

US EPA ARCHIVE DOCUMENT

3. ENVIRONMENTAL CHEMISTRY, TRANSPORT AND FATE

3.1. INTRODUCTION AND TERMINOLOGY

A general review of factors pertaining to the chemistry of metals in sediments, soils, waters, and the atmosphere is presented in this chapter in the context of risk assessment. Because the behavior of metals defies simple generalities, understanding the chemistry of the particular metal and the environment of concern is necessary. However, the factors that control metal chemistry and the environmental characteristics used to produce estimates of metal fate and effects can be generalized.

In environmental chemistry, the phase the species occurs in (gas, liquid, aqueous solution, mineral, or adsorbed on an interface between phases) generally is also included in a complete definition. In the context of the environmental chemistry of metals, chemists speak of a metal species as a “specific form of an element defined as to isotopic composition, electronic or oxidation state, complex or molecular structure” and phase (Templeton et al., 2000).

Metal speciation greatly determines the behavior and toxicity of metals in the environment. Speciation refers to the occurrence of a metal in a variety of chemical forms. These forms may include free metal ions, metal complexes dissolved in solution and sorbed on solid surfaces, and metal species that have been coprecipitated in major metal solids or that occur in their own solids. The speciation of a metal affects not only its toxicity but also its volatilization, photolysis, sorption, atmospheric deposition, acid/base equilibria, polymerization, complexation, electron-transfer reactions, solubility and precipitation equilibria, microbial transformations, and diffusivity (Bodek et al., 1988).

The following sections address the application of hard and soft acid and base (HSAB) concepts to metal behavior, including the formation of metal complexes, and the importance of pH and oxidation-reduction reactions to metal mobility. These sections also discuss the occurrence and interactions of the metals of concern in natural media (including surface and ground waters, soils and aquatic sediments, and the atmosphere). Metal sorption behavior, aging in soils, metal dissolution and transformation and transfer to plants, and methods of determining metal speciation in soils and sediments are important topics considered in these sections.

Chemical Species

The International Union of Pure and Applied Chemistry (IUPAC) defines chemical species as chemical compounds that differ in isotopic composition, conformation, oxidation or electronic state, or that in the nature of their complexed or covalently bound substituents, can be regarded as distinct chemical species.

3.1.1. Hard and Soft Acids and Bases: The Stability of Complexes

Complexes are formed between metals (acids) and ligands (bases), both in solution and at the surfaces of minerals and organisms. The toxic reaction of organisms to metals can be directly related to the nature of the metal complexes formed in solution and at the surface of the organism.

A useful concept that helps to explain the strength of metal complexing and metal toxicity is that of HSAB, which was introduced by Pearson (1973). In this concept, metal cations are Lewis acids and ligands are Lewis bases, with the metal cation and ligand in a complex acting as electron acceptor and donor, respectively. "Soft" implies that the species' electron cloud is deformable or polarizable and the electrons are mobile and easily moved. Soft species prefer to participate in covalent bonding. Hard species are comparatively rigid and nondeformable, have low polarizability, hold their electrons firmly, and prefer to participate in ionic bonds in complex formation (Langmuir, 1997). Hard acids form strong, chiefly ionic bonds with hard bases, whereas soft acids and soft bases form strong, chiefly covalent bonds when they form complexes. In contrast, the bonds formed between hard-soft or soft-hard acids and bases are weak, such that their complexes tend to be rare. Table 3-1 summarizes hard and soft acid and base relationships for the metals of concern.

Hard metals (hard acids), which are the least toxic, preferentially bind with hard bases that contain oxygen, forming weaker bonds with soft nitrogen and sulfur species. The strength of binding between hard metals and hard ligands is usually a function of pH. Many of the hard metals are macronutrients. Soft metals (acids) bind preferentially with soft S and N ligands, forming weaker bonds with hard base species such as hydroxide and sulfate. Soft and borderline metals, and Mn^{2+} , which is hard, form bonds of decreasing strength with soft ligands such as sulfide, generally in the following order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+} > Fe^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+}$. The tendency of metals to bind to soft ligands or to organic substrates (which are

Hard and Soft Acids and Bases

Hard acids and hard bases. Complexes formed between divalent hard acid cations and monovalent or divalent hard bases are ionic and relatively weak and are often termed "ion pairs." Complexes formed between Be^{2+} or trivalent hard acids and hard bases tend to be ionic and relatively strong.

Soft acids and soft bases. Relatively strong covalent bonds are formed in complexes between soft and borderline soft acid cations and soft bases. Ligand-binding sites on the external or internal surfaces of organisms are often soft base and thus bond strongly with soft and borderline soft acid cations.

Ligands

Ligands are simply anions or molecules that form in coordination complexes with metal ions. Depending on whether a ligand shares one, two, three, or more electron pairs with metals, it is called a mono-, bi-, tri-, or multidentate ligand. For ligands composed of more than one atom, the atom that directly participates in metal-ligand binding is called the donor or ligand.

Table 3-1. Hard and soft acids (metal cations) and bases (ligands)

Hard acids	Al^{3+} , Ba^{2+} , Be^{2+} , Co^{3+} , Cr^{3+} , Fe^{3+} , Mn^{2+} , Sr^{2+} , U^{4+} , UO_2^{2+} , VO^{2+}
Borderline acids (between hard and soft)	Co^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}
Soft acids	Ag^+ , Cd^{2+} , Cu^+ , Hg^{2+} , Hg^+ , CH_3Hg^+ , Tl^{3+} , Tl^+
Hard bases	F^- , H_2O , oxyanions: OH^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , $\text{C}_2\text{O}_4^{2-}$, CrO_4^{2-} , MoO_4^{2-} , $\text{H}_n\text{PO}_4^{n-3}$, $\text{H}_n\text{AsO}_4^{n-3}$, SeO_4^{2-} , H_2VO_4^- , NH_3 , RNH_2 , N_2H_4 , ROH , RO^- , R_2O , CH_3COO^- , etc.
Borderline bases (between hard and soft)	Cl^- , Br^- , NO_2^- , SO_3^{2-} , $\text{H}_n\text{AsO}_3^{n-3}$, $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_3^- , N_2
Soft bases	I^- , HS^- , S^{2-} , CN^- , SCN^- , Se^{2-} , $\text{S}_2\text{O}_3^{2-}$, $-\text{SH}$, $-\text{SCH}_3$, $-\text{NH}_2$, $\text{R}-$, C_2H_4 , C_6H_6 , RNC , CO , R_3P , $(\text{RO})_3\text{P}$, R_3As , R_2S , RSH , RS^-

“R” refers to an organic molecule.

Source: Adapted from Langmuir (1997); Huheey et al. (1993).

usually soft) is greatest for soft and borderline metals (soft acids), followed by the hard metals (hard acids), typically in the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} \gg \text{Na}^+$ (Pickering, 1986).

The tendency of metals to form solid phases, such as sulfides in sediments, is also related to their HSAB qualities. For example, extremely insoluble metal sulfides are formed in anoxic sediments by soft acid metal cations, such as Hg^{2+} ($\log K_{\text{sp}} = -57.25$) or Ag^+ ($\log K_{\text{sp}} = -49.7$), whereas borderline hard and hard metal cations such as Mn^{2+} ($\log K_{\text{sp}} = -19.25$) or Fe^{2+} ($\log K_{\text{sp}} = -22.39$) form slightly more soluble, although still highly insoluble, metal sulfides. Solubility products for all sulfides except Ag_2S are from Di Toro et al. (1990). The product for silver sulfide is from Stumm and Morgan (1970).

3.1.2. Transformations

As discussed previously, metals and metalloids can exist in the environment in several valence forms. They can also exist as organometallic compounds. Organometallic compounds are compounds that have a metal/metalloid-carbon bond. The bonds in organometallic compounds are generally covalent and between soft acid metals and soft ligands. Metal/metalloid transformation processes, such as metal methylation, occur through interactions with other chemicals and biota in the environment. Cycling and distribution of organometallic compounds between terrestrial, aquatic, and atmospheric phases may be physically, chemically,

or biologically mediated. Table 3-2 lists examples of some commonly occurring, environmentally stable organometallic compounds.

Table 3-2. Examples of organometallic compounds

Metal/metalloid	Organometallic compounds
As	Methylarsenic acid, dimethyl arsenic acid, trimethyl arsine, trimethylarsine oxide
Pb	Tetramethyl/ethyl lead, trimethyl/ethyl lead, dimethyl/ethyl lead
Hg	Methyl mercury, dimethyl mercury
Se	Dimethyl selenide, dimethyl diselenide, seleno-amino acids
Sn	Tributyltin, bis(tributyltin) oxide

As discussed in this section, organometallic methylation and demethylation rates are influenced by both the speciation and bioavailability of the metal, the microbial community, and a large number of environmental factors, many of which are interrelated. Sulfide and organic matter are important environmental variables that significantly affect methylation; however, their effect on methylation/demethylation is poorly understood. The dominant variables differ among locations and between seasons, although it is clear that methylation is predominantly a biologically mediated process. Methylation/demethylation rates are strongly influenced by metal/metalloid speciation and bioavailability.

Environmental methyl-metal concentrations reflect the net methylation rather than simple rates of methyl-metal synthesis. Table 3-3 presents metals that are involved in abiotic or biotic methylation/demethylation processes. With the exception of As and Se, the metals in the table form stable complexes with either methyl or ethyl groups. In addition to methyl/ethyl compounds, metals can also be incorporated biochemically into stable organometallic compounds (e.g., As into lipids and Se into amino acids).

Organometallic environmental transformations may affect both the mobility and toxicity of metals. The transformation rates and the organometallic products are dependent on environmental conditions and the population of microorganisms available. For example, methylation/demethylation rates are dependent on the speciation of the metal, the microbial community, the environmental variables (e.g., pH, temperature, reduction oxidation potential, organic matter, dissolved oxygen, nutrient availability, salinity, complexing agents), and the distribution of the metal between compartments (sediment, water, gaseous). The inter-relatedness of these processes has made research into unraveling the factors controlling net methylation difficult and, to date, incomplete. However, some general trends can be predicted with some certainty, as discussed in this section.

Table 3-3. Metals/metalloids involved in methylation processes

Process	Metals affected
Environmentally stable organometallics	Si, Ge, Sn, Pb, Hg, As, Sb, Se
Abiotic chemical methylation	Hg, Pb, Sn
Abiotic demethylation	Sn, Pb
Biotic methylation	As, Cd, Hg, Pb, Se, Sn
Biotic demethylation	As, Hg, Sn, Pb

Source: Bodek et al. (1988).

3.1.2.1. Biotic Methylation Transformations

Biotic methylation occurs when organisms, primarily microorganisms, transfer alkyl groups to bioavailable metals. In general, it is thought that anaerobic sulfate-reducing bacteria are the principal methylators in freshwater and estuarine environments. However, methylation rates are not always correlated with sulfate-reducing bacteria. Not all sulfate-reducing bacteria are capable of methylating, and the efficiency of methylation is dependent on the activity and structure of the bacterial community. Other bacteria may be involved in methylation. Biotic methylation occurs predominantly in the sediment column; however, because the water column by volume is much larger, water column methylation is important.

Maximum methylation rates typically occur at the redox boundary, which varies seasonally and frequently coincides with the sediment-water interface (Ullrich et al., 2001). Methylation rates decrease with increasing sediment depth, probably due to a decrease in biotic habitat. Microorganisms may also demethylate (or dealkylate) organometallic compounds. Microbial-mediated transformations are frequently the most important environmental organometallic processes. Generally, as the amount of organic material increases in a system the microbial populations also increase.

High temperatures and anaerobic conditions generally favor metal-methylation formation, and demethylation processes are generally favored under low temperatures and/or aerobic conditions. Studies on the effects of pH are not consistent. Interconnected parameters include pH effects on the microbial communities and effects on the speciation distribution of the metals/metalloids in the water and the sediment as well as adsorption rates. Organometallic compounds appear to increase in the water column in low pH environments, but this may be due to release of methylated metals from the soil and subsequent depletion of organometallic compounds in the soil. Therefore, pH effects on net methylation in a system are not fully understood. In freshwater ecosystems, where sulfate concentrations are typically low, increase

in sulfate concentration increases methylation rates. However, in reducing environments, increasing sulfide concentration decreases methylation rates. General trends in methylation/demethylation rates are outlined in Table 3-4.

Table 3-4. General trends of environmental factors affecting rates of methylation/demethylation

Organometallic transformations	Temperature		pH		SO ₄ ⁻²	Organic matter	Redox		Salinity
	High	Low	High	Low	High		Oxic	Anoxic	High
Net methylation	↑	↓	?	?	?	?	↓	↑	↓
Methylation aq	↑	↓	↓?	↑?	↓	↓↑	↓	↑	↓
Methylation sed	↑	?	↑	↓	↓	?	?	?	?
Demethylation	↓	↑	↓	↑	?	?	↑	↓	?

↑ indicates an increase in rate.

↓ indicates a decrease in rate.

? indicates conflicting data or insufficient data to indicate a likely trend.

The inhibitory effect of sulfide is probably not due to metal sulfide formation but, rather, to the formation of less bioavailable metal-sulfur complexes. High organic matter may increase abiotic methylation through humic/fulvic metal reactions; however, this mechanism is poorly understood and confounded because biotic methylation rates may increase in environments with high organic matter. In ecosystems with high dissolved organic carbon (DOC) concentrations, DOC may bind with metals/metalloids, rendering them unavailable and thereby reducing biotic methylation rates.

3.1.2.2. *Abiotic Transformations*

Some organometallic compounds, those with electronegativities greater than 1.7, are stable under environmental conditions. In a few instances, metals can undergo abiotic methylation processes. Carbon-metal bonds with more polar (metal electronegatives <1.7) will undergo hydrolysis (reaction with water). Abiotic chemical methylation can occur by three mechanisms: transmethylation reactions between mercury and tin/lead alkyls, reactions with humic/fulvic substances, and photochemical reactions.

3.1.3. Aquatic Chemistry

Exposure and risks associated with metals in aquatic environments depend on the forms of the metals and on the factors that influence the presence of these forms as well as on the fate and transport of the metals.

3.1.3.1. Processes

A number of factors influence the sorption of metals in aquatic systems. Speciation/complexation is the distribution of a given constituent among its possible chemical forms, including metal complexes, which have differing tendencies to be adsorbed or desorbed; precipitation is the process by which dissolved species exceed the solubility limits of their solids, so that some of the species precipitate from solution; colloid formation can result in metals being sorbed or

Factors Affecting Sorption of Metals
Speciation/complexation
Precipitation
Colloid formation
Biofixation
Interactions with natural organic matter
Changes in pH
Oxidation potential
Salinity
Competing ions
Nature of sorbent phases
Surface site densities

coprecipitated with colloidal-sized particles; biofixation occurs when biological processes (usually involving microorganisms or plants) result in the binding of metals to solid materials; interactions with natural organic matter can also result in sorption. In addition to these factors, sorption is influenced by changes in pH, oxidation potential, salinity, concentrations of competing ions, the nature of sorbent phases and their surface areas, and surface site densities.

3.1.3.2. Speciation and Complexes

Metal species dissolved in water may occur as free ions, or aquo-ions, or as complexes. Free metal cations are generally surrounded by coordinating water molecules and so have been termed “aquocations,” although by convention the water molecules are ignored when writing chemical reactions involving metal cations.

The total analytical concentration of a given metal in water is the sum of the concentrations of its free ion and its complexes and any metal associated with suspended solids, whether organic or mineral. For example, the total molal concentration of lead, ΣPb , in a natural water might equal:

$$\Sigma Pb = mPb^{2+} + mPbOH^+ + mPbCO_3^0 + mPbHCO_3^+ + mPbSO_4^0 + mPb(suspended\ solids)$$

In most natural waters, the concentration of free lead ion, mPb^{2+} , is less than the sum of the concentrations of its complexes, which in this case are lead complexes with hydroxyl, carbonate, bicarbonate, and sulfate ions. Other metals that are found in natural waters most often

as complexes and not as free ions include Al^{3+} , Ag^+ , Cu^{2+} , Fe^{3+} , and Hg^{2+} . The metalloids As and Se and the metals Cr, Mo, Sb, and V occur most often in aerobic waters and soils as covalently bonded to oxygen in oxyanions. Under oxidizing conditions, these include arsenate, selenate, chromate, molybdate, and vanadate, which themselves are complexes.

Complexes that incorporate metals play a major role in controlling the availability and fate of metals in the environment. Increasing the fraction of a metal that is complexed increases the solubility of minerals of that metal (Langmuir, 1997). For example, the solubility of lead sulfate is related to the molal concentrations of free lead and sulfate ions through the expression below:

$$K_{sp} = (\gamma_{Pb} \cdot m_{Pb^{2+}})(\gamma_{SO_4} \cdot m_{SO_4^{2-}})$$

where the terms γ_{Pb} and γ_{SO_4} are the activity coefficients of the ions. The product of the ion activity coefficient and the molal concentration of each species equals the activity of the ion. This equation shows that for a given total Pb concentration, the greater the amount of Pb that is complexed, the lower the concentration of free Pb ion. This means that as the extent of Pb complexing increases, the total Pb concentration must also increase to reach saturation equilibrium with lead sulfate. In other words, metal complexing increases total metal solubility.

Metal complexing also has a direct influence on metal adsorption to organic matter or mineral surfaces. For example, metal carbonate, sulfate, and fluoride complexes are usually poorly adsorbed, whereas metal hydroxide complexes are strongly adsorbed (Langmuir, 1997). In summary, metal complexing generally increases the solubility and mobility of metals in surface and ground waters (with the exception of metal hydroxide complexes).

For many metals, the free metal ion is thought to be the primary metal species that causes toxicity to aquatic organisms. This is consistent with the free ion activity model (FIAM), which carries the assumption that the free or aquo-ion is the most biologically active form of the dissolved metal. If this is true, the key parameters that can modify the degree of toxicity are those that affect speciation, such as pH and the amount of inorganic and organic ligands (e.g., DOC) that can form metal complexes and so provide alternative binding sites for the metal ion. Metal toxicity also will be affected by other dissolved ions (e.g., Na, Ca) that compete with metals for binding sites on the gills of fish or on the respiratory surfaces of other aquatic organisms. However, it should be noted that many metal complexes (whether bound to organic or inorganic ligands) are reversible, particularly if environmental conditions change (e.g., pH decreases).

3.1.3.3. *Importance of pH and Redox Conditions*

The pH is probably the single most important variable that influences the behavior of metals in the environment. Thus, metal complexes with sulfate, fluoride, chloride, and phosphate are most stable and important below pH 7, whereas metal carbonate and hydroxide complexes become increasingly more important above pH 6–8.

Also, as discussed in Section 3.1.6, hydrogen ion competes with metal cations for adsorption sites, so that adsorption of metal cations by hydrous ferric oxide (HFO), for example, is low in acid systems but increases with increasing pH. In contrast, oxyanions of As, Mo, Se, and Cr tend to be desorbed from HFO with increasing pH because of competition between the oxyanions and OH⁻ ion for sorption sites. Furthermore, the solubility of most metal-containing minerals is greatest under acid conditions, decreasing with increasing pH. Figure 3-1 shows the locus of measured values of oxidation potential (Eh) and pH in aquatic systems. The principal controls on Eh are atmospheric oxygen and organic matter. High Eh (oxidizing or aerobic) conditions are maintained in the atmosphere and in most surface waters and shallow soils in contact with atmospheric oxygen. The lowest Eh values and reducing or anaerobic conditions are found in water-logged soils and sediments that contain organic matter and in ground waters that contain a few milligrams per liter or more of DOC. Intermediate Eh conditions are found in waters and sediments that are only partially oxidized because of their relative isolation from the atmosphere. Measured Eh values may not agree with Eh values computed from the concentrations of redox-sensitive species. The difference between measured and computed Eh values is discussed at length by Stumm and Morgan (1996) and Langmuir (1997).

3.1.4. **Ground Water and Metals Mobility**

Site-specific nonorganic metal health risk assessments for EPA programs often are used to predict the rate of movement of metals through soils and their subsequent movement and concentrations in ground water. The primary processes governing the environmental fate and transport of metals in the subsurface are advection, dispersion, matrix diffusion, and retardation (U.S. EPA, 1994b). Advection and dispersion are functions of the system rather than of the contaminant. Matrix diffusion, which is a function of the contaminant, is relatively unimportant and is omitted in most model transport algorithms. Retardation depends on a number of factors (Langmuir, 1997; U.S. EPA, 1994b) and may involve or be affected by the following:

- **Sorption** - The attachment of metal species to mineral surfaces or other surfaces.
- **Speciation** - The distribution of a given constituent among its possible chemical forms, including metal complexes, which have differing tendencies to be adsorbed or desorbed.

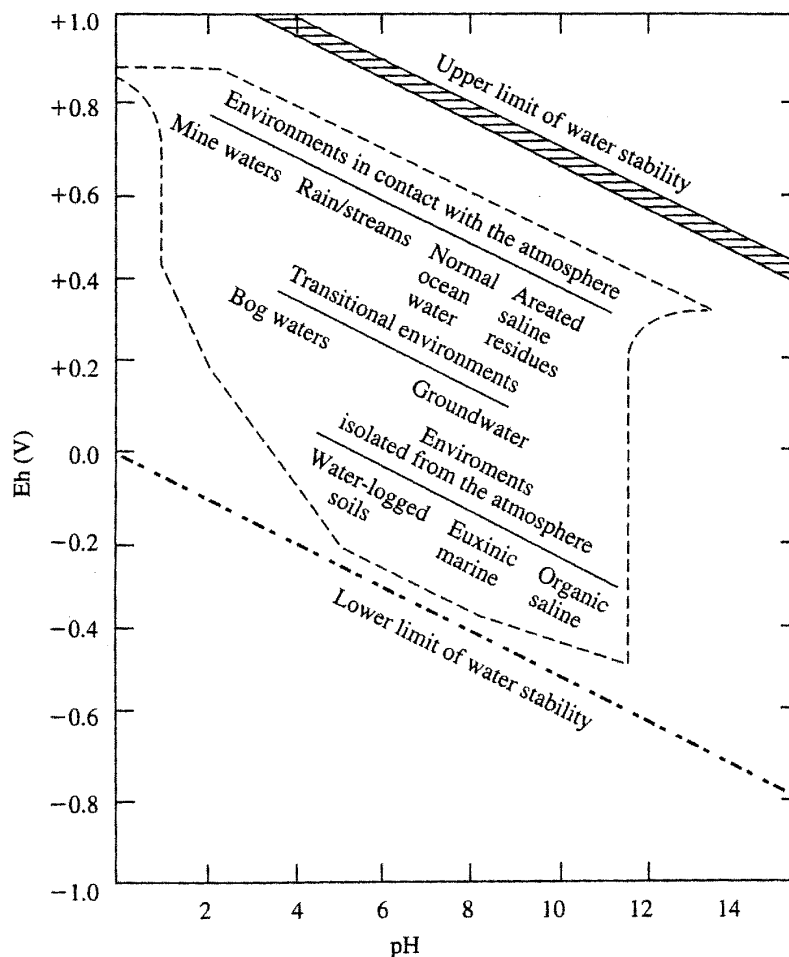


Figure 3-1. Approximate positions of some natural environments in terms of Eh and pH. The dashed line represents the limits of measurements in natural environments.

Source: Baas-Becking et al. (1960).

- **Precipitation** - The process by which dissolved species exceed the solubility limits of their solids, so that some of the species precipitate from solution. When a metal species reaches mineral saturation, addition of further amounts of the species to solution are precipitated, not adsorbed.
- **Colloid formation** - The process of forming colloids and the association of metal species with them. The metals may be sorbed or coprecipitated with colloidal-sized particles.
- **Biofixation** - The binding of metals to solid materials due to the interactions of microorganisms or plants.
- **Natural organic matter** - (NOM) interactions.

- **Other processes** - Other processes include changes in pH, oxidation potential, salinity, concentrations of competing ions, the nature of sorbent phases and their surface areas, and surface site densities.

3.1.4.1. *Application of Partition Coefficients to Metal Mobility in Ground Water*

Owing to the complexity and multiplicity of the processes involved, recourse is often made to the use of a single partition or distribution coefficient that describes the degree to which the contaminant's transport is retarded relative to water. This approach starts with defining the retardation factor:

$$R_f = \frac{v_p}{v_c}$$

where:

R_f = the retardation factor,

v_p = the velocity of water through a control volume, and

v_c = the velocity of contaminant through a control volume.

Langmuir (1997) noted that the retardation factor is related to the distribution coefficient through the below expression:

$$R_f = 1 + \frac{\rho_b}{n_e} K_d$$

where:

ρ_b is the porous media bulk density, and

n_e is the effective porosity at saturation given as a volume fraction.

Laboratory adsorption studies often find that, in simple systems, the value of $\log K_d$ for metal adsorption increases linearly with pH. For example, for Zn^{2+} adsorption by HFO, Langmuir (1997) noted that adsorption followed the log equation:

$$\log K_d = 15.48 + 1.77 \text{ pH}$$

The properties and applications of partition or distribution coefficients for metals are comprehensively reviewed in EPA (1999a). These coefficients may be obtained from the literature, estimated using mathematical models, or measured. Properly designed column

experiments generally give results more representative of the *in situ* behavior of soils and sediments than do batch tests (Langmuir, 1997).

Models using partition distribution coefficients (K_d) have significant inaccuracies for metals, and the application of single partition coefficient values for individual metals should be limited to site-specific assessments (when they can be calibrated for a specific site); to regional- and national-scale studies where bounds of potential K_d values are adequate; or reasonably representative single values that have sufficient functionality built in to account for variability due to pH and soil composition.

EPA (1999a) discusses the advantages and disadvantages of several methods for measuring partition coefficients, including laboratory batch testing, in situ field batch testing, flow-through testing, and field modeling. In many national assessments, EPA has used the MINTEQ model and its subsequent versions to generate generic partition coefficients that may be applied to regional or national mobility evaluations (<http://www.epa.gov/ceampubl/mmedia/minteq/index.htm> or <http://www.lwr.kth.se/english/OurSoftware/Vminteq/>).

For screening assessments:

- Partition coefficients have been tabulated as a function of pH by EPA (U.S. EPA, 1998b), and the Agency has also presented non-pH-dependent values for Pb (900) (Pb values have large variability and selecting meaningful values is difficult), mercuric chloride (58,000), and Hg (1,000) (U.S. EPA, 1999b).
- In simple systems, the value of $\log K_d$ for metal cation adsorption usually increases linearly with pH, whereas the value of $\log K_d$ generally decreases with pH for anion adsorption.

For definitive assessments:

- It may be possible to estimate metal adsorption with some accuracy without having to measure it in the field, depending on the information available on a specific soil, surface-water, or ground-water system. To do so, at minimum, the risk assessor will need to determine the amounts and surface areas of the potentially sorbing materials (e.g., metal oxides, clays, and organic matter [OM]) in a soil or sediment or in suspension in a stream, and the detailed chemical composition of the water, especially its pH and metal concentration. Literature information can then be used to estimate the sorption properties of these materials for use in the diffuse layer (DL) sorption model.
- If greater accuracy or site specificity is required, it may be necessary to measure metal adsorption in laboratory experiments designed to parameterize the DL model for application to a specific study area. The risk assessor could run experiments (batch tests) that attempt to reproduce the composition of waters and sorbing solids in the study area.

3.1.5. Sediment Chemistry

In addition to the challenges posed by metal chemistry, the sedimentary environment is complex and often highly heterogeneous. Fortunately, generalizations can be made about the sedimentary environment in order to progress toward a method for risk assessment. This brief review summarizes information on the composition of sediments; processes that act on sediments and their metal burden; and the chemistry of the sedimentary environment that influences the fate, bioavailability, and effects of metals. It is important to consider these factors in light of the aim of estimating potential biological effects of metals in sediments.

Sediment solids can hold up to a million times more metal than an equivalent volume of water. The exact proportion of a chemical held by sediment relative to water is a function of a metal's chemistry as well as the chemistry of the sediment solid and the surrounding environment. Further, this distribution is dynamic (Diamond and Mudroch, 1990). Because of their large capacity to "hold" metals, sediments have been characterized as "sinks." Sediments can serve as temporary sinks from which some of the metal can enter ecological and human food webs through several routes (e.g., Diamond, 1995), primarily through accumulation in benthic organisms. These organisms include those that fully or partially live in the sediments (e.g., tubificids, chironomids, trichopteran larvae) or those that feed from the sediment bed (e.g., suckers, carp). Some organisms obtain their chemical dose from both pelagic and benthic routes (e.g., lake whitefish, walleye), but because of high chemical concentrations in sediments, the benthic route can be the dominant route of uptake (Morrison et al., 2000).

For humans, the route of entry of metals from the sediments is through water used for drinking, bathing, and swimming. The availability of these metals is mediated by sediment-water exchange processes that can result in the release or remobilization of chemicals from the sediment bed. However, owing to the ability of Hg to bioaccumulate in its monomethyl form, fish consumption is the critical route of exposure to this metal for humans.²

Many important chemical reactions involving the metals of concern occur in the fine-grained materials that accumulate in the deep parts of water bodies. The controlling factors or master variables that influence metal chemistry are redox potential and pH. A depth profile of

Sediments

Bed or bottom sediments are found at the bottom of lakes, rivers, and estuaries. Sediments have several sources that influence their composition and chemistry. The type and chemistry of sediments is also determined by their location in the water body as well as the characteristics of the water body. At any given site, metals can be associated with solid-phase minerals, organic matter, colloids, and pore water. The solid phase can vary from sand (>63 μm) to silt (2–63 μm) to clay (<2 μm). Because clays have more active binding sites than do the other grain sizes and because of their high surface area-to-volume ratio, clays—or fine-grained particles—are of greatest significance in terms of metal binding.

² Marine biota can also be a significant route of exposure to arsenic in its organic forms, such as methylarsonic acid; however, these arsenic species are significantly less toxic than the inorganic forms (Fowler, 1983).

the sediments will reveal decreasing sediment porosity and concentrations of dissolved oxygen because oxygen is consumed as organic matter decomposes. The pH is often relatively constant or may decrease with depth, but alkalinity may increase owing to mineralization of organic matter (Stumm and Morgan, 1996). As dissolved oxygen is consumed, anaerobic microbes use other electron acceptors in redox or oxidation-reduction reactions in the order of nitrate, ferric iron, ammonium, sulfate, and bicarbonate to produce carbon dioxide, ammonia, sulfide, and methane.

The risk assessor can ascertain the redox status of the sediments by measuring the concentration of dissolved oxygen or other redox-sensitive species, by calculating pE (a measure of electron availability in solution), or by measuring Eh (millivolts) or the electromotive force of the pore water solution. The zone of transition from oxic to anoxic conditions is the redoxcline, which can migrate vertically, depending on the mixing of the overlying water column (e.g., Diamond and Mudroch, 1990). For example, the redoxcline may be 5-10 cm below the sediment-water interface in a well-oxygenated oligotrophic lake or river, but it may be above the sediment-water interface in a thermally stratified eutrophic lake or river.

3.1.5.1. *Metal Chemistry in Sediments*

In this discussion, the risk assessor should consider two pools of metals. The first pool consists of metals that exist as aqueous (or dissolved) species bound to colloids or DOM and those bound to sediment particles through an exchangeable binding process. This pool is often referred to as the “exchangeable” or “labile” pool. The second pool consists of metals found within the mineral matrix of the sediment solids. This pool is largely unavailable to biota, and its release will occur over geologic time scales, through diagenetic processes. Because the latter pool is largely unavailable, only the exchangeable pool of metals is considered. Note that the exchangeable pool will be composed of naturally occurring metals that are released into solution as a result of weathering and diagenetic processes as well as metals released into the environment as a result of anthropogenic activities.

The exchangeable pool of metals is subject to speciation in the aqueous phase (e.g., within the pore water) and sorption to solid phases, where sorption is a general term that includes adsorption (the accumulation of matter at the solid-water interface or a two-dimensional process) and absorption (inclusion in a three-dimensional matrix) (Stumm and Morgan, 1996). Here, speciation refers to the distribution of metal species in a particular sample or matrix or species distribution (Templeton et al., 2000). In the aqueous phase, metal will react or bind with dissolved ligands according to the pH, Eh, ionic strength, and abundance of ligands (see Section 3.1.3, Aquatic Chemistry).

The concentration of metal in the dissolved phase is controlled by sorption to the solid phase. Although sorption can occur rapidly, desorption or dissolution of metal from the solid phase may be a two-phase process, where the second phase is rate limiting (e.g., Nyffeler, 1986;

Santschi et al., 1986). If the kinetic limitation of reactions are not considered, the distribution of metals among aqueous species and between the aqueous phase and the solid phase can be estimated by using one of the speciation models. Several speciation/complexation models are available to perform this calculation, such as MINEQL+ (Schecher and McAvoy, 2001), the Windermere Humic Aqueous Model (WHAM) (Lofts and Tipping, 1998), and MINTEQA2 (Allison et al., 1991). These models work well under oxic conditions, but estimates of metal binding are less reliable under anoxic conditions, where metal concentrations are most often controlled by the solubility of metal sulfides. Furthermore, in some circumstances equilibrium may not be achieved, particularly when the redoxcline moves more quickly than the rate of metal reaction or when the reaction is governed by microbial processes, as occurs with the methylation of Hg or As.

In oxic sediment pore waters (above the redoxcline), metals will exist as aqueous species, that is, as freely dissolved ions or metal complexes (e.g., phosphate, sulfate, or carbonate complexes), and associated with colloids. Solid-phase reactions are controlled by iron oxyhydroxides and manganese oxides that may exist as colloids, sediment particles or surface coatings of particles, OM that may also exist as colloids or coat sediment particles, and clay colloids and particles.

As Eh declines, the solid-phase manganese oxides are the first to be reduced and thereby dissolve, which releases metals that have been sorbed or coprecipitated with these minerals. Some of the metals released into the pore water may then be adsorbed by iron(III) oxyhydroxides, which are the next to dissolve as the Eh continues to drop. Under reducing conditions, particularly as sulfate is consumed and the S is converted to sulfide, metal concentrations in pore waters again drop as solid-phase metal-sulfides are formed (see discussion below about the role of acid-volatile sulfides [AVSs] in regulating toxicity).

As a result of redox chemistry, metals can undergo seasonal redox-driven cycling between the water column and sediments or within the sediments, depending on the position of the redoxcline. The stages in the cycling are, first, the adsorption or coprecipitation of metals with iron and manganese hydroxides under oxidizing conditions; then with the development of moderately reducing conditions, the reduction and dissolution of the manganese and iron oxyhydroxides and consequent release of the associated metals into the water or pore water; followed by their diffusion upward toward the zone of low metal concentrations under oxidizing conditions. It is also possible for dissolved metals to diffuse downward toward the zone of low metal concentration owing to their precipitation as sulfides. As a result of this vertical cycling, the depth profile of metals in pore water may not match that of the solid phase (e.g., Carignan and Tessier, 1985). Moreover, it is possible, but less usual, that the cycling can occur relatively rapidly and involve a significant portion of the solid-phase metal. Under these conditions, the solid-phase sediment profile reflects this reworking rather than the historical record of metal loadings (MacDonald et al., 2000).

The pH controls metal speciation and binding by affecting the species distribution of dissolved ligands (e.g., phosphate, sulfate, carbonate, humic substances) and the surface charge of binding sites on DOM and solid phases such as iron oxyhydroxides. Generally, at low pH, when surface sites are protonated, the sorption of cationic metals decreases, and, hence, metal mobility increases. The converse occurs at high pH, which results in low metal solubility and greater sorption. The patterns of dissolution and sorption are reversed for metalloids, such as As, that exist as anionic species.

3.1.5.2. *Estimating Metal Distribution in Sediments*

A main objective in terms of assessing the hazard or risk posed by metals in sediments is estimating the amount of metal that is potentially bioavailable. The bioavailability of metals in sediments is a function of their distribution between the dissolved and solid phases, with dissolved metals in porewater generally considered to be the most bioavailable fraction. Accordingly, several methods have been developed to estimate the distribution of metals among dissolved and solid phases in sediments. These methods have been thoroughly reviewed by Mudroch et al. (1999, 1997). Although bioavailability is also a function of aqueous phase speciation, limited research has been conducted to estimate metal speciation in pore waters. Generally, for the purpose of ecological risk assessments, the exposure of benthic organisms to sediment-associated metal is assumed to be proportional to the metal concentrations in interstitial water, although some studies indicate that uptake from overlying water (Hare et al., 2003; Roy and Hare, 1999) or ingested sediment may be a significant source of body burdens of metals.

Distribution of metals in sediment pore waters may be determined by field measurements, experimental methods, and mathematical modeling, with the latter also requiring some field measurements. Concentrations of metals in pore waters may be determined in the field by using pore water dialysis chambers or peepers and by methods that separate the solid phase from the pore water, although the latter have been shown to be less reliable (Mudroch et al., 1997). Several extraction schemes have been developed to determine the distribution of metal among operationally defined fractions (e.g., Forstner, 1995; Tessier et al., 1979). However, sequential extraction methods do not cleanly distinguish the occurrence and speciation of different forms of metals in sediments and soils (Tye et al., 2003; Tack and Verloo, 1999). Other experimental methods include leaching tests (e.g., Reuther, 1999). The results of any of these methods are concentrations of metals in pore water, which can be related to toxicity benchmarks.

Because of the need to develop Sediment Quality Guidelines (SQGs) for metals that explicitly address toxicity and are based on readily measured parameters, several methods have been developed. For oxic sediments, Tessier et al. (1993, 1989, 1984; Tessier, 1992) compiled partition coefficients of metals that were derived from field studies of freshwater sediments. The

partition coefficients are dependent on pH (because Eh is held constant) and are generally linear over a range of pore water pH values (see above discussion under ground-water chemistry, Section 3.1.4 for the theoretical basis for development of partition coefficients).

Speciation/complexation models also may be used to estimate fractions of dissolved and bound metal species. These models rely on measurements of pH, dissolved oxygen, or Eh to establish redox conditions. The models assume that solid-phase binding is governed by sorption to iron and manganese oxides. Model estimates are less reliable when other solid-phase substrates are dominant (e.g., clay minerals) and are a function of the availability and accuracy of the stability constants for the metal-ligand reactions that are used in the calculations. Model estimates are less reliable when other solid-phase substrates are dominant (e.g., clay minerals), and they are a function of the availability and accuracy of the stability constants for the metal-ligand reactions that are used in the calculations.

For anoxic sediments, the availability of sulfide controls metal distribution and solubility. Operationally, AVSs (mainly iron monosulfide) have been considered as a measure of reactive sulfides (Forstner, 1995). Studies have demonstrated an inverse relationship between sediment acute toxicity and AVSs for marine and freshwater sediments (Di Toro et al., 1992, 1990; Ankley et al., 1991) as well as between pore water concentrations and AVSs (Brumbaugh et al., 1994; Casas and Crecelius, 1994). As a screening-level tool, the acute toxicity of anoxic sediments can be assessed by determining the ratio of AVSs to simultaneously extracted metal (SEM). Low sediment toxicity is indicated when AVSs are in excess ($AVS > SEM$), which implies sufficient capacity of the AVS to bind essentially all free metal. This topic is further discussed in Section 5.

3.1.6. Soil Chemistry

The cationic metals occur naturally in soils as oxides and hydroxides (Fe, Mn, Al); to a lesser extent they can occur as carbonates, phosphates, and sulfates; and in reducing (usually wet or waterlogged) soils as sulfides, which are highly insoluble. The soil parameters important in affecting sorption and precipitation reactions and the extent of their influence—and thus contaminant bioavailability—depend on the intrinsic properties of the contaminants. In the soil environment, metals can exist as cations (having a positive charge), anions (having a negative charge), or neutral species (having a zero charge). Their form significantly affects their sorption, solubility, and mobility. For example, most soils are chiefly negatively charged; thus, metal cations have a higher propensity to be sorbed by soil particles than do metal anions (U.S. EPA, 2003e).

Cationic metals can react with inorganic soil constituents (e.g., carbonates, sulfates, hydroxides, sulfides), forming aqueous complexes, which may be adsorbed or precipitated in mineral form. Most complexation and precipitation reactions are pH dependent (U.S. EPA, 2003e).

As, Cr, Se, and V complex with O and typically exist as anionic species under most environmentally relevant scenarios (Bohn et al., 1985; Lindsay, 1979). The most common forms of As are arsenate (As(V)) and arsenite (arsenic(III)), which are present in soil solution in the form of AsO_4^{3-} and AsO_3^{3-} , respectively. The chemistry of arsenic resembles that of phosphate (Barber, 1995; Bohn et al., 1985). Cr can exist as chromate (Cr(VI) or CrO_4^{2-}), which is usually considered more soluble, mobile, and bioavailable than the sparingly soluble chromite (Cr(III)), which is normally present in soil as the precipitate $\text{Cr}(\text{OH})_3$ (Barnhart, 1997; James et al., 1997). Similarly, Se can be present as selenates (SeO_4^{2-}) and selenites (SeO_3^{2-}). For V, vanadate (VO_4^{3-}) is the most common form (U.S. EPA, 2003e).

Metals can exist in the pore water as aquo-ions or soluble complexes. The bonding of metal species to soil particles can range from ionic to covalent. For most soils in the United States, negatively charged sites are more plentiful; less than 5% of the total available charge on the soil surface is positively charged. Metals existing as cationic species have a greater propensity to associate with such soils. This makes them less bioavailable, but it also results in greater loading of metals into the soil ecosystem. Anionic metals generally move into pore water—and so are more bioavailable—but leach out of the system much more rapidly. In summary, soil pH and availability of charged sites on soil surfaces are the primary soil factors controlling release of metals to pore water and, subsequently, bioavailability (U.S. EPA, 2003e).

3.1.6.1. Key Parameters Affecting Metal Bioavailability in Soils

From the preceding overview of how the metals and metal compounds interact with soil constituents, it is clear that soil plays a very significant role in reducing the potential bioavailability of metals in the environment. Given the types of contaminant-soil interactions presented, the primary soil factors controlling the potential bioavailability of metals are soil pH, the availability and character of sorption sites on soil surfaces, the content of Iron and aluminum oxyhydroxides and soil organic matter, and least important, the soil clay mineral content. The following discussion briefly details the key soil parameters affecting the various contaminants availability to the pore water.

Soil pH is often termed the master soil variable because it controls virtually all aspects of contaminant and biological processes in soil. These processes include dissolution and precipitation of metal solid phases, complexation and acid-base reactions of metal species, and metal sorption as well as microbial activity. Increasing soil pH also results in an increase in the number of negatively charged soil sites, with a concomitant decrease in the positively charged sites. Therefore, increasing the soil pH increases the sorption and removal from pore water (Bohn et al., 1985).

3.1.6.2. Adsorption Behavior of the Metals of Concern

3.1.6.2.1. Surface area and surface density. In porous media, the most important sorbent solids for metals are oxyhydroxides of iron and manganese. Their important surface properties are discussed in Langmuir et al. (2003). For a given weight of sorbent, metal sorption capacity is proportional to surface area and surface site density. The greatest surface site densities (positively or negatively charged sites) are those of organic material and the oxyhydroxides. These phases are the strongest and most important sorbents of trace metals. Except for kaolinite, the clays (0.02-2 mmol sites/g) have a surface charge that is largely independent of pH, whereas the surface charge of organic matter and the oxyhydroxides is strongly pH dependent.

3.1.6.2.2. Organic matter (organic carbon) content. Organic matter includes plant and animal remains in various stages of decomposition, cells and tissues of soil organisms, and substances exuded from plant roots and soil microbes (Sumner, 2000). Organic matter is primarily composed of carbon, oxygen, and minor amounts of nitrogen (N) and phosphorus (P). On average, approximately 58% of organic matter is organic carbon. Organic matter in soils ranges from <1% for a sandy soil to almost 100% for a peat soil, with most soils having organic matter contents <10% (Bohn et al., 1985). Also, organic matter content is usually higher in surface soils or in the root zone and decreases with depth in the soil profile. The organic acid functional groups typically present in organic matter have a high affinity for metal cations.

3.1.6.3. Aging of Metals in Soil

A distinction should be made between persistence of total metals in soil and persistence of bioavailable forms of the metal. As metals age in soils, they decrease in bioavailability. The aging process is partially reversible if environmental parameters change (e.g., pH decreases), although a portion of the metal ions will be securely entrapped in the soil particle lattice and not available to be resolubilized. It has been well documented that metal chemistry in solutions freshly added or spiked into soils vary from metal forms in field-contaminated soils. Typically, the metal contaminant pool requires time to diffuse into micro- or nanopores and to be absorbed into organic matter and soil particles. These slow reactions are attributed to micropore diffusion, occlusion in solid phases by (co)precipitation and (co)floculation, and cavity entrapment. Although the slow reactions play a key role in metal bioavailability, their rates, mechanisms, and controlling factors have not been comprehensively elucidated. Evidence of aging processes is provided by studies of metal extractability and lability (Tye et al., 2003; Hamon et al., 1998). It has been frequently observed that easily extractable pools revert with time (~1 year) to more strongly bound forms. Isotopic dilution provides a useful way to quantify changes associated with progressive attenuation of metals in soil. After 1 year aging reactions are almost complete and are mostly reversible. At present, information regarding the aging reactions of different

metals and metalloids and sorbing solids, is very limited, so it is not possible to generalize which metal(s) age the fastest or with greater/less reversibility.

3.1.6.4. *Dissolution and Transformation of Metals*

The dissolution and transformation of a metal compound in soil is related to a series of chemical and physical properties characteristic of the compound itself and of the soil. Environmental parameters such as temperature and humidity have a strong influence on the rate of transformation. When assessing the transformation of a compound in soil, the risk assessor should keep in mind that aging reactions may take place at the same time as transformation and dissolution. When metal salts are added to soil, the form of the salt dictates the rate and amount of soluble metal that will form in the pore water. Insoluble forms of metals (e.g., vanadium pentoxide [V_2O_5]) will transform to soluble free ion (V) at a slower rate than will soluble metal salts (e.g., Na_3VO_4). However, the rate of formation of the free ion is not proportional to the dissolution rate of the salt because aging reactions will remove the free ion from the pore water. The risk assessor should consider the relative rates of dissolution and aging simultaneously to accurately predict pore water concentrations.

3.1.6.5. *Soil Metal Transfer to Plants*

The “soil-plant barrier” concept was introduced to communicate how metal addition, soil chemistry, and plant chemistry affect risk to animals from metals mixed in soil (Chaney, 1980). Reactions and processes that take place at the soil-plant barrier are influenced by the following factors: (1) soil solid phases (e.g., iron, aluminum, and manganese oxyhydroxides and organic matter) may have adsorptive surfaces that influence soil chemistry; (2) adsorption or precipitation of metals in soils or in roots limits uptake-translocation of most elements to shoots; and (3) the phytotoxicity of Zn, Cu, Ni, Mn, As, Bo, Al, and F, for example, limits residues of these elements in plant shoots. More recently, inductively coupled plasma-mass spectrometry (ICP-MS) and other very sensitive analytical methods have been used to examine soil solution and soil-plant transfer of 60 elements as a function of soil pH (Tyler and Olsson, 2001a, b). These studies provide evidence that further supports the concept of a soil-plant barrier

Several areas for potential errors in the research methodology should be avoided when making these comparisons:

- First, comparison of application rates is valid only after the system has been equilibrated using accepted methods.
- Second, soil pH levels should be equal across rates studied; co-variance of soil pH should be used to correct for unequal soil pH (Bell et al., 1988).

- Third, the metal concentration in the source applied affects the slope of metal uptake: higher metal concentration in the source means higher phytoavailability at equal metal applications (Jing and Logan, 1992).

Strongly acidic soils increase plant uptake of Zn, Cd, Ni, Mn, and Co and increase the potential for phytotoxicity from Cu, Zn, and Ni. In alkaline soils, the high pH increases uptake of Mo and Se. Pb and Cr are not absorbed by plants to any significant extent at any pH (Chaney and Ryan, 1993). However, each element should be considered separately because of its unique chemistry. For example, arsenate is more strongly adsorbed than is arsenite; when a soil is flooded to grow rice, soil microbes can reduce arsenate to arsenite, and the higher concentration of dissolved arsenite can be phytotoxic to rice in more highly contaminated soils. Most other elements have little potential for redox change with change in the redox status of soils. Reduced soils can form sulfide, and sulfide forms low-solubility compounds with most of the metals of concern in soils, including Pb, Zn, Cd, Cu, and Ni (see above discussion on sediment chemistry Section 3.1.5). For essential elements (e.g., Zn, Cu, Ni), low-solubility species can result in deficiency syndromes. Upon oxidation of the soil, sulfide is quickly oxidized, and the metals are returned to more normal equilibrium reactions of aerobic soils.

3.1.7. Atmospheric Behavior/Chemistry

Most metals and metal compounds exist in the solid phase under normal environmental conditions and thus occur almost exclusively in the particle phase of the atmosphere, where they are ubiquitous. Anthropogenic sources include combustion from fossil fuels and metal industries as well as industrial sources employing specific metal compounds in specific processes. Some airborne metals (e.g., manganese and nickel) may derive largely from crustal sources (U.S. EPA, 1996a). Richardson (2002) included volcanic eruptions and emissions, entrainment of soil and dust, entrainment of sea salt spray, and natural forest fires as significant natural metals emission sources.

For purposes of health risk assessment, particle size is important. The aerodynamic size and associated composition of particles determine their behavior in the human respiratory system. Furthermore, particle size is one of the most important parameters in determining the atmospheric lifetime of particles, which may be a key consideration in assessing inhalation exposures as well as exposures related to exposure pathways involving deposition onto soil or water (U.S. EPA, 1996a). Metals emitted by combustion processes (e.g., the burning of fossil fuels or wastes) generally occur in small particles or fine fraction, which is often characterized by particles less than 2.5 microns in diameter ($PM_{2.5}$). In contrast, the larger sized, coarse mode particles result from mechanical disruption, such as crushing, grinding, and evaporation of sprays, or suspensions of dust from construction and agricultural operations. Accordingly, metals in coarse mode particles (i.e., those larger than approximately 1–3 μm) are primarily those

of crustal origin, such as Silicon (Si), Al, and Fe (U.S. EPA, 1996a). The *fine* versus *coarse* distinction simply differentiates two relatively distinct size distributions of particles, the separation point of which occurs in the range of 1 to 3 μm . The distinction does not refer directly to particle sampling methods or size fractionations particular to health risk assessment (U.S. EPA, 1996a).

Fine and coarse particles typically exhibit different behavior in the atmosphere; fine mode particles exhibit longer atmosphere lifetimes (i.e., days to weeks) than coarse particles and tend to be more uniformly dispersed across a large geographic region (U.S. EPA, 1996a). Relatively lower dry deposition velocities of fine particles contribute to their persistence and uniformity throughout an air mass (U.S. EPA, 1997c). The larger coarse particles (i.e., greater than 10 μm) tend to rapidly fall out of the air and have atmospheric lifetimes on the order of minutes to hours, depending on their size and other factors (U.S. EPA, 1996a).

In most cases, metals do not undergo transformation while in the particle phase; thus, their removal from the atmosphere is regulated by the rate at which the particles themselves participate in wet and dry deposition processes. For example, metals such as As, Be, Cd, and Pb are generally found in airborne compounds with a single predominate oxidation state (As(III), Be(II), Cd(II), Pb(II)). Some metals (e.g., the transition metals Cr, Mn, and Ni) present the possibility of changing oxidation state *in situ* in the particle, although little is known of these processes (U.S. EPA, 2003d). This is an important consideration for health risk assessment as the different oxidation states also differ in toxicity (such as for Cr).

For metals that can change oxidation states, much of the atmospheric chemistry takes place in the aqueous phase, such as cloud droplets or water films on particles. Metal salts and oxides that dissolve in water can undergo several reversible reactions, including hydration, hydrolysis, polymerization, and reaction with other anions. The equilibrium between these forms depends on the atmospheric conditions, the equilibrium and solubility constants, and the concentrations of other chemicals. Transformations between oxidation states can occur either to increase the oxidation state (such as oxidizing Cr(III) to Cr(VI)) or to reduce it. These oxidation or reduction reactions can occur through reaction with other species, such as dissolved metals, reduced sulfur species, and organic compounds (Seigneur and Constantinou, 1995). Although models exist that can be used to estimate metal speciation in aerosols with liquid water, the reactions are still highly uncertain.

Hg is an exception among the commonly occurring metals; it exists primarily in the vapor phase under most conditions but can also occur in particle and aqueous phases. The risk assessor should consider at least three species of Hg: elemental Hg, which is largely present as a gas; divalent (Hg(II)) inorganic Hg compounds, which are more water soluble; and particulate-phase Hg (Schroeder and Munthe, 1998; U.S. EPA, 1997b). The behavior of Hg in the atmosphere depends strongly on the oxidation state. Elemental Hg is capable of being transported long distances, even globally; divalent Hg deposits within a few hundred kilometers of sources; and

particulate mercury is deposited at intermediate distances, depending on the particle size (Schroeder and Munthe, 1998). Elemental Hg that is deposited can be reemitted from the surface, as can divalent and particulate Hg after biological or chemical reduction to the elemental form.

In the gas phase, elemental Hg can be oxidized to divalent Hg by O₃, OH, H₂O₂, and molecular chlorine (Cl), although other halogen atoms also might be important (Schroeder and Munthe, 1998). In the aqueous phase, elemental Hg can be oxidized by OH, O₃, and dissolved chlorine, and divalent mercury can be reduced by processes such as reaction with HO₂ and S(IV). Both vapor-phase and aqueous atmospheric chemistry may involve multiple phases.

EPA has made a substantial effort to evaluate the atmospheric fate of Hg as a result of the requirements of the Clean Air Act. EPA (1997b) contains a comprehensive evaluation of mercury's atmospheric fate, but this is an area of ongoing research and controversy. EPA continues to actively investigate Hg behavior in the atmosphere (e.g., Landis and Stevens, 2003; Jaffe et al., 2003; Bullock and Brehme, 2002; U.S. EPA, 2001a; Bullock, 2000a, b).

Most sampling and analytical techniques published by EPA for metals in air are oriented toward evaluation of particular-phase total metals rather than metal species (U.S. EPA, 1999a). These methods involve collection of a particular size fraction of particles (e.g., PM_{2.5}, PM₁₀, and total suspended particulates), with subsequent analysis by x-ray fluorescence, atomic absorption, inductively coupled plasma, proton-induced x-ray emission, or neutron activation analysis gamma spectroscopy techniques. The one notable exception is a method for Hg (Method IO-5) that speciates vapor and particulate forms. To the extent that metals are sorbed to particulate phases, analysis of individual metal species can, at least theoretically, be accomplished by the same techniques used to analyze those species in other solid media.

Potential for Inhalation

Inhalation of metals is addressed in Section 4.2.5.1. Particle size is likely to be the most important determinant of potential exposure. Particle size also influences the overall fate of metals in the atmosphere.

3.2. METAL FATE AND TRANSPORT

Major metal sources to water and land include diverse manufacturing, mining, combustion, and pesticide activities. Major atmospheric sources are oil and coal combustion, mining and smelting, steel and iron manufacturing, waste incineration, phosphate fertilizers, cement production, and wood combustion (Haygarth and Jones, 1992). Metals from these atmospheric sources can find their way into soils, sediments, and water. Other major sources to aquatic and terrestrial systems include chloralkali, acid, pigment, electronics, and copper sulfate production.

Some exposure assessments do not involve anthropogenic releases of metals to the environment. Rather, they focus on changes in exposure to environmental metals that result from other aspects of human activities. For example, acidification of freshwater changes Al phase association and speciation, resulting in an increased dose of naturally occurring metals to aquatic biota (e.g., Campbell et al., 1992). Intensive irrigation mobilizes Se that is naturally present in relatively high concentrations in western soils, and consequent evaporative concentration in wetlands, impoundments, and other low-lying areas in arid regions of the U.S. can lead to toxic exposures (e.g., Wu et al., 1995).

3.2.1. Aquatic and Terrestrial Transport Pathways for Metals

When an exposure assessment is completed for a site, the available data are usually limited in their coverage with respect to the characterization of exposure levels over both time and space. Depending on the situation, it may be advantageous to use a transport and fate model (i.e., a computational model) to fill in the data gaps, such that an improved characterization of exposure levels is available for use by the risk assessor. Models are also useful in situations where it is desirable to have an estimate of future exposure levels that are expected to result from the implementation of remediation measures. These results can be used to quantitatively evaluate the effectiveness of alternative remediation scenarios that are being considered. The models can also be used to refine the design of the viable alternatives so that the risk assessor can develop an optimal remediation strategy.

Although numerous models are available for use, most are based on the same two fundamental principles: (1) metals are ubiquitous in the environment, as they are found in the aquatic, terrestrial, and atmospheric compartments; (2) within each compartment, they are present in association with water (freely dissolved metal or as organic and inorganic metal complexes), particles (sorbed, precipitated, or incorporated within a mineral phase), and air. The evaluation of metal transport therefore requires evaluation of the distribution of the metal among these phases, within each compartment (air, water, soil), as well as the movement (i.e., the transport) of each of these within and among the various compartments. It is important for the assessor's model to simulate the movement of water and particles explicitly because this provides a way to evaluate differences in the degree to which various chemicals/metals may be transported in association with particles (i.e., via settling and resuspension) or in association with the dissolved phase (diffusive flux of dissolved metal). The analyst represents the environmental setting of interest as a series of discrete, interconnected volumes. Mass balance equations for air, water, solids, and metal are then formulated for each volume to obtain a system of mass balance equations that may then be solved for the concentrations of interest over both time and space. Including all compartments in every model is not necessary. For example, models for a site that is impacted by a smelter might call for use of a model of an atmospheric compartment (e.g., to simulate transport of a release from a stack) and a terrestrial compartment (to simulate fate of

atmospheric inputs to the soil). Alternatively, for an aquatic setting dominated by previously contaminated sediments, it may be sufficient to consider water and sediment transport alone and to neglect the atmospheric and terrestrial compartments.

Although the underlying principles of most models are similar, the included features vary widely from one model to the next. The output from a relatively simple model may be adequate for decision-making purposes in some instances. Some relatively simple models are limited in their applicability to steady-state analyses and spatially uniform conditions, but if this will provide a reasonable and/or conservative representation of conditions at a site, it may provide the analyst with a useful and cost-effective modeling alternative. In other cases, the analysis may require the completion of time-variable simulations to properly represent conditions that vary over time, such as daily or seasonal variations in flow and upstream boundary concentrations, point source loads, and pulse exposures. The analyst should select an appropriate model because not all models will be applicable to every situation. Although, in principle, the more sophisticated models provide the risk assessor with the capability to complete a more detailed and mechanistically based analysis than will a simple model, successful application of these models will require greater resources (data, time, and funding) than will the use of a simpler model. The analyst must also possess a relatively high level of modeling expertise to use the more sophisticated modeling approaches. It is for this reason that the more sophisticated models are usually reserved for use in higher level, definitive assessments.

Many of the models available for use in evaluating the transport and fate of metals were originally developed for application to neutral organic chemicals. As a result, these models frequently include a variety of reactions that are not necessarily relevant to an analysis of metal transport and fate (e.g., biodegradation, photo-oxidation, and volatilization). Although these models still may be of use in an exposure assessment for metals (the nonapplicable processes often may be bypassed), a more significant problem is that they often fail to represent some important metal-specific processes. For example, the evaluation of metal speciation and metal partitioning between dissolved and particulate phases will be represented only in a very simple manner in such models. This limitation may be overcome, at least in part, by performing the requisite metal-specific analyses with a stand-alone chemical equilibrium model, but this approach will place an added burden on the analyst to integrate the results of the two models in a technically defensible manner.

Although models that include some metal-specific capabilities will be discussed as part of this Framework, no single model that is currently available for use includes all the metal-specific features that would be desirable for use. More detailed discussions of these and other transport and fate models, as well as a number of chemical equilibrium models, may be found in Paquin et al. (2003) for aquatic systems and Allen (2002) for terrestrial systems. Additionally, work is in progress to develop updated models that will offer improved metal-specific capabilities (e.g., the

Unit World model (Di Toro et al., 2001). As a result, metal fate and transport models should be viewed as an evolving tool, and new models may be expected in the near future.

3.2.1.1. Aquatic Transport Models

Modeling of metal transport and fate within aquatic systems involves the representation of hydrodynamic transport to simulate movement of water, particulate transport to simulate the movement of particles, and chemical transfers and kinetics to simulate exchange of metal between dissolved and particulate phases and between the water column and benthic sediment (Figure 3-2). The risk assessor has the option of using independent hydrodynamic transport, sediment transport and chemical fate models, or an integrated model that incorporates all these processes.

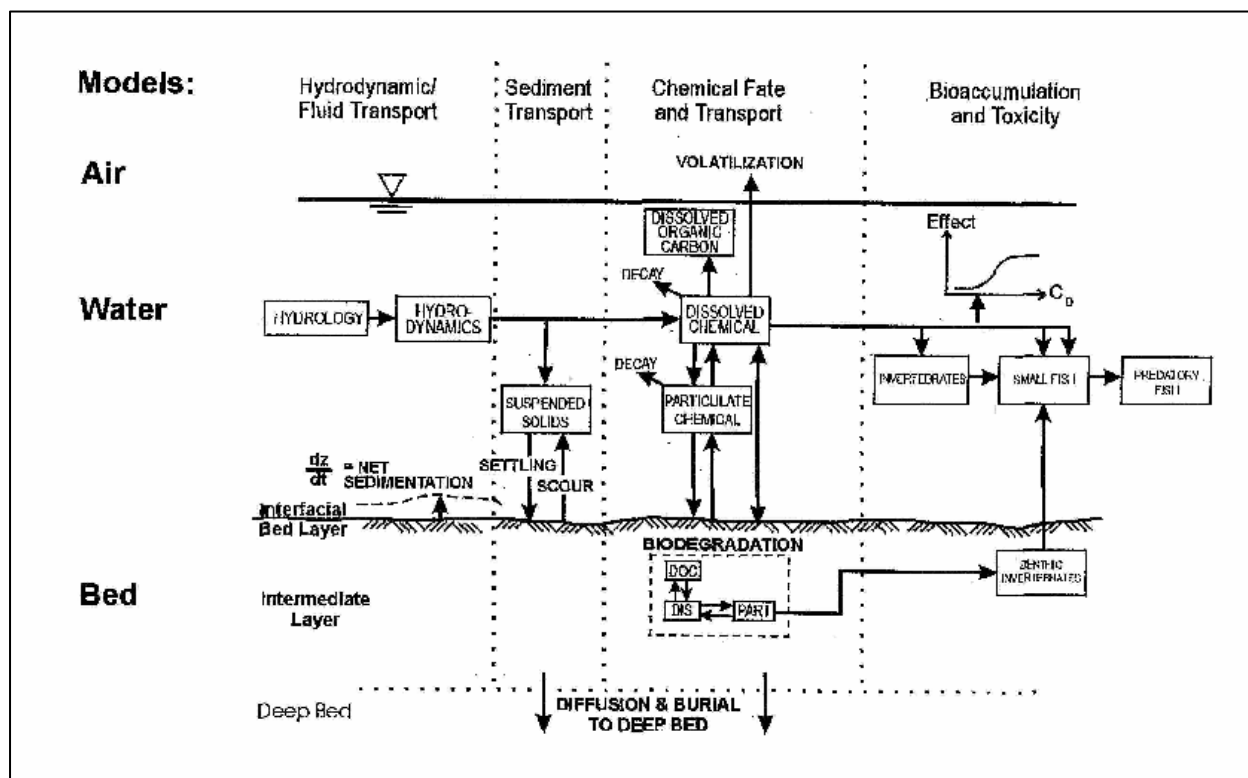


Figure 3-2. A generalized model framework for chemical fate and transport in an aquatic system.

Source: Paquin et al. (2003).

Modeling the movement of metals through an aquatic system begins with a characterization of the water movement through the system. The time scale for the hydrodynamic analysis should be represented in a way that will satisfy the needs of the sediment transport and chemical fate analyses that are also being performed. For example, low-flow

conditions associated with minimum dilution may be judged to be the most critical conditions in a setting involving a point source discharge, while peak flow conditions may need to be simulated in a setting where resuspension of contaminated sediments is the primary concern. A steady-state model might be appropriate for use in the former case, and a time-variable model would likely be needed in the latter case. Thus, the details of the specific problem setting will necessarily have an influence on both model selection and how the model will be used.

Integrated Models

The fate and transport of metals in aquatic systems is most reliably predicted using integrated models rather than stand-alone hydrodynamic or sediment transport models.

The risk assessor also should be aware of several reviews of fate and transport models that have been completed since the early 1980s. In earlier reviews, Delos et al. (1984) reviewed models for wastewater load allocations, and Mills et al. (1985) described screening-level analyses for water quality assessments of conventional pollutants. The Agency subsequently prepared an updated summary of the features included in the water quality models that were available for use in exposure assessments (U.S. EPA, 1987). Schnoor et al. (1987) simultaneously published their review and included detailed descriptions of fate and transport models and their required input parameters. Later, EPA published a review describing the use of modeling tools for the development of Total Maximum Daily Loads (TMDLs) in watersheds (U.S. EPA, 1997a). More recently, Paquin et al. (2003) completed a review of exposure, bioaccumulation, and toxicity models for aquatic systems, with a focus on their applicability to metals (exclusive of organometallics). Because of the advances that have been made since the mid-1990s with regard to the development of fate and transport models, including some recent efforts to couple these models with metal speciation models and more sophisticated stand-alone hydrodynamic and sediment transport models, the latter reviews by EPA (1997a) and Paquin et al. (2003) tend to include the most up-to-date information with regard to the availability of models that are appropriate for use. These reviews also include example applications of many of the models discussed.

Fate and transport analyses may be performed by using an integrated hydrodynamic, sediment, and chemical transport model or by employing what tend to be relatively sophisticated stand-alone versions of these three submodels. The advantage of the former approach is that integration of the hydrodynamic, sediment, and chemical transport results takes place in a seamless manner with limited need for an assessor's intervention. This is in contrast to the use of stand-alone models, where the output of one model should be formatted in a way that ensures it is amenable to use with the other models that are to be applied. A distinct advantage of the latter approach is that it has the potential to reduce the time needed to complete a model run, an important consideration for a multiyear simulation of a large and complex problem setting. For example, it may not be necessary to repeat the simulation of hydrodynamic and sediment transport if the model input being modified affects only chemical transport (e.g., partition

coefficient). A similar line of reasoning would apply to the use of an integrated transport model that includes metal speciation versus one that uses a stand-alone chemical equilibrium model to satisfy this need.

The partition coefficient, which controls the distribution of metal between the dissolved and particulate phases, is considered to be a key model parameter in chemical/metal fate and transport evaluations (see Section 3.1.4). It is important for several reasons. First, the distribution of metal between the dissolved and particulate phases has a direct impact on the magnitude of particulate fluxes of metal that occur in association with the settling and resuspension of sorbed metal. Second, the partition coefficient also controls the magnitude of diffusive fluxes of metal between the sediment interstitial water and the overlying water column, as this flux is proportional to the concentration gradient of total dissolved metal (free ionic metal + metal-DOC and metal-inorganic ligand complexes) between these compartments. Partitioning reactions also affect the metal bioavailability and the route of exposure to a metal (food vs. water). Given its importance, the risk assessor should recognize that the assumption of equilibrium partitioning is a potential oversimplification in some situations (e.g., near a point source discharge to a receiving water or immediately following a pulse exposure, such as an overflow from a storm sewer system). Under these conditions, the assumption of equilibrium between the dissolved and particulate phases may be less appropriate than is otherwise the case and additional uncertainty will necessarily be associated with the model results. If this situation exists, consideration should be given to conducting special studies (e.g., measurement of free metal concentrations over time in a water sample) to test the validity of the equilibrium assumption.

Analytical Solution Models

Analytical solution models of aquatic system fate and transport are the simplest models with the lowest computational requirements. They are solved analytically to provide concentrations over metal of time or space.

Modeling of Hg and metalloids, such as As and Se, is complicated by transformation processes that change the form of the metal. Similarly, metals that readily change oxidation state (e.g., Cr) also require additional considerations in fate modeling. Many of the same transport models can be used, but input parameters will require modification. Such models are beyond the scope of this framework, which is focused on inorganic forms of metals. See, for example, the Hg cycling model by Hudson et al. (1994) for further guidance on fate and transport models for Hg. All modeling exercises are limited by the validity of the model Framework, the accuracy of input parameters, and the experience of the analyst (Dzombak and Ali, 1993). Therefore, all exposure assessments should include an explicit description of model assumptions and associated uncertainties.

3.2.2. Terrestrial Fate and Transport

Movement of metals through soils is dependent on the chemical properties controlling speciation, the presence of ligands that control complexation of metals within pore water (and ground water) and adsorption onto mineral surfaces, and the rate of water flux through the soil. Metals are lost from the soil by leaching into ground water and through metal specific uptake by plants (see Section 3.1.6.5). Sections 3.1.4 and 3.1.6 review the processes and models that predict movement of chemicals through soils or partitioning onto mineral surfaces (i.e., partition coefficients). These serve the same role as the fate and transport models discussed above for aquatic systems and therefore are not repeated here.

3.3. ATMOSPHERIC FATE AND TRANSPORT

Fine and coarse particles typically exhibit different behavior in the atmosphere: fine mode particles exhibit longer atmospheric lifetimes (i.e., days to weeks) than coarse particles and tend to be more uniformly dispersed across a large geographic region (U.S. EPA, 1996a). Relatively lower dry deposition velocities of fine particles contribute to their persistence and uniformity throughout an air mass (U.S. EPA, 1997c). The larger coarse particles (i.e., greater than 10 μm) tend to rapidly fall out of the air and have atmospheric lifetimes on the order of minutes to hours, depending on their size and other factors (U.S. EPA, 1996a).

In the atmosphere, the behavior of Hg depends strongly on its oxidation state. Elemental Hg is capable of being transported long distances, even globally; divalent Hg deposits within a few hundred kilometers of sources; and particulate Hg is deposited at intermediate distances, depending on the particle size (Schroeder and Munthe, 1998). Elemental Hg that is deposited can be reemitted from the surface, as can divalent and particulate Hg after biological or chemical reduction to the elemental form.

Deposition

Because most metals occur as particulate matter (hereinafter referred to as *particulates*), their removal from the atmosphere is governed by the rates of wet and dry deposition. These deposition processes represent an important route of exposure for plants, animals, and humans. Some of the deposited metals can come to reside on the surfaces of vegetation, resulting in potential exposure to the plants and to animals that eat the plants. Metals deposited from the atmosphere also come to reside in the leaf litter and uppermost soil surfaces, where they can be a source of exposure for soil organisms, people, and wildlife.