REQUIREMENTS FOR MODELING TRACE METAL PARTITIONING IN OXIDIZED ESTUARINE SEDIMENTS

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ABSTRACT

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The fate of particulate-bound metals is of particular importance in estuaries because major biological energy flows involve consumption of detrital particles. The biological impact of particulate-bound metals is strongly influenced by the partitioning of metals among sediment components at the oxidized sediment—water interface. Adequate methods for directly measuring this partitioning are not available, thus a modeling approach may be most useful. Important requirements for such a model include: (1) determinations of metal binding intensities which are comparable among sediment components important in oxidized sediments; (2) comparable determinations of the binding capacities of the several forms of each component; (3) operational determinations of the abundance in natural sediments of components of defined binding capacity; (4) assessments of the influence of particle coatings and multicomponent aggregation on the available binding capacity of each substrate; (5) consideration of the effect of Ca and Mg competition on binding to different components; and (6) determinations of the kinetics of metal redistribution among components in oxidized sediments.

INTRODUCTION

Estuaries act as efficient traps for potentially toxic trace metals (Turekian, 1977). Negatively charged particles and mixed colloidal aggregates of iron hydroxides and organic materials flocculate near the freshwater—seawater interface (Sholkovitz, 1976; Murray and Gill, 1978; Sholkovitz et al., 1978). These and other types of particles readily scavenge metals from solution, sequestering high metal concentrations in suspended and bed sediments. However, the impacts upon estuarine ecosystems of particle-bound metals are difficult to predict. One of the reasons is that differences in metal bio-availability occur when metals are bound to different types of binding sites on particles (Luoma and Jenne, 1977), but quantitative methods for describing metal partitioning among binding sites in natural sediments are not available. Realistic predictions of the biological significance of metals in estuarine sediments would be greatly facilitated by the development of such methods.

Historically, efforts to quantitatively describe metal partitioning in natural sediments have involved a search for extractants which selectively remove specific forms of metals from sediments. Although such extraction data are

not without value (Luoma and Bryan, 1981), studies with well-defined components of sediments have amply demonstrated that few, if any, extractants specifically remove metals from only one component (Luoma and Jenne, 1976; Guy et al., 1978).

Quantitative models have been employed to describe metal adsorption to well-defined component surfaces, but such models have seldom been extended to the multiple component systems typical of nature. However a modeling approach may be necessary to help unravel the complexities of the partitioning process, in lieu of useful direct extraction techniques. A metal partitioning model for sediments could also be very useful in facilitating predictions of metal bioavailability from sediments.

The objective of this paper is to discuss the concepts of a multicomponent metal partitioning model for the biologically important, fine-grained, oxidized sediments of estuaries. The modeling approach should employ laboratory-derived metal binding intensities and binding site densities for individual sediment components, combined with relevant measurements of component abundance in natural sediments, to calculate competitive metal partitioning in a multi-component system with clean component surfaces. We will attempt to evaluate the available literature on metal binding intensities, binding site densities and abundance measurements for the major metal binding components of estuarine sediments. We will also discuss the effects of particle coatings and particle aggregation on partitioning, and the influence of the kinetics of metal redistribution among phases. A major goal is to help provide a focus for a synthesis of laboratory and field studies of the partitioning process.

BIOLOGICALLY IMPORTANT SEDIMENTS

To be of use in assessing metal bioavailability, a partitioning model must be relevant to the types of sediment most important to biota. The major flow of energy from primary production to consumer organisms in most estuaries is through the detrital food web, i.e., through deposit-feeding and suspension-feeding organisms (Odum and de la Cruz, 1967; Odum, 1980). These animals directly ingest metal-enriched particles and may transfer any available metals from such particles to higher trophic levels.

Although exceptions occur, detritus feeders are most commonly exposed to oxidized sedimentary particles. Suspended particles are oxidized in all but the most eutrophic estuaries. In the sediment bed, an oxidized layer of sediment usually separates anoxic subsurface sediments from the water column. This oxidized interface, operationally definable as a brown layer of sediment with a positive redox potential, is the most important zone of contact between the detritus-based food web and metals bound to the bed sediments (Johnson, 1974). Many deposit feeders, which reside deep in the sediment, use their siphons to ingest particles from the sediment surface. Others have tubes or burrows which cycle oxidized water and particles from the surface.

Meiofauna, small benthic invertebrates, live almost exclusively above the redox interface (Coull, 1979). Epifauna are exposed directly to interfacial conditions, and many benthic predators obtain their prey from at, or near, the sediment—water interface, simultaneously ingesting oxidized surface particles.

Some detritus feeders (e.g., some nereid polychaetes; Goerke, 1971) may selectively choose only specific organic particles when feeding. However, most feed "non-selectively"; mechanically separating particles on the basis of particle size or, perhaps, specific gravity (Newell, 1965; Bubnova, 1974; Whitlatch, 1974; Self and Jumars, 1978). Since the objective of such sorting is often to maximize ingestion of adsorbed bacteria and surface organic coatings, the smaller available particles are most commonly preferentially ingested (Tahgon et al., 1978). Differences occur among species in preferred mean particle size, but maximizing energy intake by maximizing ingestion of particle surface area is a relatively generalized strategy of detritus feeding.

One reason that chemical selection of particles is rare among detritus feeders is that few fine particles in estuaries occur as single, discrete minerals. Nearly all silt—clay particles in bed sediments, for example, are organic-mineral aggregates (Johnson, 1974). The end result is that most detritus feeders are exposed to all the organic and inorganic components which may bind metals in sediments. Thus, ths chemical processes controlling metal partitioning in sediments play an important role in controlling biological exposures to metals.

The type of site to which a metal is bound greatly affects the passage of metals from particles to organisms. For example, deposit-feeding clams accumulate ^{110m}Ag associated with Mn oxides 100 times more rapidly than when the metal is bound to amorphous Fe oxides, or to marsh grass detritus (Luoma and Jenne, 1977). Differences in metal uptake from different types of sediment as large as 1000-fold have been observed in clams (Luoma and Jenne, 1977). Statistical studies suggest that the nature of metal binding in sediments is similarly important in determining metal concentrations in detritus feeders in nature (Luoma and Bryan, 1978, 1979, 1982). Binding to different components also affects sediment—solute distribution coefficients and thus, may influence organisms other than detritus feeders (Luoma and Jenne, 1977).

From these generalizations it may be concluded, that, with some exceptions, the metal particle reactions which are biologically most important in estuaries are those that affect metal distributions among the organic and inorganic components of fine-grained, oxidized sediments. The remainder of our discussion will be confined to such reactions.

A MULTICOMPONENT METAL PARTITIONING MODEL

The predominant components of fine-grained, oxidized estuarine sediments which bind trace metals include the hydrous oxides of iron, aluminum and

manganese, aluminosilicate minerals, organic matter and carbonates. At equilibrium, the partitioning of a metal ion among these components is influenced by: (1) the binding capacity of each component; (2) the binding intensity of the metal ion to each component; (3) the abundance of each component in the sediment; (4) solution parameters such as pH and dissolved ligand concentrations which may influence the speciation of dissolved metal ions; and (5) the concentration of other metal ions which may compete with trace metals for the available binding sites.

Empirically, metal binding may be expressed as a simple complexation reaction

$$M_i^{z+} + S_j \xrightleftharpoons{\bar{K}_{M_iS_j}} M_iS_j \tag{1}$$

where M_i^{z+} represents metal ion i, S_j represents a surface site of component j, and M_iS_j is the surface complex. $\bar{K}_{M_iS_j}$ is a measure of the binding intensity and may be defined by analogy with equilibrium constants as

$$\bar{K}_{M_iS_j} = [M_iS_j]/([M_i^{z+}][S_j]) \tag{2}$$

where $[M_i^{z+}]$ is the activity of the free metal ion i; $[S_j]$ is density of uncomplexed surface sites on component j; and $[M_iS_j]$ is the density of surface sites of component j complexed with the metal ion i. The activity coefficients of the surface species are assumed to be one.

The total amount of metal i complexed with component j in a given sediment is the product of the abundance of component j (A_j, expressed as a weight % of the sediment) and the density of the surface complex, $[M_iS_j]$

$$\bar{M}_{i,j} = A_j [M_iS_j] \tag{3}$$

Then, the total amount of metal i bound is the sum of $\bar{M}_{i,j}$ over all j components

$$\bar{M}_i = \sum_1^j \bar{M}_{i,j} = \sum_1^j A_j [M_iS_j] \tag{4}$$

The binding capacity of component j (B_j) can be defined as the sum of uncomplexed surface sites plus those complexed with ions

$$B_j = [S_j] + \sum_1^i [M_iS_j] + \sum \text{ other complexed sites} \tag{5}$$

where other complexed sites include those which are bound to anions or other molecules. The binding capacity of the sediment (B_{sed}) then is simply the product of the abundance of each component j (A_j) and its binding capacity (B_j) summed over all j components

$$B_{sed} = \sum_1^j A_j B_j \tag{6}$$

With the above concepts defined, determination of the model parameters can now be discussed.

Binding capacity (B_j*)*

A variety of methods exist for quantifying the density of binding sites on a component. Typically, each sedimentary component has unique characteristics which make one method more appropriate than others.

Methods

(1) A frequently used method is to determine a metal adsorption isotherm at constant pH (Gadde and Laitinen, 1974; Dempsey and Singer, 1980; McKenzie, 1980). Unfortunately, it is usually difficult to saturate a surface with bound metal without exceeding the solubility of a metal hydroxide phase during the experiment. However, many studies have ignored the precipitation problem.

Precipitation of a metal hydroxide phase can be avoided by estimating the binding capacity of an adsorbent at low pH. This approach also has problems, because (a) the capacity at low pH may differ from the capacity of the component in the pH range of interest, or (b) the low pH may cause partial dissolution of the component itself, e.g., Al_2O_3, aluminosilicate minerals. Perhaps the best approach has been employed by Swallow et al. (1980), who estimated B_j by incrementally decreasing the amount of adsorbent employed, rather than increasing the metal ion concentration. With this method the authors were able to determine the binding capacity of amorphous iron oxyhydroxide at pH 8.

Many authors, assuming that their adsorption data fit a Langmuir isotherm, have determined B_j by a mathematical fitting procedure. However, few studies have verified that the Langmuir isotherm is applicable over a wide range of metal concentrations, and one recent study (Benjamin and Leckie, 1981) suggest that the Langmuir isotherm is rarely applicable for metal adsorption on hydrous oxides.

(2) James and Healy (1972) and Murray (1975) have calculated B_j by dividing the specific surface area of a solid by the estimated surface area covered by an adsorbed metal ion. This method will not be appropriate for components where factors other than surface area influence metal binding, as in metal substitution reactions (e.g. with Mn oxides), or in layered minerals with an interior surface area which is unavailable to large cations (McKenzie, 1980).

(3) The total number of hydrogen exchangeable sites can be determined by rapid tritium exchange (Yates and Healy, 1976; Davis et al., 1978). On hydrous oxides the method yields the number of surface hydroxyls present. This method might be expected to overestimate the metal binding capacity, but Swallow et al. (1980) found close agreement between the two values for amorphous iron oxyhydroxide (explained in detail below).

(4) For aluminosilicate minerals, B_j has usually been determined by ion exchange with univalent cations (van Olphen, 1977). This method is limited by the experimental conditions under which it is applied (pH, etc.) and the

assumption that one cation at saturation coverage may be fully exchanged with another cation. It also is difficult to clean aluminosilicate minerals in a way that guarantees that all coordination sites are occupied by the exchanging ion. The presence of adsorbed Fe (III) or Al (III) at exchange sites may be a significant problem (Bolland et al., 1976).

Determination of B_j *for specific components*

Hydrous iron oxides. Iron oxides occur in oxidized estuarine sediments in a continuum of states, ranging from a highly amorphous (or microcrystalline) oxyhydroxide, which forms upon precipitation, to increasingly crystalline solids which form as the initial precipitate ages. Crystallization reduces the surface area of the solid, and may alter the types of surface hydroxyls present. Davis and Leckie (1978a) estimated that the total number of surface hydroxyls on amorphous $Fe(OH)_3$ was $8 \times 10^{-3} \, mol \, g^{-1}$, but the crystalline iron oxide, goethite, has a site density of only $0.9–1.3 \times 10^{-3} \, mol \, g^{-1}$. The difference reflected the greater specific surface area of the amorphous material ($\sim 600 \, m^2 \, g^{-1}$) compared to that of goethite ($30–50 \, m^2 \, g^{-1}$). When computed on the basis of surface area, the total site densities were comparable. Characterization of the surface area of iron oxides is thus essential in studies of metal adsorption, since computations of binding capacities on a weight basis will be biased by the form of the oxide present.

Swallow et al. (1980) found that the capacity of amorphous iron oxyhydroxide for Pb(II) or Cu(II) in seawater was about equal to the total number of surface hydroxyls found by rapid tritium exchange ($\sim 8 \times 10^{-3} \, mol \, g^{-1}$). Binding capacities of this magnitude could be explained by adsorption of the unhydrated ion (Table I), but are more likely due to the loose, highly hydrated structure of the amorphous material (Swallow et al., 1980). Kurbatov et al. (1951) estimated a binding capacity of $4 \times 10^{-3} \, mol \, g^{-1}$ for adsorption of Co (which does not readily precipitate) on amorphous iron oxide at pH 8. Other estimates of binding capacity from adsorption isotherms have yielded lower values. For example, McKenzie (1980) measured adsorption densities of $10^{-4} \, mol \, g^{-1}$ for Pb(II) and Cu(II) on goethite and $4 \times 10^{-5} \, mol \, g^{-1}$ on hematite at pH 5. However, such studies may underestimate the total binding capacity at pH 8, because they were either made at low pH to avoid precipitation, or ignored precipitation.

A binding capacity can be calculated for iron oxides with the ionic radius of the metal ion and estimates of the specific surface area, as in Table I. The calculated capacity depends on whether one assumes that an unhydrated or hydrated form of the metal ion is adsorbed. The values for monolayer coverage of the hydrated metal ions lie between the experimental estimates of McKenzie (1980) and Kurbatov et al. (1951). Total binding sites for Mg on goethite are in good agreement with the area occupied by the hydrated Mg ion (Balistrieri and Murray, 1981).

TABLE I

Calculated metal binding capacity of hydrous iron oxides

Adsorbing cation	Goethite ($50 \, m^2 \, g^{-1}$) ($mmol \, g^{-1}$)	Iron oxyhydroxide ($600 \, m^2 \, g^{-1}$) ($mmol \, g^{-1}$)
Pb(II), unhydrated	1.9	22
Pb(II), hydrated	0.17	2
Co, Zn, or Cu (II), unhydrated	5.2	62
Co, Zn, or Cu (II), unhydrated	0.22	2.6
Mg (II), unhydrated	6.1	73
Mg (II), hydrated	0.22	2.7
Tritium exchange method and crystallographic calculations (Yates, 1975; Davis et al., 1978)	~ 1	~ 8

Hydrous manganese oxides. Metals bind to manganese oxide by interaction with surface hydroxyl groups (McKenzie, 1980; Balistrieri and Murray, 1982b), by exchange of the metal for Mn(II) in the solid, or by oxidation of the trace metal by Mn(IV) (Loganathan and Burau, 1973; Burns, 1976; Hem, 1978; Murray and Dillard, 1979; McKenzie, 1980). Interlayer penetration by metals may result in binding capacities which exceed predicted monolayer coverage (McKenzie, 1980). However, monolayer calculations are also affected by difficulties in the measurement of the surface area of manganese oxides (McKenzie, 1980; Balistrieri and Murray, 1982b).

Adsorption isotherms can easily be conducted in the absence of metal precipitation, because metals are bound to hydrous manganese oxides at low pH. The results for metal binding capacity are similar among various investigators. Most workers have reported metal capacity values in the range 2—$3 \times 10^{-3} \, mol \, g^{-1}$ MnO_2 (Guy et al., 1975; Murray, 1975; Dempsey and Singer, 1980; Balistrieri and Murray, 1982b). A higher capacity for Pb(II) ($6 \times 10^{-3} \, mol \, g^{-1}$ MnO_2) was observed by Gadde and Laitinen (1974). McKenzie (1980) compared the binding capacities of nine preparations of manganese oxides with different surface areas. Capacities ranged from 0.4 to $2.4 \times 10^{-3} \, mol \, g^{-1}$ MnO_2 and no correlation of binding capacity with specific surface area was observed. Thus, the binding capacities of hydrous manganese oxides are similar to those for amorphous iron oxyhydroxide (on a weight basis), but significantly greater than the capacities of crystalline iron oxides.

Organic matter. The binding capacity of the organic material in sediments is perhaps the most difficult to quantify. The sources of organic matter in estuarine sediments include autochthonous primary production, microorganisms and their exudates, and allochthonous material entering from

terrestrial watersheds. The contribution from each source may vary widely among estuaries, and hence, generalizations about the chemical properties of sediment organic matter are not easily made.

Most metal complexation studies with natural organic material have considered dissolved compounds. Such studies show dissolved natural organic material typically contains $0.6-1.2 \times 10^{-2}$ mol g^{-1} of weakly acidic functional groups, primarily carboxylic and phenolic groups (Reuter and Perdue, 1977; Perdue et al., 1980). These groups are involved in the complexation of trace metals, but the metal complexation capacity is often only about 10% of the total acidity (Chau and Lam-Shue-Chan, 1974). Reuter and Perdue (1977) suggested that most of the complexing sites were occupied by very strongly bound Fe(III) or Al(III) ions. Gamble et al. (1980), however, measured a copper complexation capacity of 5.4×10^{-3} mol g^{-1} for a soil fulvic acid.

In some cases the organic material derived from estuarine sediments by alkaline extraction has been studied (Mantoura et al., 1978). The organic matter solubilized by alkaline extraction has been operationally defined as humic substances by soil scientists (Schnitzer and Khan, 1972), a term often associated with terrestrial organic material. However, it is important to realize that an alkaline extraction of an estuarine sediment will also result in the desorption and lysis of bacterial cells and partial hydrolysis and solubilization of their exudates (Corpe, 1974; Scheraga et al., 1979). The contribution of microbial organic carbon to the extract may be dependent on the depth of sediment sampled, since the highest concentration of microorganisms is often found at the sediment—water interface. In surficial intertidal estuarine sediments, bacteria may constitute from 1 to 50% of the organic carbon (Dales, 1974; Tunnicliffe and Risk, 1977). Furthermore, living bacteria may sequester metals in sediments, not only by complexation, but also by active transport, or by actively initiating precipitation at the cell surface (Harvey, 1981). Studies of the binding capacity of a bacterial extract will not include the latter processes.

Rashid (1974) measured a capacity of 10^{-3} mol g^{-1} at pH 7 for humic acids extracted from marine sediments, but the possibility of precipitation during the experiments was not carefully considered. Guy et al. (1975) estimated that the capacity of Aldrich humic acids (extracted from peat) was 4×10^{-3} mol g^{-1} at pH 5.

Other components. The binding capacities of aluminosilicate minerals are usually determined by a cation exchange method. The capacities of most clays are not related simply to the chemistry of their exposed surfaces, but are instead manifestations of charge deficiencies within the solid phase from isomorphic substitution. The range of cation exchange capacities of some clay minerals is given in Table II. Clay minerals most abundant in estuarine sediments of eastern U.S.A. include kaolinite, illite and chlorite (Biggs, 1967; Edzwald et al., 1974). Low percentages of montmorillonite, however, may

TABLE II

Cation-exchange capacities of clay minerals

Mineral	Exchange capacity (mequiv. g^{-1})
Kaolinite	0.02—0.1
Illite	0.15—0.4
Chlorite	0.1—0.4
Smectites	0.8—1.5
Vermiculite	1.0—2.0

provide the major portion of cation exchange capacity in a sediment, and montmorillonite clays may be more abundant in other regions.

Although carbonates and sands may constitute a significant portion of the mass in some estuarine sediments, their low specific surface areas greatly reduce their metal binding capacities on a weight basis (Jenne, 1977), and they are of less concern in the finer size fractions of sediments that are more likely to be ingested by organisms.

Binding intensity ($\bar{K}_{M_i S_j}$)

In theory, the binding intensity of a metal ion may be defined by the free energy of its reaction with the surface of a given component. Unfortunately, an evaluation of the various components of the net free energy change is complex. Components may include: (1) electrostatic forces due to the presence of charge; (2) ion exchange reactions, which occur near the surface or by substitution for cations on the solid phase; or (3) formation of co-ordinative bonds with a specific surface site.

It is important to note that eq. 1 does not contain H^+ or any other ex-changeable ion as a product, and thus $\bar{K}_{M_i S_j}$ is a conditional constant, rather than a true thermodynamic constant. The major advantage of this approach is that is allows for the elimination of complex details of pH dependence, which may involve both the release of protons from surface sites and the variation of charge and potential at the surface (Davis and Leckie, 1979). Another advantage is that the surface may be treated in a fashion analogous to ligands in solution, which compete for coordination of metal ions.

It should be emphasized that a stability constant determined by eq. 2 is valid only for constant solution conditions, including pH, electrolyte com-position and concentration, temperature, etc. As a first approximation, this approach is ideal for modeling marine systems (where solution conditions are relatively constant), if the conditional stability constants are determined in a well-defined, artificial seawater mixture. Unfortunately, the requirement of constant solution conditions has not been universally recognized in the literature.

Competition of major cations, e.g., Na^+, Ca^{2+} and Mg^{2+}, for surface sites on hydrous iron oxides is probably ineffective under freshwater conditions,

since trace metals are bound very strongly (Dempsey and Singer, 1980). However, competition for surface sites could be more pronounced in seawater. A detailed study of the speciation of the goethite surface in artificial seawater has recently been completed (Balistrieri and Murray, 1981). The authors estimated that 37% of the surface sites were occupied by adsorbed Mg, Ca and Na ions. In a subsequent paper (Balistrieri and Murray, 1982a), it was shown that Cu, Pb, Cd and Zn adsorption on goethite (in seawater at pH 8) was decreased slightly by competition with Ca and Mg ions. The competitive effect was modeled with the site-binding model of Davis and Leckie (1978a).

Competition for binding sites by Ca^{2+} and Mg^{2+} ions may be more significant for organic matter than for oxide surfaces. Mantoura et al. (1978) concluded that dissolved organic compounds may play an important role in the speciation of trace metals in freshwater systems, but in seawater it was estimated that organic complexes accounted for only 10% of the dissolved Cu (II) and virtually nil for other trace metal ions, due to competition from Ca and Mg ions for the organic ligands. Rashid (1974) found that marine sediment humic acids and peat complexed large amounts of trace metals when suspended in simple electrolyte solutions. When the same materials were equilibrated with seawater, high concentrations of Ca, Mg and Na were found associated with the solids, but very low concentrations of trace metals were present. Thus, competition for complexing sites by Ca and Mg may limit the binding of many metals by organic matter in estuarine or marine sediments.

These studies emphasize the importance of determining the binding intensity ($\bar{K}_{M_i S_j}$) in a solution with composition similar to the system which is to be modeled. In situations where the concentration of major ions varies dramatically, it is necessary to know the binding intensities of both trace metal ions and major ions (Balistrieri and Murray, 1982a).

Although studies of the adsorption of metal ions on single solid phases under well-controlled laboratory conditions are numerous, it is surprisingly difficult to compare conditional stability constants among solid substrates. The greatest problem arises from the different methods employed to define the total binding site density (B_j) for a given component. The selection of units for $[S_j]$ is not important if the reaction is defined as in eq. 2, since the concentration of the complex $[M_i S_j]$ would be defined with identical units. The amount of metal i adsorbed, $[M_i S_j]$, is usually evaluated by direct analytical method. However, the density of uncomplexed sites, $[S_j]$ in eq. 2, is usually determined by subtracting the density of complexed sites, $\sum_{1}^{i} M_i S_j$, from the total site density (B_j). Thus, different methods of determining B_j affect the value of $[S_j]$, and hence, the value of $\bar{K}_{M_i S_j}$, the conditional stability constant. Another important limitation is the assumption that all sites of a component bind the metal ion i with equal intensity. It has been shown

TABLE III

Comparison of conditional stability constants of metal complexation with amorphous iron oxyhydroxide and natural organic matter at pH 8

	$Fe(OH)_3$[a]		Organics[c]	
Reactions:	$FeOH + M \underset{\longleftarrow}{\overset{K_{MOH}}{\longrightarrow}} FeOM\,(OH)$		$L + M \underset{\longleftarrow}{\overset{K_M}{\longrightarrow}} ML$	
			Seawater organics	Lake sediment organics
Metal	$\log K$ (pH 8)		$\log K$ (pH 8)	$\log K$ (pH 8)
Cu (II)	K_{MOH} 7.9		K_M 8.9	K_M 11.4
Pb (II)	K_{MOH} 9.6			
Zn (II)	K_{MOH} 6.7		K_M 5.3	K_M 5.9
Cd (II)	K_{MOH} 5.7		K_M 4.7	
Ca (II)	K_M 3.0 [b]		K_M 4.1	K_M 4.7

[a] Constants recalculated from Davis and Leckie (1978a) with total binding sites of 10^{-3} mol g^{-1}.
[b] Ca constant recalculated from Murray and Balistrieri (1981a) for goethite.
[c] Constants from Mantoura et al. (1978).

that dissolved natural organic ligands exhibit a distribution of binding intensities (Mantoura and Riley, 1975; Gamble et al., 1980), and a similar heterogeneous site model has been proposed for hydrous oxides (Benjamin and Leckie, 1981).

Despite the limitations, it is instructive to compare binding intensities among sedimentary components, employing consistent assumptions whenever possible. Table III contains conditional stability constants of metal ions with amorphous iron hydroxide (Davis and Leckie, 1978a) and dissolved natural organic matter (Mantoura et al., 1978) at pH 8. The data for $Fe(OH)_3$ were recalculated for a metal binding capacity of 10^{-3} mol g^{-1}; no correction for charge on the surface was necessary at pH 8 since this is very near the pH of zero charge for $Fe(OH)_3$.

The data in Table III indicate that Zn(II) and Cd(II) are bound more strongly to amorphous iron oxide than to dissolved organic matter at pH 8. This is also expected to be the case for Pb(II), based on stability constants with organic matter isolated from freshwater environments (Saar and Weber, 1980). Cu(II) and Ca(II) exhibit a different behavior and are bound more strongly to the organic material. The conclusions for Cu(II) and Cd(II) are consistent with the relative binding stabilities found by Oakley et al. (1981) for humic acid and iron oxyhydroxide. However, it is to be remembered, that the conditional stability constants alone are insufficient to calculate partitioning in the sediment; component abundance (A_j) is another important variable (eq. 3) which will be discussed below. Another important note is that Mantoura et al. (1978) found significant differences in binding stabilities for organic materials isolated from different environments. Stability constants for metals were greater with organics isolated from lake sediments than those for dissolved organic material in lakes, rivers and seawater.

Table III also illustrates an interesting point with respect to competition between trace metals and Ca ions for binding sites. The apparent stability constants for surface complexes of trace metals with the iron oxyhydroxide are several orders of magnitude greater than that of Ca. This behavior can be contrasted with the stability constants of these metals with organic matter (with the exception of Cu(II)). Ca-organic complexes are only slightly weaker than complexes formed by Zn(II) and Cd(II). Thus, these stability constants are qualitatively consistent with the premise presented earlier that Ca and Mg ions are effective competitors for binding sites on organic material (Mantoura et al., 1978) but not as significant when competing for oxide surface sites (Dempsey and Singer, 1980; Balistrieri and Murray, 1982a).

A constant binding intensity was assumed for all sites (S_j) in these calculations, therefore, the binding intensities ($\bar{K}_{M_iS_j}$) represent the average binding per metal ion for the particular adsorption density at which the measurement was made. Since measurements in the laboratory are usually made at greater metal concentrations than are found in nature, the conditional stability constants in Table III may be underestimates.

Metal binding to clay minerals is generally less strong than to the hydrous oxides of iron and manganese (Jenne, 1977; Oakley et al., 1981). The surfaces of clay minerals may be broadly divided into two groups: (1) the siloxane type, which are typically those of the basal planes; and (2) the hydrous oxide type, which occur at edges, in defects of structure surface and in hydrous oxide impurities on clay mineral surfaces (Greenland and Mott, 1978). Whereas many trace metals are believed to form a strong coordinative bond at hydrous oxide type surfaces (Stumm et al., 1976), the siloxane type surfaces are relatively inert. Metal ion uptake at siloxane surfaces, especially in the smectites and vermiculites, is related to the charge deficiencies of the minerals, rather than coordinative bonding, and hence is comparatively weak. Little work has been done to assess the metal binding capacity of the hydrous oxide type in clay minerals, although some authors have speculated that hydrous oxide contaminants are important (Jenne, 1968).

Abundance of sediment components (A_j)

The number of sites of a given component in a sediment sample is the product of the binding capacity of the component (B_j) and its abundance in the sediment (A_j). Defining the abundance of each type of component in a natural sediment requires measuring concentrations of the major forms of sedimentary components. Operational methods are available for a number of such measurements, although the binding capacities and intensities of many of the operationally defined forms have not been established.

Organic materials extractable from sediments by alkaline solutions (usually by 0.5 N NaOH) have been characterized in a few instances in terms of their metal binding capacity and intensity (Nissenbaum and Kaplan, 1972; Mantoura et al., 1978), but additional work is necessary. Since the abundance

of these materials can be simply measured by calibration of weight with the absorbance of the extractant, an estimate of the abundance of a characterized ligand in this operationally defined form of organic material is possible. However, specific information is needed on the consistency of absorbance per g organic carbon among different sediments.

Characterization of the organic material which is not extractable is more difficult. Less than 30% (and as little as 1%) of the organic material in estuarine sediments may be solubilized by single alkaline extractions (Luoma and Bryan, 1981). Pre-treatment of sediments to remove iron oxides (Luoma and Bryan, 1981), repeated washes with alkaline extracts, or iterative extractions with oxidizing and reducing extractants (Jenne, 1977), all result in greater extraction of organic matter than do single treatments with an alkaline extractant. Furthermore, the yield of a single batch extraction of sediment with alkaline solution is highly dependent upon the ratio of solid to extractant used, the buffer capacity of the sediment, and the method and time of equilibration, as well as other variables. Thus, single extractions are nearly always incomplete and it is inappropriate to assume that all the remaining organic material should not be considered "humic substances".

It is important to differentiate (operationally) between the amorphous and crystalline states to quantify iron oxide sites in a sediment. Since a continuum of forms of different crystallinity probably exist, no operational definition will be perfect. Partial extractions of sediments with acid ammonium oxalate remove substantial quantities of iron, but do not attack goethite, or oxide forms more crystalline than goethite (Schwertmann, 1964). Experiments suggest 25% acetic acid and $0.1 N$ hydroxylamine hydrochloride attack less crystalline states of Fe oxide than does acid ammonium oxalate (Luoma and Bryan, 1979), but no attempts to estimate the surface area of the iron oxide extracted by any of these operational methods have been accomplished.

Separation of the forms of manganese in natural sediments will be necessary to quantify the abundance of manganese oxides, since manganese oxide, manganese carbonate and organically bound manganese may all occur in estuarine sediments (Wangersky, 1962; Luoma and Bryan, 1981). Acidic extractants appear to efficiently remove all three forms of manganese, dissolving manganese oxides and manganese carbonates, and desorbing bound manganese (Luoma and Bryan, 1981). Extraction of manganese oxides at neutral (or near neutral) pH with sodium acetate (Wangersky, personal communication, 1981) or ammonium acetate may eliminate the dissolution of manganese carbonate. However, such methods probably do not remove all the manganese oxides and may desorb some bound manganese (Luoma and Bryan, 1981). Furthermore, no operational scheme quantitatively differentiates the forms of manganese oxide itself, even though differences in form have some effect on binding capacities (McKenzie, 1980).

From the above, it is obvious that the development of partitioning models will require assumptions regarding the binding characteristics of sedimentary

TABLE IV

A comparison of the range of binding capacities for several components in a variety of oxidized estuarine sediments with capacities taken from the text and abundances from Luoma and Bryan (1981)

Substrate	Apparent binding capacity ($M g^{-1}$)	Abundance Method of estimation	Concentration ($\mu g\, g^{-1}$)	Binding capacity sediment ($\mu M\, g^{-1}$)
Amorphous iron oxide [a]	10^{-3}	Acid ammonium oxalate	2000–28 000	2.0–28
	5×10^{-3}	Hydroxylamine hydrochloride	200–2800	1.0–14
Crystalline iron oxide [b]	10^{-4}	Unextracted Fe	10 000–40 000	1.0–4.0
Manganese oxide [c]	2.5×10^{-3}	Concentrated HNO_3 reflux	100–2000	0.25–5.0
Extractable organic material	10^{-3}	NaOH	400–15 000	1.4–15
Unextractable organic residue [d]	10^{-4}		2000–60 000	0.2–6.0

[a] Assume acid ammonium oxalate extract includes a fraction of more crystalline iron oxide while hydroxylamine extracts only highly amorphous iron oxide (e.g., 600 m^2 g^{-1}).
[b] Assume binding capacities of goethite.
[c] Assume all manganese is manganese oxide — a liberal estimate.
[d] Assume half of total organic carbon is plant residue, and a very low density of binding sites, as observed on cellulose and lignins (Somers, 1978).

components with concentrations measured by operational techniques. Reasonable assumptions may be extrapolated initially from laboratory characterizations of model components. In the future, however, direct studies of the characteristics of operationally-defined forms of components would be valuable.

It is instructive to compare the metal binding capacities of some of the components of estuarine sediments over the range of component concentrations observed in different estuarine environments (Table IV; data from Luoma and Bryan, 1979, 1981). Assumptions regarding site densities of each component are listed in the table. The range of binding capacities for each component of the sediment is determined by multiplying field determinations of component concentration by binding site densities determined on model phases of each component in laboratory studies.

The estimates in Table IV suggest that amorphous iron oxide and extractable organic material commonly have the largest binding capacity in oxidized estuarine sediments. The capacity of manganese oxides in sediments is generally low, because of their low abundance. Crystalline iron oxide is quite abundant, but due to its small specific surface area, this substrate has a low capacity in most sediments. The uncharacterized organic material in sediments could have a substantial binding capacity if greatly abundant, or if the density of binding sites is greater than estimated.

The data in Table IV show the wide variability in concentration which is characteristic of most components of estuarine sediments. Oxides of iron and manganese differ in concentration as the processes which affect their precipitation, coagulation or remobilization change. Humic substances, which differ in their input to aquatic environments, are highest during periods of high runoff (Wangersky, 1978) and often decline in concentration from the head to the mouth of estuaries (Wangersky, 1978). Unextractable organic residues (i.e. cellulose and lignins) are more important in estuaries with short, simple tributary systems, than in estuaries with extensive tributary systems which provide time for intensive biological reprocessing. The abundance of bacteria is strongly dependent upon the surface area of particles (Newell, 1965; Tunnicliffe and Risk, 1977).

Figure 1 compares binding capacities of several components within several specific estuaries (using the techniques employed in Table IV). Estuaries are sufficiently variable, that no one component consistently has the greatest binding capacity and there are instances where amorphous iron oxide, extractable organic substances, or uncharacterized organic materials each dominate the binding capacity (Fig. 1). There are also instances where the total binding capacity is evenly divided among several components (including manganese oxides), or, in contrast, where one component has a capacity an order of magnitude greater than any other component. Furthermore, the total binding capacity of the sediment differs considerably among estuarine environments.

From the variability in binding capacities observed in Table IV and Fig. 1
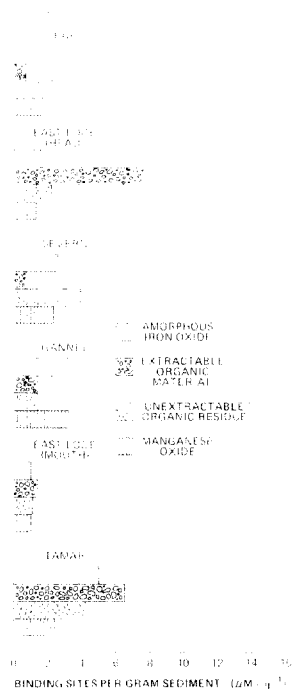
Fig. 1. Comparisons of binding site densities (as defined in Table IV) of four components in sediments of six different estuaries.

it may be concluded that the partitioning of a specific metal is highly dynamic in both space and time in estuaries, except where binding intensity to a generally abundant component greatly exceeds that for other components. Such a conclusion is consistent with statistical assessments of metal partitioning in estuarine sediments reported by Luoma and Bryan (1981). The competitive effects of Ca and Mg may also be expected to play an important role in balancing the large binding capacities of some organic materials in estuaries, driving the partitioning of many metals (Cu excluded) to components where Ca and Mg competition is less effective than would be expected from measured capacities alone. This effect is consistent with the sequences of apparent binding intensities observed in seawater by Oakley et al. (1981)

$$Cu(II): MnO_2 \gg humics > Fe(OH)_3$$
$$Cd(II): MnO_2 > Fe(OH)_3 \gg humics$$

COATINGS AND AGGREGATED PARTICLES

The multicomponent model derived above implicitly assumes that the components of the sediment do not interact with each other. In fact, fine grained sediment particles most commonly occur as complex aggregates,

containing interlayered and intermeshed iron oxide coatings, organic coatings, and discrete manganese oxide particles, often surrounding a clay particle (Jenne, 1977). In this case, the binding capacities of pure phases would not necessarily equal the capacities available to compete in trace metal partitioning in a real sediment.

A number of lines of evidence support the common occurrence of coatings and aggregate particles. Microscopic observations show that nearly all clay--silt particles in estuarine surface sediments resemble aggregates (Johnson, 1974). Concentrations of iron and organic materials correlate with the abundance of fine particles in sediments, suggesting both components occur, at least partially, as surface coatings on particles (Jenne, 1977). Relatively rapid (several days) coating of particles by bacteria and their exudates has been observed in the laboratory (Corpe, 1975). Simultaneous flocculation of colloidal iron oxides and organic material at the freshwater—seawater interface has been observed, generating complex, aggregated particles in which these two components are intermixed (Sholkovitz, 1976).

Although manganese concentrations are not always correlated with particle surface area, manganese oxides may be an important component of aggregate particles. Sundby et al. (1981) demonstrated that 80% of the manganese in near-bottom suspended sediments occurred as, "weak enrichments ($<1\%$) on a background of otherwise undistinguished particles". Manganese was also observed as a stronger enrichment (1--20%) in 10--20 μm-sized particles.

Particle aggregation and the formation of surface coatings may strongly influence the availability of a given component to metal ions. The total metal binding capacity may not change significantly, but the types of surface sites available and their binding intensity could be greatly affected (Davis and Leckie, 1978b; Hunter, 1980). For example, many particles rapidly assume a common surface charge when immersed in low concentrations in seawater or lakewater (Neihof and Loeb, 1972; Davis and Gloor, 1981). The charge assumed may differ greatly from the intrinsic surface charge observed when the particles are suspended in artificial lakewater or artificial seawater. Several lines of evidence suggest the original surface sites on suspended particles may be covered by adsorption of dissolved organic matter from solution. Both viable (Corpe, 1975) and non-viable organic material (Davis and Gloor, 1981; Tipping, 1981; Davis, 1982) are capable of rapidly coating particles. Balistrieri et al. (1981) presented evidence that the scavenging of trace metals by suspended marine particulate matter is better correlated with the complexation properties of organic ligands than the properties of oxide surfaces.

Although adsorption of organic matter may cover surface sites on suspended inorganic particles, this effect may be balanced at the sediment--water interface by the continuous regeneration of fresh amorphous oxides. In estuaries, iron and manganese may be solubilized in the reducing environment of subsurface sediments and reprecipitate as amorphous forms near the surface. Sundby et al. (1981) estimated that 32--75% of Mn deposited in

the sediments of the St. Lawrence Estuary was remobilized after burial. Movement of Mn^{2+} from the subsurface to the surface in the St. Lawrence sediments occurred both by diffusion and by mixing of surface and interstitial waters. Manganese oxide then precipitated near the surface, at the redox interface, resulting in a cyclic enrichment of the surface sediment in Mn oxide. A similar process for continually regenerating and enriching the amorphous iron oxide component in surface sediments was suggested by Gobeil et al. (1981). Hem (1978) suggested that the cycle of burial → dissolution → diffusion → reprecipitation could be very important in regenerating manganese oxide sites available for metal binding. Eaton et al. (1980) observed an instance of site regeneration of metal partitioning among suspended sediments in Chesapeake Bay. During most of the year, statistical correlations suggested zinc in the suspended matter of the bay was associated with an iron oxide component. However, during a period of manganese release from sediments and precipitation of manganese oxide in the water column, the Fe—Zn correlation became insignificant. Generation of available manganese oxide sites in the water column appeared to cause at least some redistribution of zinc from iron oxide to manganese oxide.

Perhaps the most obvious net effect of coating and aggregate formation is to reduce the sites of aluminosilicate minerals which are available to metals. Aggregate particle formation appears to occur most often around a clay "nucleus" (Khailov and Fenenko, 1968; Jenne, 1977). Iron oxide coatings on clay minerals are especially evident in situations where amorphous iron oxide is precipitating (Fordham, 1973; Greenland and Mott, 1978). Davis (1982) has shown that the reactive edge sites of kaolinite may be coated with adsorbed organic matter. Thus, clays occur as coated carriers of other sediment components important in metal binding, but are unlikely to have a large number of unoccupied binding sites (Jenne, 1977). Furthermore, no mechanism analogous to the redox sensitivity of iron and manganese oxides is available in estuarine sediments for regenerating available binding sites on clays.

Oakely et al. (1981) concluded from model calculations that clays would dominate Cu and Cd partitioning in oxidized sediments. Their model included multicomponent calculations, as suggested here, using binding capacities estimated from natural sediment abundances and binding intensities assumed from (Langmuir) adsorption isotherms determined in the laboratory. The dominating effect of the clays was based upon their abundance in the sediment, without consideration of the availability of the surface. Given the aggregated nature of natural particles and the tendency of clays to become coated with layers of other components, it is likely their conclusion is not applicable to many estuaries.

Interactions among sediment components to form aggregates in nature undoubtedly result in differences between available site densities and site densities measured on pure components. Processes occur which would: (1) favor a substantial reduction of sites on clays (coatings with other substrates);

(2) coat surface sites with adsorbed organic ligands (Davis, 1982); and (3) continuously regenerate available oxide surfaces (precipitation of Fe and Mn hydroxides at the sediment—water interface). The net result of these processes on available binding capacities must be better understood before a realistic model of metal partitioning in natural sediments is possible.

METAL REDISTRIBUTION

Another important question which must be resolved concerns the rate of metal redistribution in response to temporal changes in component abundance. Changes in the abundances of particle components such as iron, manganese and organic carbon often accompany seasonal hydrologic changes in estuaries. Whether metal partitioning in surface sediments reflects the form in which metals are scavenged from the water column, or the characteristics of the surface sediments themselves, is not well known. Metal ions eventually redistribute among forms if they are buried beneath the redox interface in sediments. Oakley et al. (1980) suggested that the distribution of metals in anoxic sediments was independent of the form of introduction to the sediments and that redistribution occurred within 2 –3 days. However, ambiguities exist in the interpretation of their selective extraction procedures which led to these conclusions. Moreover, their conclusion may not apply to oxidized sediments. Thus, the kinetics of redistribution remains an important and unresolved question.

CONCLUSIONS

A quantitative model of metal partitioning in multicomponent natural sediments would be an important aid in assessing the biological impact of the large reservoir of particle-bound metals in estuaries. Such a model is relatively simple to describe conceptually, but determination of model parameters is more difficult. Inconsistencies in methodology deter precise comparisons of binding capacities and binding intensities among the important components of sediments. Operational measures of component abundances in natural sediments have seldom been combined with descriptions of the binding characteristics of the measured components. Little is known about the effects of coating and particle aggregation on the partitioning process, or about the kinetics of repartitioning when sediment characteristics change.

On the optimistic side, solutions to many difficulties of parameter determination are within the capabilities of available geochemical techniques. Such solutions will require combining the specific interests of the surface chemist with the more general interests of field-oriented workers. The value of such a merger lies in focusing the divergent approaches of these groups on a single problem of biological, geochemical and environmental relevance.

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