

THE EFFECT OF RESIDUALS ON AVAILABILITY—WHAT WE KNOW

- Solubility and availability of trace elements are directly related to sorption capacity of residuals and soil. Soil pH, Fe and Mn oxides, and NOM are very important factors controlling metal solubility in these systems. Many scientific studies have gener-

ated a large body of information on benefits and environmental impacts associated with land application of biosolids and other residuals (Basta, 2000; National Research Council, 1996; Power and Dick, 2000). Results from these studies have shown that trace element solubility and availability in land-applied residuals is governed by fundamental chemical reactions between metal constituents and soil and residual components. Sorption is an important chemical process that regulates partitioning of trace elements between solution and solid phases in soils. Iron, aluminum, and manganese oxide soil minerals are important sinks for trace elements in soil and residual-amended soils. Trace element cations sorb to soil organic matter (SOM) and other forms of humified NOM. Trace element cations form sparingly soluble phosphates, sulfides, and precipitates with other anions in soil-residual systems. Metal sorption and many metal precipitation processes are highly pH dependent. Sorption of metal cations increases with pH. The pH of the soil-residual system is often the most important chemical property governing sorption and precipitation of trace elements.

- Key concepts that describe phytoavailability of trace elements in residual-treated soil are (i) the soil-plant barrier, (ii) the plateau effect, and (iii) the salt effect. Application of residuals to soil affects phytoavailability by introducing trace elements into the soil and/or redistributing trace elements into different chemical pools that vary in phytoavailability (Alloway and Jackson, 1991). Soil extraction methods are available to access changes in trace element availability in soils treated with residuals. Application of metal-enriched residuals (i.e., biosolids, manure) increases trace element solubility and availability in soil. Increases in availability are a function of residual type and metal loading. Plant bioassays show that metal-enriched residuals (i.e., biosolids, manure) increase extractability and plant uptake. Transmission of trace elements through the food chain is limited by the soil-plant barrier (Chaney and Giordano, 1977). The barrier limits transmission of metal through the food chain either by soil chemical processes that limit solubility (e.g., soil barrier) or by plant senescence from phytotoxicity (e.g., plant barrier). Corey et al. (1987) hypothesized that metal bioavailability in residual-treated soils would show a “plateau” at high residual loadings. The plateau is influenced by the metal concentration of the residual and the trace element sorption capacity of the residual. The plateau effect hypothesis was tested and confirmed by Jing and Logan (1992). Metal bioavailability studies should be based on residual addition to soil and not based on spiking studies where trace element salts are added to soils. The “salt effect” in soils spiked with metal salts overestimates trace element bioavailability.
- Oxide mineral surfaces are important to determine the long-term environmental fate and bioavailabil-

ity of trace elements in residual-treated soils. Trace elements do not degrade in soil and many are considered persistent toxins. The risk to human and ecosystem health from land application of metals in residuals depends on solubility and availability of these contaminants in the residual-treated soil. Uncertainties remain regarding the effect of decomposition of organic matter complexes and the effect of long-term reactions of metals adsorbed to inorganic oxide surfaces on metal solubility and availability. Trace elements sequestered to oxide surfaces will probably remain sequestered longer than metal complexed by organic matter.

RESEARCH NEEDS TO ADVANCE OUR UNDERSTANDING

- Determine sorbent properties and relative trace element retention capacities of residuals and residual-treated soils for establishment of risk-based trace element loading limits. The risk associated with land application of trace elements is a function of their availability in the residual, which is dependent on trace element solubility and trace element retention capacity of the residual or soil-residual system. Thus, a fundamental understanding of these relationships is required to move past limits based on total metal content or cumulative metal loading. Trace element loading limits developed for biosolids probably will not be transferable to other residuals with very different chemical properties and behavior.
- Determine the effect of residuals on ecological receptors in soil ecosystems, including the ability of residuals to reduce or eliminate ecotoxicity in heavy-metal-contaminated soils. The effect of residual application on organism health and important biological processes (organic residue recycling, nitrogen fixation, respiration) is a growing concern. We know very little regarding the effect of residuals on ecological receptors in soil ecosystems or of the ability of residuals to reduce or eliminate ecotoxicity in heavy-metal-contaminated soils.
- Research the long-term environmental fate focused on predicting the long-term bioavailability of trace elements in residual-amended soils. The Council for Science and Technology (1980) reported that long-term availability of Cd and Zn in biosolids-treated soil was indeterminate. A great deal of progress has been made in advancing our understanding of the long-term fate of trace elements in residual-treated soils in the last 20+ years. However, uncertainty in the environmental fate of trace elements remains, and several important issues remain "indeterminate." Environmental chemistry has seen great advances in analytical instrumentation that allows molecular-based spectroscopic studies. Application of advanced spectroscopic methods has the potential to derive fundamental information on the molecular environment of the trace

elements in residual and residual-treated soils. Information is needed on the molecular level regarding trace element sequestration to answer many long-term environmental fate questions (Ryan et al., 2004).

- Research a wider array of residuals or conduct "residual-specific" research. Most research on land application of residuals has been on land application of biosolids. Land application of municipal, industrial, and agricultural wastes will continue to grow because of economic and societal benefits. Research on many residuals is limited or nonexistent and may prevent development of guidelines that allow land application of these materials. Research and guidelines used for biosolids will not be transferable to many residuals with very different chemical properties and behavior. In fact, fundamental properties of biosolids (e.g., lower metal content and chemical and physical properties) continue to evolve and will require study to modify existing guidelines.

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