

A COMPARISON OF TWO METHODS FOR DETERMINING COPPER PARTITIONING IN OXIDIZED SEDIMENTS

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ABSTRACT

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Model estimations of the proportion of Cu in oxidized sediments associated with extractable organic materials show some agreement with the proportion of Cu extracted from those sediments with ammonium hydroxide. Data were from 17 estuaries of widely differing sediment chemistry. The modelling and extraction methods agreed best where concentrations of organic materials were either in very high concentrations, relative to other sediment components, or in very low concentrations. In the range of component concentrations where the model predicted Cu should be distributed among a variety of components, agreement between the methods was poor. Both approaches indicated that Cu was predominantly partitioned to organic materials in some sediments, and predominantly partitioned to other components (most probably iron oxides and manganese oxides) in other sediments, and that these differences were related to the relative abundances of the specific components in the sediment. Although the results of the two methods of estimating Cu partitioning to organics correlated significantly among 24 stations from the 17 estuaries, the variability in the relationship suggested refinement of parameter values and verification of some important assumptions were essential to the further development of a reasonable model.

INTRODUCTION

Sediments constitute a concentrated reservoir of trace metals in aquatic environments. The distribution of metals among specific components in a sediment (defined here as metal partitioning) largely determines the fate of sediment-bound metals (i.e. the extent to which the sediment acts as a permanent repository for metals or a temporary reservoir from which metals are recycled to solution or food webs). For example, Luoma and Jenne (1977) showed that sediment–solute distributions varied by orders of magnitude when Ag, Co and Zn were bound to different components of the sediments such as iron oxides, manganese oxides or carbonates. Controlled studies have also shown that metal availability from sediments to deposit feeding animals differs greatly when such organisms ingest metals bound to different sedimentary components (Luoma and Jenne, 1976, 1977; Harvey and Luoma, 1985, 1986).

The characteristics of metal binding in well-defined media to specific well-defined surfaces (oxides and organic materials) have been described conceptually.

ally and quantitatively (James and Healy, 1972; Hohl and Stumm, 1976; Davis and Leckie, 1978). However, extrapolating those descriptions to the aggregated, multi-ligand, multi-component surfaces (Luoma and Davis, 1983) that occur in natural sediments is difficult. Only relatively crude 'operational' methods are available to separate metals from specific components of the sediment or empirically define metal-component associations in sediments. These include sequential extractions (Engler et al., 1977; Tessier et al., 1979) and statistical correlations (Luoma and Bryan, 1981), both of which require assumptions that may not always hold in natural sediments.

In lieu of precise empirical methods, equilibrium modelling, analogous to the methodology employed to describe metal speciation in solution quantitatively, ultimately could prove very useful in defining metal partitioning in sediments. However, at the present state of knowledge, even the simplest partitioning models require assumptions that have not been verified, and approaches to estimating parameter values that do not thoroughly consider the complex realities of nature (Luoma and Davis, 1983). Nevertheless models describing metal partitioning in natural and experimental settings have begun to appear in the literature.

Oakley et al. (1981) calculated Cu and Cd partitioning among a mixture of clays, organic materials, iron oxides and manganese oxides in laboratory experiments. Davies-Colley et al. (1984) extended that work to mixtures of components with empirically defined binding characteristics and to a hypothetical natural sediment. They concluded that iron oxide was the most important component binding Cd in all systems, and that Cu was predominantly bound to organic materials and, to a lesser extent, iron oxides. Tessier et al. (1985) employed a partitioning model to calculate binding intensities for Cd, Cu, Ni, Pb and Zn in three lake sediments. They then compared the results with values that were assembled from empirical studies by other authors for binding intensities to iron oxides alone. The calculated lake sediment values generally fell within the 100-fold variation characteristic of the iron oxide values (the large variation in the empirical iron oxide binding intensities resulted from the use of different types of iron oxides and different media in the various studies cited). The authors concluded iron oxides were important in the partitioning of all the metals involved.

Adequate verification of conclusions that are drawn from model calculations, such as those above, is inherently difficult because of the limitations of the available empirical methods. Oakley et al. (1981) employed a sequential extraction for verification of calculated partitioning in their experiments. However, the approaches were compared only in experiments with synthetic sediments and the extractions required assumptions of questionable validity regarding phase selectivity. Davies-Colley et al. (1984) attempted no verification of the partitioning they described in the hypothetical natural sediment; and Tessier et al. (1985) indirectly assessed the validity of their conclusions by comparing pore water metal concentrations to concentrations predicted to be in equilibrium with (undefined) iron oxide phases. Similarly, none of the stu-

dies published to date have tested the sensitivity of their conclusions to differences in model parameters.

The work presented here attempts to test the validity of the calculated partitioning of Cu to organic and inorganic components of 24 different oxidized estuarine sediments by comparison with the results of an empirical method of assessing that partitioning. Because both methods are simplistic and operational in nature, the inherent assumptions of both are emphasized. The sensitivity of the model results to variations in parameter values also is assessed. The goal of the paper is to determine how seriously the assumptions and simplistic methods of parameter value determination distort the results of partitioning models, relative to extraction results. This comparison will then be used as a vehicle to discuss types of future studies that might improve the available methods of determining partitioning.

METHODS AND MATERIALS

The sediments employed were those discussed in Luoma and Bryan (1981), and data on concentrations of metals and components in specific samples are published there. The samples were collected from the intertidal surface-oxidized layer of sediment from 24 stations in 17 estuaries in southwest England. The estuaries differed widely in their physicochemical characteristics, thus no more than two stations from any single estuary were considered here to avoid biasing the results toward any specific type of geochemical environment.

Extraction techniques

Copper was chosen for this comparison because extraction of Cu by the methods employed is more likely to be semi-selective than for most other metals. The concentration of Cu associated with extractable organic materials was determined by extraction of freshly collected sediments for one week employing 1 N ammonia (ammonium hydroxide; Luoma and Bryan, 1981). At high pH, Cu complexes sufficiently strongly with at least some organic ligands that precipitation as a hydroxide (Luoma, unpublished data) or resorption to undissolved sedimentary materials (Rendel et al., 1980) should be minimal within the extract (i.e. at least the Cu most strongly associated with extractable organic materials should be taken into solution). Inorganically associated Cu was estimated independently (i.e. from a separate aliquot of sediment) by extraction with 25% acetic acid (pH = 2.2; 2 h extraction; sediment:extractant = 50:1). The extraction could desorb Cu from weakly bound organic ligands (non-specific desorption is a serious problem with low-pH extractions of metals that bind less strongly than Cu to organics; Luoma and Jenne, 1976; Guy et al., 1977). However, Luoma and Bryan (1981) showed that the sum of acetic-acid-extractable and ammonia-extractable Cu equalled the Cu extractable by 1 N HCl in the set of estuarine sediments that will be employed to

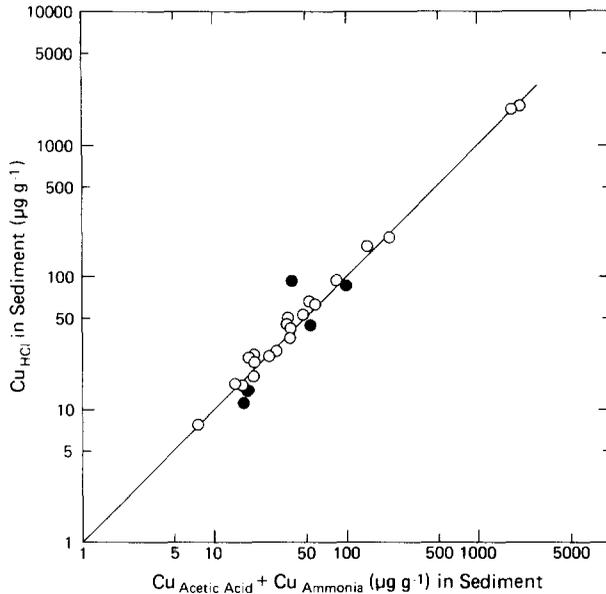


Fig. 1. Relationship of the sum of two independent sediment extractions, Cu extracted by ammonia and Cu extracted by acetic acid, with Cu extracted by a third independent extraction of the same sediment (Cu extracted by 1.0N HCl). Data are the same as employed in comparison of model calculations with extraction results.

compare Cu extractability with computed partitioning in this paper (Fig. 1). This suggested little overlap occurred between the fractions of Cu removed by the two extraction methods, and thus they might be useful indicators of organic/inorganic Cu partitioning within the HCl-soluble fraction of Cu in these sediments. When the proportion of Cu extracted by either ammonia or acetic acid is presented in this paper, it will be defined relative to 'adsorbed' (i.e. HCl-soluble) metal.

Model methodology

Model calculations followed the approach suggested by Luoma and Davis (1983), and are similar to calculations of partitioning reported by Davies-Colley et al. (1984). The model assumes that at equilibrium, metal binding may be expressed as a simple complexation reaction



where M_i represents metal ion i , S_j is a surface site of component j and $M_i S_j$ is the surface complex. $K_{M_i S_j}$ is a measure of the binding intensity and may be defined by analogy with equilibrium constants as

$$K_{M_i S_j} = [M_i S_j] / ([M_i] [S_j]) \quad (2)$$

where $[M_i]$ is the activity of the free metal ion i , $[S_j]$ is the density of uncomplexed surface sites on component j and $[M_iS_j]$ is the density of surface sites per unit mass of component j that are complexed with the metal ion i . The activity coefficients of the surface species are assumed to be one. Equation 2 can be rearranged to illustrate the factors that determine the concentrations of metal i associated with component j

$$[M_iS_j] = K_{M_iS_j} \cdot [M_i] \cdot [S_j] \quad (3)$$

To calculate the concentration of metal i associated with component j in a multi-component sediment sample the binding capacity of the component must be estimated per unit mass of sediment (B_j). Both the number of sites per unit mass of component (S_j) and the mass of component per unit mass of sediment (A_j) must be included in that estimate, i.e.

$$B_j = [A_j] \cdot [S_j] \quad (4)$$

then the concentration of metal associated with that component is

$$M_iS_j = K_{M_iS_j} \cdot [M_i] \cdot [S_j] \cdot [A_j] \quad (5)$$

The total amount of metal bound in the sediment is the sum of M_iS_j over all j components

$$\Sigma M_iS_{1\dots j} = M_iS_1 + M_iS_2 + \dots M_iS_j \quad (6)$$

Proportional partitioning of the metal to any specific component (P_j) can be calculated from estimates of $K_{M_iS_j}$ and B_j for each component, for any M_i , from, for example

$$P_1 = M_iS_1 / \Sigma M_iS_{1\dots j} \quad (7)$$

Although the partitioning model itself is relatively straightforward, obtaining the values to conduct the calculations necessitates some important assumptions. For the calculations in this paper we will assume the following:

(1) The most important sedimentary components competing for Cu partitioning in oxidized sediments are the more amorphous fraction of iron oxides, manganese oxides and the extractable fraction of organic materials. Clay surfaces are unlikely to be able to compete in most partitioning processes (Jenne, 1977; Luoma and Davis, 1983; Davies-Colley et al., 1984), and both unextractable organic materials and crystalline iron oxides contain orders of magnitude fewer sites per unit mass than the above components.

(2) All components behave independently, and are not affected by interactions with other components or by different states of dispersion.

(3) Binding to each component can be characterized by a single value of $K_{M_iS_j}$.

Values for specific model parameters were obtained as follows. Values for $K_{M_iS_j}$ were those obtained empirically by Davies-Colley et al. (1984) reported as $\log K_p$ at pH 7.9 in 35‰ seawater (Table I). A_j was obtained empirically from

TABLE I

Values employed in calculating Cu partitioning in oxidized estuarine sediments

	$\log K_j$	Extractant used in determining A_j	Site density (S_j) (M g^{-1})
Fe oxide _{am}	3.5	Acid ammonium oxalate	10^{-3}
Mn oxide	3.80	Concentrated nitric acid	2.5×10^{-3}
Extractable organic material	3.80	1 N Ammonia	10^{-3}

each sediment sample. Concentrations of amorphous iron oxides were determined from concentrations of Fe in acid ammonium oxalate extractions of recently collected sediment (particles $< 100 \mu\text{m}$). This extractant removes most Fe less crystalline than goethite, and some magnetite from oxidized sediments (Schwertmann and Fisher, 1973; Chao and Zhou, 1983). Manganese oxide concentrations were estimated from total Mn concentrations in the sediments (assumes all Mn in oxidized sediment is manganese oxide). Extractable organic materials were obtained from absorbance measurements calibrated to milligrams of organic material by Luoma and Bryan (1981). S_j were those reported by Luoma and Davis (1983, Table I). To obtain the S_j for amorphous iron oxide it was assumed that the iron extracted by acid ammonium oxalate contained five-fold sites per unit mass than freshly precipitated iron oxide (reported by

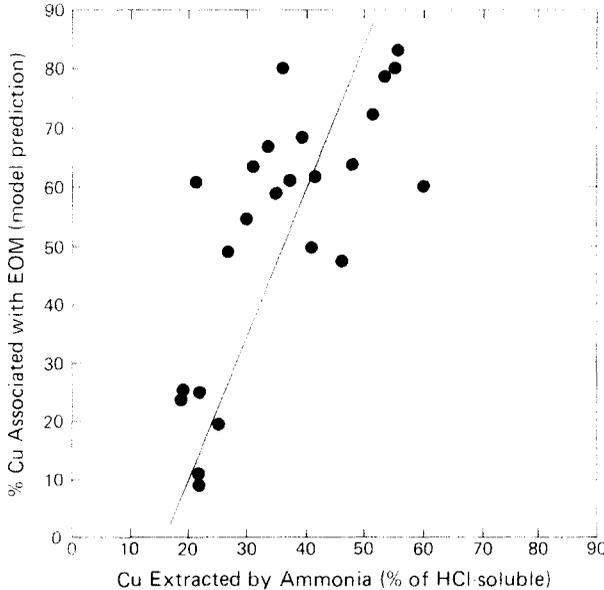


Fig. 2. Correlation of the percentage of Cu calculated to be associated with extractable organic material (EOM) with the percentage of HCl-soluble Cu extracted by ammonia. $r = 0.62$; $p < 0.001$.

Davis and Leckie, 1978, as $5 \times 10^{-3} \text{Mg}^{-1}$), and five-fold more sites per unit mass than the values for goethite measured by Davis and Leckie (1978). An example calculation employing these parameters is shown in Appendix I.

RESULTS

The overall correlation between model results and extraction results among the 24 stations showed substantial variability (Fig. 2; data tabulated in Appendix II). The proportion of Cu predicted to be associated with EOM from the model was correlated significantly with the proportion of adsorbed Cu extracted with EOM ($r = 0.62$; $p < 0.001$; Fig. 2). The significance of the correlation was driven by the consistently low extractability of Cu by ammonia at those stations where computations suggested substantially less Cu should be partitioned to the organic phase than to inorganic phases (i.e. stations where iron and manganese concentrations were high compared to concentrations of EOM). Similarly, at most stations where the computations suggested Cu should be partitioned predominantly to EOM, Cu was much more extractable by ammonia than by acetic acid. However, the extractability of Cu by ammonia was never as great as predicted from the model in these latter sediments. At stations where the model suggested a relatively even distribution of Cu among components (where differences between EOM and iron plus manganese were

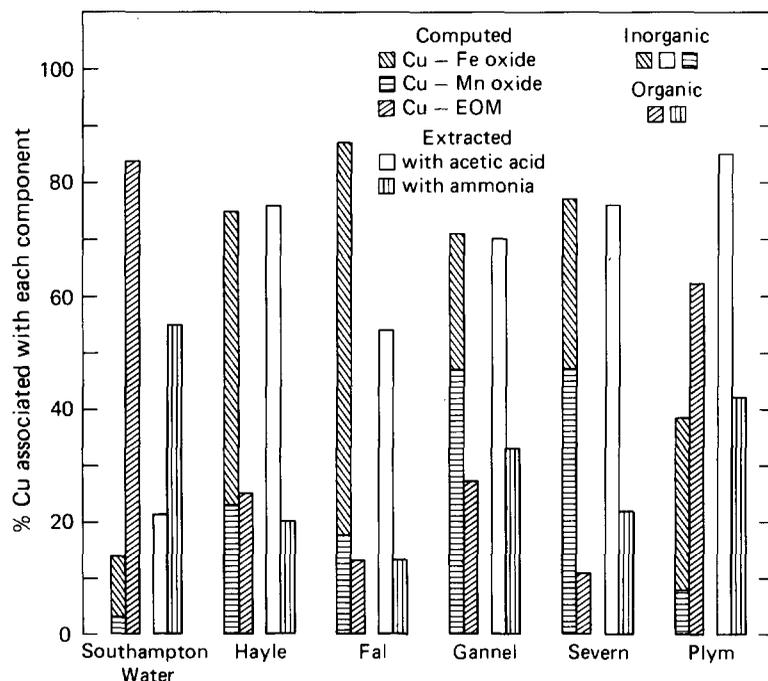


Fig. 3. The calculated distribution of Cu between extractable organic material (EOM), iron oxide (ammonium oxalate-soluble Fe) and manganese oxides and the proportion of Cu extracted by ammonia (organic) and acetic acid (inorganic) from the sediments of six estuaries.

less extreme), consistent agreement between model and extraction results was not observed.

The above results are more clearly demonstrated in Fig. 3 where computed Cu partitioning and Cu extractability are shown for several individual sites. For example, concentrations of EOM at Southampton Water were as high as anywhere in the study, and concentrations of Fe and Mn in the sediment were moderate. The calculations suggested that 83% of the Cu might be partitioned to EOM. The extractions also showed that substantially more of the adsorbed Cu was extracted by ammonia (56%) than by acetic acid (22%). In contrast, the fraction of Cu calculated to be associated with iron and manganese oxides together at sites in the Hayle, the Fal, the Gannel and the Severn estuaries was much larger than the fraction of Cu calculated to be associated with EOM (because these estuaries contain high concentrations of the former components and low concentrations of EOM in their sediments). A much higher proportion of the 'adsorbed' Cu also was extracted from these sediments by acetic acid than by ammonia. It is also interesting to note that the model suggested that manganese oxides might dominate the partitioning of Cu in the Gannel or the Severn, while iron oxide was dominant in the Hayle and the Fal. However, extraction techniques that might validate such results are not available.

The poorer agreement between model-calculated partitioning to EOM and ammonia extraction results in sediments where Cu was not predicted to be

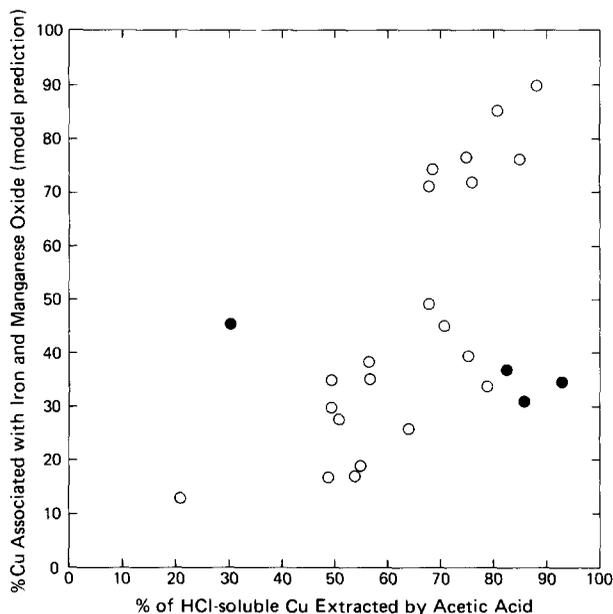


Fig. 4. Correlation of the percentage of Cu calculated to be associated with iron oxides and manganese oxides with the percentage of HCl-soluble Cu extracted by 25% acetic acid. $r = 0.48$; $p < 0.05$.

predominantly distributed to any component is illustrated by the Plym estuary results in Fig. 3.

The proportion of acetic-acid-extractable Cu correlated more weakly with the calculated partitioning of Cu to iron and manganese oxides (Fig. 4; $r = 0.48$; $p < 0.05$). In general, the acetic acid extractability of Cu was greater than predicted by the calculations where the model suggested only one-third to one-half of the Cu should be associated with iron oxide and manganese oxide together. Thus, as with EOM, agreement between the extraction and the model was most evident where calculated distribution to the specific component was very high and agreement was poor where the calculations suggested Cu was relatively evenly distributed among components.

To test the sensitivity of the correlation to variations in model parameters, partitioning was recalculated assuming a 2.5-fold increase in K_{M,S_j} for iron oxide (from 3.25 to approximately 3.65) or a 2.5-fold greater number of sites extracted per unit mass (i.e. 2.5×10^{-3} instead of 10^{-3} M g^{-1}). These changes increased the importance of the iron oxide component in binding Cu at the expense of the other two components. However, the changes were small where iron oxide already dominated partitioning or where a strong domination by EOM occurred. Thus the effect on the correlation was insignificant (an increase in the correlation for organic partitioning from $r = 0.62$ to $r = 0.64$). Where the methods agree best, therefore, the conclusions of the model calculations were relatively insensitive to small errors that might occur in estimating model parameters.

DISCUSSION

Both the model calculations and the extractions clearly indicate that Cu is not partitioned exclusively to a single component of estuarine sediment, and that Cu distribution among components may change from sediment to sediment as component concentrations change. Statistical assessments of Cu distributions in the same sediments led to similar conclusions in earlier studies (Luoma and Bryan, 1981). This general conclusion held when 2.5-fold changes in model parameters were introduced, because of the very large differences among some sediments in the relative concentrations of components. Thus all available approaches suggest that Cu competitively partitions among a variety of components in oxidized estuarine sediments, and that partitioning is driven by the highly variable chemical characteristics of those sediments.

Some agreement was evident between the fraction of Cu calculated to associate with extractable organic materials and the fraction actually extracted with that material; but this agreement was restricted primarily to situations where either the organic or inorganic component occurred in very high concentration relative to the other and thus strongly dominated partitioning. This also was the reason why the correlation of model and extraction results was insensitive to changes in model parameters.

Even if restricted to instances where partitioning is heavily dominated by a single component, agreement between calculated partitioning and an extrac-

tion in natural sediments is surprising given the weaknesses inherent in both. The organic extraction is not completely efficient at removing all organically complexed Cu (Luoma and Bryan, 1981), and if it is selective it is only so for Cu and metals with similarly strong binding intensities for organic materials. The acetic acid extraction is probably of even poorer selectivity. Especially where the model suggests Cu may be distributed among a number of components, acetic acid appears to desorb more metal than expected from the calculations or from the HCl extractions. Enhanced acetic acid extractability could result from desorption of Cu bound to weak organic ligands in these sediments or of Cu associated with sites other than amorphous iron or manganese oxides (e.g. with clays, lignins, cellulose or crystalline iron oxides). Whatever the mechanism, weaknesses in the assumption of selectivity probably contribute to the weakness of the correlations.

Inaccuracy of assumptions and in the methods for obtaining values for parameters undoubtedly limit the accuracy of the model calculations; although the extent of such effects in natural systems is unknown. Several potential problems with the model calculations are possible.

(1) The model assumes equilibrium conditions. In many systems, especially estuaries and rivers, equilibrium in metal reactions, whether between sediments and water or among sedimentary components, may be the exception rather than the rule. On the other hand, the accuracy of model predictions will improve as a system approaches equilibrium. Because complete equilibrium is not necessary for a reasonable estimation of partitioning, the equilibrium assumption may not be debilitating to model accuracy where chemical conditions change more slowly than the reactions that control partitioning.

(2) The accuracy of the equilibrium assumption will be determined by the kinetics of metal partitioning. Oakley et al. (1980) suggested that the ultimate distribution of metals in an anoxic sediment mixture was independent of the form of introduction to the sediments, and that redistribution occurred within 2-3 days. The relevance of their results in oxidized systems remains to be established, however. In highly dynamic estuarine locations the largest changes in major sediment characteristics such as particle size, iron oxide concentrations and organic carbon concentrations occur on time scales of weeks to months (Thomson-Becker and Luoma, 1985). If the kinetics of metal exchange among sediment components are sufficiently rapid that equilibrium is approached within several days, then the assumption of equilibrium may be sufficiently valid to allow reasonable estimation of partitioning from an equilibrium model in many situations in nature. Obviously, obtaining further information about the kinetics of metal exchange between competing solid surfaces remains an important goal in development of a partitioning model.

(3) The model assumes that binding intensity can be described by discrete coefficients for each metal-component combination. In fact a continuum of binding intensities between iron oxides and Cd was observed by Benjamin and Leckie (1981) over a range of adsorbent/adsorbate ratios, and may be true of many types of component surfaces. The critical question for model develop-

ment is whether metal concentrations in natural systems saturate specific component surfaces sufficiently to cause changes in binding intensity large enough to drastically affect model results. Tessier et al. (1985) suggested that metal concentrations in several lake sediments were within a small enough range that a single value adequately described metal binding intensity to iron oxides. However, further study of this complexity is essential to development of a realistic partitioning model.

(4) Most model calculations of partitioning depend (implicitly or explicitly) upon some estimate of site density for each component involved. Laboratory determinations of site densities on the surfaces of individual components such as manganese oxides, amorphous iron oxides, humic substances, cellulose/lignin organic materials, clays and various forms of crystalline iron oxides have been made (reviewed in Luoma and Davis, 1983). These estimates are not always comparable; and much room for improvement and increased consistency remains in developing such estimates. Compared to other potential errors in model calculations the available numbers can be useful, however, and presumably will become more reliable if future work emphasizes applications to natural systems.

(5) The methodology for estimating the site density for each component in natural sediments is one of the weakest parts of the modelling approach. Although component abundances can be measured, the site density of each of the components in such a multi-component mixture is difficult to determine directly, partly because components occur as aggregated mixtures. Davies-Colley et al. (1984) estimated component abundances from total concentrations of iron and manganese, and from an assumption that 50% of total organic carbon was humic substance. The use of total concentrations is an obvious source of error because site densities per unit mass of both iron and manganese oxides vary greatly with the characteristics of the oxide (Davis and Leckie, 1978; McKenzie, 1980). The proportion of total organic material that occurs as humic substance (EOM) also varies greatly among sediments (e.g. Mayer, 1985; Thomson-Becker and Luoma, 1985). Extractable organic material can be selectively removed from sediments and its binding characteristics determined (Gamble et al., 1980; Perdue et al., 1980; Davies-Colley et al., 1984). It is more difficult to determine the exact quantity and especially the form of manganese oxide in a natural sediment. However, the characteristics of the iron oxides extracted from sediments and soils by different partial leachates have been well studied (Chao, 1984; Chao and Zhou, 1983). Thus, extracting freshly collected, oxidized sediments (Thomson et al., 1980) with an extractant such as acid ammonium oxalate more closely satisfies the assumption that the fraction of iron extracted from each sediment has a similar site density per unit mass of iron than does measuring total concentrations. The next step is a more accurate definition of the site density in the actual fraction of iron soluble in the extractant. Ultimately, definition of component abundances in natural sediments on the basis of site density rather than mass would be the optimum approach to providing accurate parameter values for modelling.

(6) The model calculations also assume that all components behave independently and are not affected by interactions associated with aggregation (i.e. they assume aggregation of multiple components has no effect upon the surface of specific components available for binding metals). Davies-Colley et al. (1984) reported that the adsorption behaviour of Cd in a mixture of clays with iron oxide and organic materials was similar to what would be predicted if the metal were adsorbed by each component alone. They concluded that occlusion of adsorption sites by interaction of components did not detectably affect metal binding as long as a linear solid/solution distribution prevailed for the contributing adsorbents. This would suggest that components do not interfere with each other's adsorption properties, as long as the sites available for metal binding are not saturated. It was not possible to determine from their data whether this experiment was conducted over a range of component abundances where interactions might cause large deviations in adsorption characteristics, however. Thus, further study of this very important problem also is warranted before generalization is possible.

(7) One additional problem with model estimates is that almost nothing is known about the influence on metal binding in the sediments by some components. The most important of these is viable microorganisms. Microorganisms may constitute a significant fraction of the organic matter in sediments (in fact, microbial tissue is extracted with humic substances; Luoma and Davis, 1983); and may sequester metals in ways that are not consistent with the thermodynamic assumptions of equilibrium models (e.g. Harvey, 1981).

The degree of agreement between model calculations and extraction methods reported here is consistent with results reported in previous studies. The modelling studies of both Davies-Colley et al. (1984) and Tessier et al. (1985) found that an overall metal binding intensity of natural sediments agreed within an order of magnitude with intensities predicted from model calculations. Except in sediments where a single sedimentary component is especially dominant, model calculations are not sufficiently accurate to be taken verbatim as measures of metal partitioning. It does appear, however, that some apparent limitations to the modelling approach may be less significant in nature than previously thought (Luoma and Davis, 1983), and perhaps amenable enough to resolution that approximations of metal partitioning from a modelling approach may be possible with a reasonable development effort. Even if relatively crude, such approximations would be useful in broader studies attempting to determine the fate of metals in aquatic environments.

APPENDIX I. AN EXAMPLE OF THE CALCULATION OF COPPER PARTITIONING IN A NATURAL SEDIMENT

To calculate the concentration of Cu partitioned among the different sediment components at a site relatively enriched in EOM (Southampton Water,

Totten; partitioning shown in Fig. 3), eq. 5 must first be solved. The values of $K_{M_i S_j}$ were determined by Davies-Colley et al. (1984) at metal concentrations less than that necessary to saturate the solid surfaces (i.e. on the linear part of the adsorption isotherm). Thus all calculations assume that component surfaces are not approaching saturation in these natural sediments. If this is the case, then partitioning (to one component *relative* to another) should be independent of M_i , and that term can be omitted from the calculation (again because the goal is only to compare the proportion of partitioning among components).

To solve eq. 5 for EOM, B_j is obtained as the product of the site density per gram of EOM (best estimate from Luoma and Davis, 1983; Table I) and the milligrams of EOM per gram of sediment found at this station (19.6 mg).

Thus, from eq. 5 the Cu that could be associated with EOM is calculated as

$$\begin{aligned} \text{Cu}_{\text{EOM}}(\text{M/g sed.}) &= (\log 3.80) (10^{-6} \text{ M/mg EOM}) (19.6 \text{ mg EOM/g sed.}) \\ &= 0.124 \text{ M/g} \end{aligned}$$

Manganese concentrations at the Totten site were 0.301 mg/g; thus the Cu that could be associated with Mn is calculated as

$$\begin{aligned} \text{Cu}_{\text{Mn}}(\text{M/g}) &= (\log 3.80) (2.5 \times 10^{-6} \text{ M/mg Mn}) (0.3 \text{ mg Mn/g sed.}) \\ &= 0.0047 \text{ M/g} \end{aligned}$$

The Cu that could be associated with iron was calculated similarly employing the values in Table I and the extractable concentration of Fe in the sediments of 8.56 mg/g. That is

$$\text{Cu}_{\text{Fe}} = (\log 3.25) (10^{-6} \text{ M/mg}) (8.56 \text{ mg/g}) = 0.015 \text{ M/g}$$

Because the metal concentration available for binding (M_i) is not included in the calculation, the absolute values of Cu_{EOM} , Cu_{Fe} and Cu_{Mn} are not accurate. However, employing the sum of the values, we can calculate the proportion of Cu that should be associated with each of the individual components:

$$\% \text{Cu}_{\text{EOM}} = (0.124/0.144)(100) = 86\%$$

$$\% \text{Cu}_{\text{Mn}} = (0.005/0.144)(100) = 3.5\%$$

$$\% \text{Cu}_{\text{Fe}} = (0.015/0.144)(100) = 10.4\%$$

APPENDIX II

Percent of Cu extracted by ammonia compared to calculated estimate of percent Cu associated with EOM. Note that concentrations of Fe, Mn and EOM are available in Luoma and Bryan (1981).

Estuary	Calculated estimate of Cu_{EOM} (% of bound Cu)	Cu extracted by ammonia (% of HCl- extractable)
Fal (Old Mine)	9	22
Severn (Watchet)	11	22
Gannel (lower)	19	25
Hayle	24	19
Gannel (upper)	26	33
Hamble	47	46
Poole Harbor	49	27
Camel	50	42
Tamar (lower)	55	30
West Looe (lower)	57	38
East Looe (midway)	59	35
Beaulieu	60	60
Itchen	61	37
Tamar (upper)	61	21
Plym (upper)	62	42
Plym (lower)	63	48
Tavy	63	30
Fowey (lower)	66	33
Erme	72	51
West Looe (upper)	78	51
Fowey (upper)	80	37
East Looe (upper)	80	55
Totten	84	56

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