BIOAVAILABILITY OF METALS

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INTRODUCTION

The fate of various metals, including chromium, nickel, copper, manganese, mercury, cadmium, and lead, and metalloids, including arsenic, antimony, and selenium, in the natural environment is of great concern (Adriano, 1986; 1992), particularly near former mine sites, dumps, tailing piles, and impoundments, but also in urban areas and industrial centers. Soil, sediment, water, and organic materials in these areas may contain higher than average abundances of these elements, in some cases due to past mining and (or) industrial activity, which may cause the formation of the more bioavailable forms of these elements. In order to put elemental abundances in perspective, data from lands and watersheds adjacent to these sites must be obtained and background values, often controlled by the bedrock geology and (or) water-rock interaction, must be defined.

In order to estimate effects and potential risks associated with elevated elemental concentrations that result from natural weathering of mineral deposits or from mining activities, the fraction of total elemental abundances in water, sediment, and soil that are bioavailable must be identified. Bioavailability is the proportion of total metals that are available for incorporation into biota (bioaccumulation). Total metal concentrations do not necessarily correspond with metal bioavailability. For example, sulfide minerals may be encapsulated in quartz or other chemically inert minerals, and despite high total concentrations of metals in sediment and soil containing these minerals, metals are not readily available for incorporation in the biota; associated environmental effects may be low (Davis and others, 1994). Consequently, overall environmental impact caused by mining these rocks may be much less than mining another type of mineral deposit that contains more reactive minerals in lower abundance.

In aquatic environments where chemically reducing conditions may prevail, metals from mining activities may be associated with sulfide minerals. These sulfide minerals are present either in the ore deposit or formed by bacterial reduction of the sulfate in oxidized tailings. Most metal sulfide minerals are quite immobile, as long as they remain in a chemically reducing environment, and they may have little impact on biota despite anomalous metal concentrations.

BIOAVAILABILITY

Metals of major interest in bioavailability studies, as listed by the U.S. Environmental Protection Agency (EPA), are Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Sb (McKinney and Rogers, 1992). Other metals that are presently of lesser interest to the EPA are Ag, Ba, Co, Mn, Mo, Na, Tl, V, and Zn. These metals were selected because of their potential for human exposure and increased health risk. Some highlights concerning the bioavailability of As, Cd, Cu, Hg, Mo, Pb, Se, and Zn in water and (or) sediment are discussed in the section below entitled "Specific metals of interest."

Metals can be dispersed in soil, water, and air. Geoscientists are mainly concerned with metals dispersed in soil and sediment, dissolved in ground and surface water, suspended as particles in surface water, and in pore fluid in sediment (fig. 1). In addition, metals can be dispersed into the atmosphere, by natural geochemical cycling and by other anthropogenic processes (such as smelting and burning leaded gasoline and coal) and by microbial activities; these metal fluxes must be considered in overall metal bioavailability studies. Bioaccumulation of metals by biota in surface water and by plants and animals in terrestrial environments can adversely affect humans. In surface and ground water, sediment and air, bioavailability is a complex function of many factors including total concentration and speciation (physical-chemical forms) of metals, mineralogy, pH, redox potential, temperature, total organic content (both particulate and dissolved fractions), and suspended particulate content, as well as volume of water, water velocity, and duration of water availability, particularly in arid and semi-arid environments. In addition, wind transport and removal from the atmosphere by rainfall (frequency is more important than amount) must be considered. Many of these factors vary seasonally and temporally, and most factors are interrelated. Consequently, changing one factor may affect several others. In addition, generally poorly understood biological factors seem to strongly influence bioaccumulation of metals and severely inhibit prediction of metal bioavailability (Luoma, 1989). Some of the major controls on the bioavailability of metals in surface water and soil and data concerning potentially hazardous metals are described below.

In order to understand bioavailability, plant materials and selective chemical leaches of soil must be analyzed and the results compared. Elemental suites for which analyses are performed and the type of selective leaches utilized must be tailored to bedrock and soil types, and to suspected anthropogenic inputs. Soil pH, organic matter,

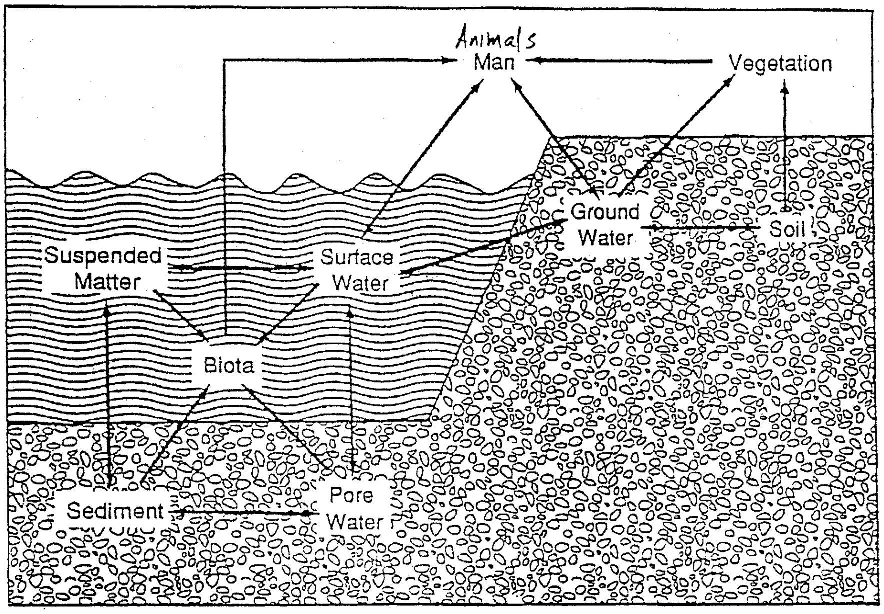

Figure 1. Interrelationships of man, metals, and the environment. Modified from Salomons and Forstner (1988).

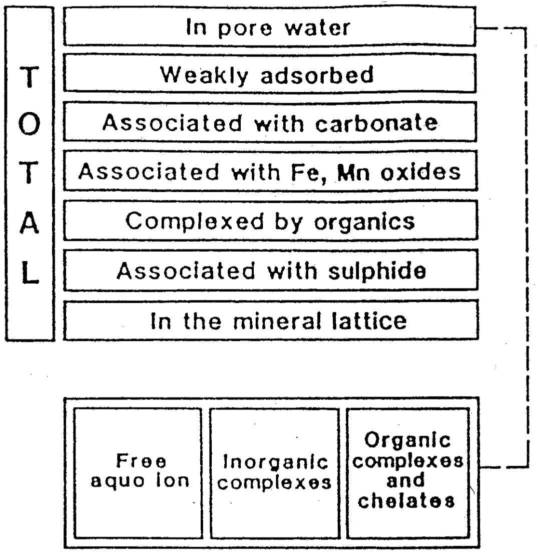

Figure 2. The chemical forms of metals in solid phases. Modified from Gunn and others (1988).

and sulfur and carbonate contents should be determined to enable accurate assessment of elemental reservoirs, mobility, and bioavailability. Additional work on mineralogical residences of metals is also important because metals can be associated with several sites (fig. 2).

Soil scientists involved in agriculture havebeen studying the chemistry of nutrient elements in soil for more than 100 years. Soil testing methods are used to determine sixteen essential elements for plant growth, but nitrogen, phosphorous, and potassium, along with pH and salinity are the most often measured properties (Peck and Soltanpour, 1990). Physical-chemical aspects of nutrient availability are discussed by Corey (1990) and soil testing correlations are reviewed by Dahnke and Olson (1990).

FACTORS THAT INFLUENCE BIOAVAILABILITY IN SOIL

Plant uptake of trace elements is generally the first step of their entry into the agricultural food chain. Plant uptake is dependent on (1) movement of elements from the soil to the plant root, (2) elements crossing the membrane of epidermal cells of the root, (3) transport of elements from the epidermal cells to the xylem, in which a solution of

Table 1. Relative mobility and availability of trace metals (modified from Salomons, 1995)

Metal species and association	Mobility
Exchangeable (dissolved) cations	High. Changes in major cationic composition (e.g. estuarine environment) may cause a release due to ion exchange
Metals associated with Fe-Mn oxides	Medium. Changes in redox conditions may cause a release but some metals precipitate if sulfide mineral present is insoluble
Metals associated with organic matter	Medium/High. With time, decomposition/oxidation of organic matter occurs
Metals associated with sulfide minerals	Strongly dependent on environmental conditions. Under oxygen-rich conditions, oxidation of sulfide minerals leads to release of metals
Metals fixed in crystalline phase	Low. Only available after weathering or decomposition

elements is transported from roots to shoots, and (4) possible mobilization, from leaves to storage tissues used as food (seeds, tubers, and fruit), in the phloem transport system. After plant uptake, metals are available to herbivores and humans both directly and through the food chain. The limiting step for elemental entry to the food chain is usually from the soil to the root (Chaney, 1988). This critical step usually depends on element concentrations in soil pore solutions, which are controlled by local soil physical and chemical conditions including water content, pH, Eh, and other factors.

Climate strongly influences soil types; these two factors largely control element (metals and metalloids) mobility and availability. Arid climates in the western United States often result in small soil organic matter abundances and large salt and carbonate abundances. These phases often contain the metals of interest. In the eastern United States, humid climates prevail and large amounts of organic matter require determination of organic matter-associated metals and their residence times or turn-over rates, because after some time, much of the organic matter is oxidized and associated metals may be released or available. In tropical climate conditions, accumulation of oxide minerals of iron, manganese, and aluminum in soil profiles may limit the mobility and bioavailability of both metals and metalloids.

Plant species and relative abundance and availability of necessary elements also control metal uptake rates. Abundant bioavailable amounts of essential nutrients, including phosphorous and calcium, can decrease plant uptake of non-essential but chemically similar elements, including arsenic and cadmium, respectively. More complex interactions are also observed: bioavailability may be related to multi-element amounts or ratios. For example, copper toxicity is related to low abundances of zinc, iron, molybdenum and (or) sulfate (Chaney, 1988). Many agricultural studies have been completed on this subject (see Adriano, 1986; 1992).

In the scientific literature, many studies describe anthropogenic (industrial or mining) contributions to elemental abundances, and their bioavailability controls, in the environment. Examples include: occurrence of heavy metals in soil near and far from urban pollution (Pouyat and McDonnell, 1991); formation of acid mine drainage (Filipek and others, 1987); uptake of heavy metals by plants in lab experiments (Brown and others, 1995); and uptake of metals by vertebrates in the vicinity of zinc smelters (Storm and others, 1994).

FACTORS THAT INFLUENCE PARTITIONING OF METALS IN SURFACE WATER AND SEDIMENT

After discharge to an aquatic environment but before uptake by organisms, metals are partitioned between solid and liquid phases. Within each phase, further partitioning occurs among ligands as determined by ligand concentrations and metal-ligand bond strengths. In solid phases, soil, sediment, and surface water particulates, metals may be partitioned into six fractions: (a) dissolved, (b) exchangeable, (c) carbonate, (d) iron-manganese oxide, (e) organic, and (f) crystalline (Elder, 1989; Salomons, 1995). Various metals partition differently among these fractions as shown by sequential partial extraction procedures. Partitioning is affected strongly by variations in pH, redox state, organic content, and other environmental factors (Elder, 1989; Salomons, 1995). The relative mobility and bioavailability of trace metals associated with different fractions are shown in Table 1. The dissolved fraction consists of carbonate complexes, whose abundance increases with pH, and metals in solution, including metal cation and anion complexes and hydrated ions whose solubilities are affected strongly by pH and tend to increase with decreasing pH (Elder, 1989). Exchangeable fractions consist of metals bound to colloidal or particulate material.

Metals associated with carbonate minerals in sedimentary rocks and soil constitute the carbonate fraction, which can be newly precipitated in soil. The iron-manganese oxide fraction consists of metals adsorbed to iron-manganese oxide particles or coatings. The organic fraction consists of metals bound to various forms of organic matter. The crystalline fraction consists of metals contained within the crystal structure of minerals and normally not available to biota.

Hydrogen ion activity (pH) is probably the most important factor governing metal speciation, solubility from mineral surfaces, transport, and eventual bioavailability of metals in aqueous solutions. pH affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubilities under pH conditions in natural water. Because hydroxide ion activity is directly related to pH, the solubility of metal hydroxide minerals increases with decreasing pH, and more dissolved metals become potentially available for incorporation in biological processes as pH decreases. Ionic metal species also are commonly the most toxic form to aquatic organisms (Salomons, 1995).

Adsorption, which occurs when dissolved metals are attached to surfaces of particulate matter (notably iron, manganese, and aluminum oxide minerals, clay, and organic matter), is also strongly dependent on pH and, of course, the availability of particulate surfaces and total dissolved metal content (Bourg, 1988; Elder, 1989). Metals tend to be adsorbed at different pH values, and sorption capacity of oxide surfaces generally varies from near 0 percent to near 100 percent over a range of about 2 pH units.

The adsorption edge, the pH range over which the rapid change in sorption capacity occurs, varies among metals, which results in precipitation of different metals over a large range of pH units. Consequently, mixing metal-rich, acidic water with higher pH, metal-poor water may result in dispersion and separation of metals as different metals are adsorbed onto various media over a range of pH values. Cadmium and zinc tend to have adsorption edges at higher pH than iron and copper, and consequently they are likely to be more mobile and more widely dispersed. Adsorption edges also vary with concentration of the complexing agent; thus, increasing concentrations of complexing agent increases pH of the adsorption edge (Bourg, 1988). Major cations such as Mg^{+2} and Ca^{+2} also compete for adsorption sites with metals and can reduce the amount of metal adsorption (Salomons, 1995).

Particulate size and resulting total surface area available for adsorption are both important factors in adsorption processes and can affect metal bioavailability (Luoma, 1989). Small particles with large surface-area-to-mass ratios allow more adsorption than an equivalent mass of large particles with small surface-area-to-mass ratios. Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water. The size of particles released during mining depends on mining and beneficiation methods. Finely milled ore may release much smaller particles that can both be more widely dispersed by water and wind, and which can also serve as sites of enhanced adsorption. Consequently, mine tailings released into fine-grained sediment such as silty clays found in many playas can have much lower environmental impact than those released into sand or coarse-grained sediment with lower surface area and adsorption.

Temperature exerts an important effect on metal speciation, because most chemical reaction rates are highly sensitive to temperature changes (Elder, 1989). An increase of 10ºC can double biochemical reaction rates, which are often the driving force in earth surface conditions for reactions that are kinetically slow, and enhance the tendency of a system to reach equilibrium. Temperature may also affect quantities of metal uptake by an organism, because biological process rates (as noted above) typically double with every 10ºC temperature increment (Luoma, 1983; Prosi, 1989). Because increased temperature may affect both influx and efflux rates of metals, net bioaccumulation may or may not increase (Luoma, 1983).

In recent organic carbon-rich sediments, trapped interstitial fluids can commonly form a strongly reducing (anoxic) environment. Low redox potential in this environment can promote sulfate reduction and sulfide mineral deposition. During diagenesis, much of the non-silicate-bound fraction of potentially toxic metals such as arsenic, cadmium, copper, mercury, lead, and zinc, can be co-precipitated with pyrite, form insoluble sulfides, and become unavailable to biota (Morse, 1994). Seasonal variation in flow rates or storms that induce an influx of oxygenated (sea)water can result in rapid reaction of this anoxic sediment and thereby release significant proportions of these metals. Pyritization and (or) de-pyritization of trace metals probably can be an important process in controlling bioavailability of many trace metals, especially in the marine environment (Morse, 1994).

METAL UPTAKE PATHS INTO AQUATIC ORGANISMS

Metal uptake by plants (discussed above) and partitioning in the soil (above) are combined in the aquatic environment. Two major pathways or uptake vectors are available for metal incorporation in deposit- and (or) detritus-feeding aquatic species:(1) ingestion of metal-enriched sediment and suspended particles during feeding, and (2) uptake from solution (Luoma, 1989). Consequently, knowledge of geochemical reactions of metals in both water and sediment is necessary to understand controls on metal bioavailability in natural water. Unfortunately, many biological factors controlling metal bioaccumulation in aquatic organisms are not understood; this fact severely limits our understanding of metal bioavailability (Luoma, 1989).

Bioavailability studies indicate that aquatic organisms uptake free metal ions (metal hydroxides) from solution quite efficiently; similarly, terrestrial animals uptake metal from solutions more efficiently than via direct particulate matter ingestion (Luoma, 1983). Consequently, geologic and (or) environmental conditions that enhance dissolved metal abundances (for example, lower pH) result in greater metal bioavailability. Indirect controls, such as larger particle or sediment size, also can result in greater bioavailability of metals by reducing adsorption and increasing dissolved metal contents. Metal assimilation from ingested particulate matter is also important, however, because metals are highly concentrated in this form (Luoma, 1989).

The efficiency of bioaccumulation via sediment ingestion is dependent on geochemical characteristics of the sediment. Luoma (1989) describes variation of cadmium uptake from sediment by clams as a function of sediment iron content; cadmium uptake from iron oxide-rich sediment was not detected, but a significant proportion of total cadmium uptake was a consequence of iron-poor sediment ingestion by clams.

GEOCHEMICAL AND ENVIRONMENTAL PROCESSES THAT AFFECT BIOAVAILABILITY

Numerous geochemical environmental factors may affect metal availability to aquatic organisms and plants (discussed in previous sections). The most important factors appear to be: (1) metal concentrations of solutions, (2) solute metal speciation, (3) metal concentration in food, (4) metal partitioning among ligands within food, (5) influence of other cations, (6) temperature, (7) pH, and (8) redox potential (Louma, 1983). Several of these factors are described above and others are discussed in the following paragraphs.

Interaction among metals can result both in stimulation and antagonism, as described by Luoma (1989). Stimulation occurs when uptake of one metal induces synthesis of binding sites that affect accumulation of both metals. Stimulation of cadmium uptake by lead exposure and of zinc by cadmium exposure have been observed in rats. Antagonism is commonly observed in simultaneous exposure to several metals. Antagonism to zinc uptake occurs during exposure to cobalt in clams and to copper in phytoplankton and microalgae. Antagonism between zinc and cadmium occurs in phytoplankton and macroalgae. Antagonism between copper and lead and between cadmium and mercury has also been reported in some types of organisms. In addition, more widespread elements, such as calcium and magnesium, can inhibit some types of metal-organic interactions. Zinc uptake by fish is influenced by this phenomenon but uptake of copper and cadmium are not affected.

Empirical studies suggest that bioavailability of several potentially toxic cationic metals (cadmium, cobalt, copper, nickel, and zinc) in anaerobic sediment is dependent on the total concentration of these elements in pore fluids (Ankley and others, 1994). They suggest that bioavailability of these metals can be predicted by measuring the acid volatile sulfide (AVS) and the simultaneously extracted metal (SEM) contents of sediment. AVS is the fraction of sulfide extracted by cold HCl and consists primarily of iron-sulfide complexes, whereas SEM is a sum of the concentrations of metals simultaneously extracted with AVS. High toxicity levels in benthic invertebrates and presumably high bioavailability of these metals are present when the SEM-AVS ratio exceeds one.

As noted above, temperature can strongly influence the rate of biological processes; rates double for every 10ºC-temperature increment. The increase in biological process rates does not necessarily result in increased bioaccumulation of metals, because both influx and efflux rates of metals may increase.

Transport of metals may vary between relatively unpolluted systems and disturbed or polluted systems. Particulate transport is dominant in unpolluted systems where metal inputs are principally from erosion of watershed substrates (Elder, 1989). In disturbed or polluted systems, for example, those affected by acid-mine drainage, point sources commonly deliver metals in a soluble phase, or associated with organic matter, and the proportion of dissolved metals and their bioavailability tends to be higher (Salomons and Forstner, 1984).

DETERMINATION OF BIOAVAILABILITY BY SELECTIVE CHEMICAL EXTRACTION

The extent of bioavailability is largely controlled by elemental speciation or chemical siting in soil, which determine solubility. A number of soil testing methods and partial or sequential chemical extraction techniques and methods are used to determine element behavior (Chao, 1984; Gunn and others, 1988). Some of the chemical extractions are: (1) water or $MgCl_2$ at neutral or ambient soil pH for easily soluble metals, (2) solubility in weak base (pH 9) for humic materials, (3) weak acid or dilute acid in buffer solution (pH 2 to 5) to release metals associated with carbonate phases, and (4) a chelating (or complexing) agent such as EDTA (ethylenediaminetetraacetic acid) (Borggaard, 1976) or DPTA (diethyenetriaminepentaacetic acid) buffered to a pH of 7 (Crock and Severson, 1980). Other possible extractants include (5) hydroxylamine hydrochloride for the "reducible" fraction associated with iron and manganese oxides/hydroxides, (6) strong acid (HCl, pH 1) to identify maximum mobility of most metals (Leventhal and Taylor, 1990), (7) oxidation by hydrogen peroxide to release metals associated with organic matter and (or) sulfide minerals, (8) a strong oxidizing acid (HNO_3) to execute steps (6) and (7) simultaneously, and (9) a mixture of strong acid and HF to dissolve residual silicate minerals. The choice of extractants and the order in which they are used depends on the sediment/soil type, environmental conditions, and metals of interest.

However, these sequential/partial extractions are all "operational", that is they are not completely specific to metals or chemical phases. Therefore any determination of bioavailability should be carefully calibrated, by direct measurement, with the actual behavior of metals in soil and plants. For example, O'Connor (1988) cautions about the use of the DPTA method and shows that it sometimes gives results comparable to plant uptake and sometimes it does not. As a consequence, he advises direct analysis of the total plant and (or) its component parts in addition to chemical leaches in order to determine bioavailability.

SPECIFIC METALS OF INTEREST

Brief summaries of some factors controlling bioavailability of several metals and two metalloids are given below. Additional data are available in the references listed for each metal.

Arsenic: Arsenic mobility, bioavailability, and toxicity are dependent on speciation: arsenite (AsO_3^{-3}) forms are much more toxic to biological species and are more mobile than arsenate (AsO_4^{-3}) forms (Kersten, 1988). Arsenic is chemically similar to phosphorous. Arsenate interferes with phosphate metabolism that is widespread in the biosphere. Metallo-organic forms of arsenic also may be much more bioavailable than inorganic forms; however, organic-bound arsenic is excreted by most species and does not appear to be highly toxic (Luoma, 1983). Adsorption-desorption on iron and aluminum oxide minerals is the main factor controlling arsenic behavior in soil and sediment. Maximal adsorption occurs at different pH for As{III} (pH 9.2) and As{V} (pH 5.5) as a function of the adsorbing mineral; As^{+3} mobility is enhanced under oxic conditions. Arsenic is apparently highly mobile in anoxic sediment-water systems. Development of acidic and oxidizing conditions tends to release large amounts of arsenic into solution due to decreased sorption capacity of both forms of arsenic (see Léonard, 1991).

Cadmium: The redox potential of sediment-water systems exerts controlling regulation on the chemical association of particulate cadmium, whereas pH and salinity affect the stability of its various forms (Kersten, 1988). In anoxic environments, nearly all particulate cadmium is complexed by insoluble organic matter or bound to sulfide minerals. Greenockite (CdS) has extremely low solubility under reducing conditions thereby decreasing cadmium bioavailability. Oxidation of reduced sediment or exposure to an acidic environment results in transformation of insoluble sulfide-bound cadmium into more mobile and potentially bioavailable hydroxide, carbonate, and exchangeable forms (Kersten, 1988). Studies of lake and fluvial sediment indicate that most cadmium is bound to exchangeable site, carbonate fraction, and iron-manganese oxide minerals, which can be exposed to chemical changes at the sediment-water interface, and are susceptible to remobilization in water (Schintu and others, 1991). In oxidized, near neutral water, $CdCO_3$ limits the solubility of Cd^{2+} (Kersten, 1988). In a river polluted by base-metal mining, cadmium was the most mobile and potentially bioavailable metal and was primarily scavenged by non-detrital carbonate minerals, organic matter, and iron-manganese oxide minerals (Prusty and others, 1994). Elevated chloride contents tend to enhance chloride complex formation, which decreases the adsorption of cadmium on sediment, thereby increasing cadmium mobility (Bourg, 1988) and decreasing the concentration of dissolved Cd^{+2} and bioavailability (Luoma, 1983). Also see, Stoeppler (1991) for additional data.

Copper: In a river polluted by base-metal mining, copper is most efficiently scavenged by carbonate minerals and iron-manganese oxide minerals and coatings and is less mobile than cadmium, lead, and zinc (Prusty and others, 1994); in most other situations lead is less mobile than copper. Elevated chloride contents decrease adsorption of copper on sediment, due to chloride complexation, which results in greater solubility and mobility (Bourg, 1988; Gambrell and others, 1991). In systems with high total copper contents, precipitation of malachite controls dissolved copper contents at low pH (Bourg, 1988; Salomons, 1995). Sometimes, elemental substitution is more complex; for example, copper toxicity is related to low abundances of zinc, iron, molybdenum, and (or) sulfate (Chaney, 1988).

Lead: The main sources of lead in the aquatic environment are leaded gasoline and mining (Prosi, 1989). Leaded gasoline results in introduction of organometallic lead compounds, which eventually reach surface water, into the atmosphere. Mining releases inorganic lead compounds. Both organic and inorganic forms of lead pose serious health risks to all forms of life (Ewers and Schlipköter, 1990). Inorganic lead compounds (sulfide, carbonate, and sulfate minerals) are commonly abundant in sediment but have low solubilities in natural water. Naturally-occurring lead in mineral deposits is not very mobile under normal environmental conditions, but becomes slightly more soluble under moderately acidic conditions. Soluble lead is little affected by redox potential (Gambrell and others, 1991). Lead is tightly bound under strongly reducing conditions by sulfide mineral precipitation and complexion with insoluble organic matter, and is very effectively immobilized by precipitated iron oxide minerals under well-oxidized conditions (Gambrell and others, 1991). In the aquatic environment, total dissolved lead abundances in water and pore water control primary uptake by organisms. Lead bioaccumulation is primarily dependent on the amount of active lead compounds (predominantly aqueous species) in the environment and the capacity of animal species to store lead (Prosi, 1989). Particulate lead may contribute to bioaccumulation in organisms. For humans, particles that are inhaled but not exhaled are especially important. Variations in physiological and ecological characteristics of individual species lead to different enrichment factors and tolerances for each organism. Studies of bottom dwelling organisms suggests that iron-rich sediment inhibits lead bioavailability (Luoma, 1989). In a study of lake and fluvial sediment, most lead was bound to a carbonate fraction or to iron-manganese oxide minerals, both of which respond to chemical changes at the sediment-water interface, and are susceptible to remobilization in water (Schintu and others, 1991). In a polluted river environment, lead is most efficiently scavenged by non-detrital carbonate and iron-manganese oxide minerals and is less mobile than cadmium (Prusty and others, 1994).

Mercury: Mercury has three valence states in natural sediment-water systems: elemental mercury (Hg^o), Hg^{+1}, and Hg^{+2} (Kersten, 1988). Hg^o is considerably more bioavailable for certain organisms than Hg^{2+} because of the solubility of Hg^o in lipid-rich tissue (Louma, 1983). However, Hg^{+2} is readily available to plants, but under reducing conditions and in presence of free sulfide ligands, mercury is stabilized in the Hg^{+2} state as extremely insoluble sulfide mineral precipitates or is bound as surface complexes with organic matter containing sulfur. Methylation of Hg^{2+} in natural environments leads to formation of volatile organic complexes that are several times more bioavailable than inorganic forms of mercury. Methylated mercury species are also one of the most toxic pollutants in the biosphere. Natural production of methyl mercury occurs under anoxic conditions and is probably mediated by microbes, but methylation of Hg^{+2} is inhibited by elevated sulfide contents (Kersten, 1988). Increased pH appears to increase availability of mercury to marsh plants possibly by causing conversion of Hg^{+2} to Hg^o. Sediment can serve as a sink for mercury discharged to the environment; partition coefficients, between suspended matter and water, are usually in the range of 10^5 (Kersten, 1988). Sorption is the main process for enrichment of mercury in sediment. Sorption can be influenced by chloride ligand concentration due to formation of chloro-mercurial complexes; in seawater, only organic matter retains its sorption capacity for mercury. Most particulate mercury in natural aquatic environments is associated with humic and other organic materials as well as oxide and sulfide minerals. Several studies have shown that mercury is less bioavailable in sediment that is rich in organic matter (Luoma, 1989). Most mercury released from point sources during mining is bound to sulfide compounds and is relatively non-bioavailable. However, a large percentage of mercury becomes associated with organic complexes downstream from point sources, possibly due to mobilization of mercury from pore fluids by humic acids. In natural water, suspended matter is the main transporting medium for mercury. In oxic sediment, most mercury is bound in unknown (complexed?) chemical forms that are readily susceptible to transformation, thereby affecting its mobilization and bioavailability.

Molybdenum: Molybdenum is an essential element for many animals and plants as it is required in their enzyme system. Molybdenum can be present in molybdate anions, MoO_4^{-2}, in soil where it can be mobile and bioavailable, because it is geochemically similar to sulfate. Molybdate ion is often associated with iron oxyhydroxide minerals, where it competes with phosphate and organic matter. Molybdenosis in animals is associated with soil that contains large amounts of available molybdenum, especially in forage plants with low sulfur and copper contents (Neuman and others, 1987).

Selenium: In the arid western United States, a number of environmental problems are related to high selenium abundances. These problems are mainly due to irrigation practices that allow selenium to accumulate in drains, reservoirs, and wetlands. Under these conditions, selenium can be bioavailable to plants and birds and accumulate to toxic levels (Severson and Gough, 1992). Extensive work has been done by the U.S. Geological Survey to determine the geochemistry of selenium, most of which is associated with (adsorbed on) oxide minerals, such as goethite (Balistrieri and Chao, 1987), amorphous iron oxyhydroxide and manganese oxide minerals (Balistrieri and Chao, 1990), and is relatively immobile. A chemical leach using 0.1 M KH_2PO_4 can be used to determine the soluble-available selenium (mainly as $Se0_4^{-2}$) content of soil with low oxide mineral contents and high pH (Chao and Sanzolone, 1989).

Zinc: In slightly basic, anoxic marsh sediment environments, zinc is effectively immobilized and not bioavailable (Gambrell and others, 1991). Substantial amounts of zinc are released to solution if this sediment is oxidized or exposed to an acidic environment. Very high abundances of soluble zinc are present under well oxidized conditions and at pH 5 to 6.5, whereas low abundances of soluble zinc are present at pH 8 under all redox conditions and at pH 5 to 6.5 under moderately and strongly reducing conditions (Gambrell and others, 1991). In polluted river environments, most zinc is scavenged by non-detrital carbonate minerals, organic matter and oxide minerals and is less mobile than cadmium (and perhaps less mobile than lead) (Prusty and others, 1994). Elevated chloride contents decrease adsorption of zinc on sediment (Bourg, 1988).

SUMMARY

Bioavailability of metals released from mineral deposits is very complex and dependent on many interrelated chemical, biological, and environmental processes. These processes may vary over time and among micro-organisms, plants, and animals. In soil and surface water, the mining method, presence or absence of sulfide minerals, quantity of water, acid-buffering capacity, presence of organic matter and iron and manganese oxide minerals, element speciation, and concentrations of other constituents in water may impact dissolved and bioavailable metal and metalloid contents. Field and laboratory studies of particular sites using soil, plants, and selective chemical extraction methods may enhance understanding this environmental concern.

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