

A STATISTICAL ASSESSMENT OF THE FORM OF TRACE METALS IN OXIDIZED ESTUARINE SEDIMENTS EMPLOYING CHEMICAL EXTRACTANTS

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ABSTRACT

The thin layer of oxidized sediment at the sediment–water interface plays an important role in the chemical and biological interactions of trace metals in estuaries. Chemical extractants can be useful in defining trace metal interactions in sediments. Extractions may aid in determining the abundance of the operationally-defined forms of substrates which are the most active in binding metals in sediments; in operationally-defining an “extractable” phase of trace metals in sediments; and in providing information necessary for determining the bioavailability of sediment-bound metals. Comparison of 10 techniques for metal and substrate extractions among the sediments of 19 estuaries from south and west England indicate substrate characterization is best accomplished by Fe and Mn extractions with acid ammonium oxalate or 1N HCl, and humic substances extraction with 0.1N NaOH or 1N ammonia. Partial fractionation of trace metals is best accomplished with 1N HCl. Statistical relationships indicate the extractable phase of Fe is more important than total Fe in binding Ag, Cd, Cu, Pb and Zn in oxidized sediments, and the operationally-defined humic substance fraction of organic materials is highly important in binding Ag and Cu. Statistical analysis within specific subsets of data indicate trace metals are partitioned among several substrates in most sediments, the substrates compete with one another for the metals, and the outcome of the competition is strongly influenced by the concentrations of the different substrates in the sediment.

INTRODUCTION

Sediments constitute one of the most concentrated sinks of trace metals in aquatic environments. Within sediments, metals may partition among several different types of binding sites (substrates). This partitioning is greatly influenced by the physical and chemical characteristics of the sediment. Partitioning among different physicochemical forms plays an important

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role in determining the biological significance of sediment-bound metals and in determining metal exchange between sediments and water (Luoma and Jenne 1977; Luoma and Bryan, 1978; 1979).

Determining metal partitioning in the layer of sediment at the interface of the sediment bed and the water column is especially important in estuaries. The sediment–water interface plays several roles in the chemistry of trace metals: (1) The surficial layer of sediment is usually predominantly oxidized, and thus acts as a diffusion barrier for solutes migrating upward from reducing zones of sediment. Precipitation of manganese oxides and ferric hydroxides (with an associated coprecipitation of available trace metals) at the interface will control the exchange of trace elements between sediments and the water column (Hem, 1977; 1978). (2) Surface sediments on the bed of many estuaries exchange readily with suspended sediments (Conomos and Peterson, 1977); and (3) The sediments at the water–sediment interface are more important to biological fauna than are subsurface sediments. Meiofauna live exclusively above the reduced zone in sediments. Suspension feeding and epibenthic organisms are exposed directly to metals in the environment of the sediment–water interface; and most macroscopic infauna use tubes, burrows or siphons to obtain the bulk of their food and oxygen (and thus their metal burden) from the sediment surface.

The trace metal chemistry of oxidized sediments such as those at the sediment surface is more complex than that of anoxic sediments. Sulfides dominate the processes controlling metal form in reducing sediments (Morel et al., 1975). However, in oxidized sediments, organic materials, carbonates and hydrous oxides of both Fe and Mn may all compete for the binding of trace metals. (For the purposes of this discussion we will assume the term binding encompasses adsorption, complexation, coprecipitation and ion exchange.) Clays and other silicate mineral surfaces also have some capacity for binding metals. However, the strength of metal association with clay surfaces is weak relative to metal associations with substrates which would complete for binding in oxidized sediments. Thus, the most likely role of the clays in such sediments is that of a carrier for the substrates which bind metals more strongly (Jenne, 1977).

The binding substrates themselves occur in a variety of forms; and the forms of the substrates in any given sediment greatly influence the strength of metal–substrate binding processes. In estuarine sediments, major classes of organic materials include humic substances, bacteria, bacterial metabolites and refractory, non-viable organic material (e.g. cellulose and lignins). Oxides of Fe exist in layers on particle surfaces or as particles of mineralogic Fe. The crystallinity of the Fe oxides varies over a continuum from highly amorphous to highly crystalline. Manganese may occur as Mn oxides of varying structure or Mn carbonate. In turn, both Fe and Mn may also occur associated with each other or with other binding sites.

Mathematical models may be the most realistic approach to predicting metal partitioning in sediments of varying character (analogous to models of metal speciation in solution). Partitioning models would require constants

describing the strength of metal—substrate binding, and values for the relative abundances of the different forms of the different substrates present in natural sediments. Extraction of sediments with established geochemical techniques may provide information useful in such modeling efforts. Extractions could be used to describe the abundances of operationally-defined forms of substrates in different sediments. Statistical relationships between trace metal concentrations and the different substrate forms defined by the extractants may also indicate which of these substrate forms to employ in models (or the development of constants for the models).

Most recent studies employing chemical extractions have attempted to directly define metal partitioning, often implying a degree of specificity for extracting metals from single substrates which probably cannot be obtained with most procedures. Studies with chemically well-defined sediments suggest extractants which selectively remove metals from a single substrate (much less from a given form of a substrate) are the exception rather than the rule (Luoma and Jenne, 1976; Guy et al., 1978). The useful information provided by the direct extraction of trace metals may be limited to determination of a general, operationally-defined "extractable phase" of the metals, and to providing information about the biological availability of bound metals (Luoma and Bryan, 1978; 1979).

In this paper, we compare the extraction of metals and substrates from surficial estuarine sediments by 9 commonly employed geochemical techniques, and determine statistical relationships between extractable metals and extractable substrates. Our objectives are: (1) To compare the usefulness of different extractants in determining an operationally-defined "extractable" fraction of metals in oxidized sediments. (2) To assess the characterization of the different forms of some substrates (Fe oxides, Mn oxides, the humate fraction of organic materials) by different extractants, both in terms of the relative concentration of substrate extracted and the statistical correlation of extractable fractions of substrates with trace metals; and (3) To test the hypothesis, implicit in previously reported statistical models coupling metal partitioning and metal availability to deposit feeders (Luoma and Bryan, 1978; 1979), that the partitioning of metals in sediments may vary with variations in the concentrations of substrates (i.e. that substrates actively compete for metals in a sediment and that competition is concentration-dependent).

METHODS AND MATERIALS

Sample collection and treatment

Sediment samples were collected from 50 stations in 19 estuaries in south and west England (for precise geographical locations see Luoma and Bryan, 1978). Estuaries and stations were chosen to give the widest possible variability in physicochemical conditions to facilitate statistical analyses. Metal concentrations differed among stations by 1–3 orders of magnitude (Table 1);

TABLE 1

REPRESENTATIVE DATA FROM SELECTED STATIONS IN 19 ESTUARIES, UPPER REACH - SALINITY ~10‰; LOWER REACH - SALINITY 25‰. GEOGRAPHIC LOCATION OF EACH ESTUARY IN LUOMA AND BRYAN (1978).

Estuary	Reach	Organic carbon (%)	Inorganic carbon (%)	Humic material (absorbance/g), ammonia	Particle size (% < 14μ)	Fe total amorphous (percent)	Mn total (μg/g)	Total metal concentrations (μg/g)					
								Ag	Cd ^a	Co	Cu	Pb	Zn
Bristol Channel	lower	3.92	1.36	1.77	27.3	2.60	0.53	0.38	0.20	17.4	39	99	278
Torridge	lower	2.04	1.37	4.02	24.9	2.32	0.48	0.24	0.37	12.2	26	50	137
Camel	mid	2.17	2.78	6.20	19.5	2.34	0.54	0.49	0.33	10.9	88	53	190
Gannel	upper	1.40	1.69	3.46	14.0	2.71	0.62	1.75	0.61	36.1	176	1602	812
	lower	1.98	3.00	3.68	15.2	2.42	0.44	0.65	0.32	25.0	109	422	346
Hayle	lower	2.01	0.91	4.25	15.4	3.61	1.55	3.60	0.91	24.7	1170	188	943
Restronguet Creek	mid	2.49	0.10	1.79	7.0	4.84	2.65	4.52	0.83	23.2	3052	323	3544
Fowey	upper	2.46	0.007	17.35	14.9	2.23	0.32	0.52	0.32	9.1	142	75	207
	lower	2.22	0.12	8.75	13.9	2.19	0.34	0.31	0.27	8.9	120	70	180
Looe (West)	upper	2.34	0.06	18.90	15.8	3.13	0.36	1.61	0.24	12.9	64	408	176
	lower	1.26	0.41	5.06	15.9	2.68	0.25	0.26	0.16	10.4	43	123	131
Looe (East)	upper	2.24	0.05	20.03	10.0	3.15	0.33	1.71	0.35	14.2	35	92	186
	lower	1.14	1.02	3.55	18.4	2.57	0.20	0.21	0.17	10.3	37	64	108
Tamar	upper	4.32	0.04	20.66	27.8	3.23	1.02	1.22	1.03	26.9	410	186	456
	lower	3.10	0.02	11.08	27.4	3.63	0.86	0.71	0.44	18.0	282	179	363
Tavy	mid	2.77	0.09	13.54	35.1	3.79	0.72	0.35	0.42	18.0	314	190	370
Plym	upper	2.29	0.05	5.43	21.8	1.07	0.35	1.81	0.52	4.68	73	177	68
Erne	mid	3.85	0.85	19.22	22.0	3.25	0.71	0.21	0.19	13.5	31	66	141
Poole Harbor	lower	3.78	0.58	6.58	34.1	3.57	0.87	3.81	10.80	15.6	98	145	386
Beaulieu	upper	2.94	0.05	17.3	46.5	2.92	1.55	0.29	0.06	16.0	24	57	142
Test	upper	6.31	2.23	39.2	47.7	2.53	0.86	0.50	1.52	15.2	42	171	510
Itchen	mid	4.51	1.25	12.1	35.8	3.09	0.97	1.51	0.63	9.4	131	253	266
Hamble	mid	2.02	0.58	6.98	35.5	2.92	1.55	0.29	0.21	16.0	24	57	142
Elorn	upper	3.28	1.15	9.29	35.8	2.50	0.78	0.56	1.32	7.0	64	85	309
	lower	2.31	2.00	5.69	29.7	2.31	0.69	0.26	0.26	8.1	39	67	175

^a Concentration in HCl.

substrate concentrations (Fe, Mn, humic substances, total organic carbon, carbonates) varied by 1–3 orders of magnitude; metal inputs included agricultural, urban, industrial and mining wastes; and the nature of the estuaries varied from broad, sandy sediment estuaries dominated by marine processes (e.g. Gannel River) to more protected estuaries with silt–clay sediments (e.g., Tamar River).

Samples of surficial sediment were scraped from the surface layers (~5 mm deep) of intertidal sediments at low tide. For comparison, subsurface sediments were collected at 5 cm depth below the redox interface at 7 of the stations. Within 4 h of collection, sediments were sieved through 100 μ m polyethylene mesh using diluted seawater, to remove particle size biases caused by large sand grains (de Groot, 1976). Following overnight settlement (within 24 h of collection) the 100 μ m sediments were either extracted wet or dried at room temperature.

In the interest of developing sediment characterization schemes that were of maximum use in correlations with biological variables (Luoma and Bryan, 1978; 1979) and that allowed collection of statistically useful quantities of data, every effort was made to keep the chemical treatments as simple as possible. Subsamples of wet sediment were collected from a slurry using a pipette sampler while swirling. Each subsample was treated with a different extractant, i.e., samples were not extracted sequentially. Duplicate subsamples were washed with distilled water then dried at 80°C to obtain salt-free weights. Dry weights (250–550 mg) seldom varied by more than 10 mg between replicates. Salt-free weights were calculated for the dried samples from the salinity of the water used in the sieving procedure. Extractions were carried out in 20-ml glass scintillation-counting vials, which were shaken at frequent intervals. The extract was separated from the sediment by filtration under pressure through a 0.45- μ m membrane filter. The filtrates were analyzed for Ag, Cd, Co, Cu, Fe, Mn, Pb and Zn by atomic absorption spectrophotometry. Background correction was used in Ag, Cd, Co and Pb analyses. Because of low concentrations in sediments, Cd is reported only in HCl (HCl-soluble Cd equalled totals) while Ag is reported only in total, HCl, ammonia and NaOH extracts.

Extractions

Concentrated nitric acid (Total). Samples were wet ashed using the procedure of Bryan and Uysal (1978). Oxidation with concentrated nitric acid of sediments from the Tamar estuary resulted in nearly 100 percent extraction of Cu, Pb and Zn, and over 90 percent extraction of Mn and Fe compared to total sample dissolution in hydrofluoric acid (Bryan and Hummerstone, 1971).

1N hydrochloric acid (HCl). Subsamples of 1 g air-dried sediments were extracted for 2 h with 10 ml of 1N HCl. Preliminary experiments showed similar concentrations of metal were extracted from air-dried and wet sediment. Weaker solutions of HCl (0.1N) were neutralized by carbonates in the sediments, which greatly inhibited the action of the extractant.

25 percent acetic acid. Subsamples (2 ml) of wet sediment were extracted for 2 h in 20 ml of acetic acid. A slight neutralization of the acid (from pH 2.2 to pH 2.6 in the most extreme cases) was observed in sediments with the highest concentrations of carbonates. Dried subsamples of these sediments were re-extracted and titrated back to pH 2.2 with concentrated nitric acid shortly after initiation of the extraction. Only the extraction of Cu was detectably affected by the slight neutralization of the acetic acid. The copper values from the re-extraction were used in our data analysis.

0.4N ammonium oxalate in 0.4N oxalic acid at pH 3.3 (acid ammonium oxalate — Schwertmann, 1964). Subsamples (2 ml) of wet sediment were extracted for 2 h in 20 ml of extract and preserved for analysis by injecting 25 μ l of concentrated HNO_3 into the filtrate.

0.1N hydroxylamine hydrochloride in 0.01N nitric acid at pH 2 (hydroxylamine — Chao, 1972). Subsamples (2 ml) were extracted for 30 min in 20 ml of extractant. Hydroxylamine was extremely sensitive to the presence of any CaCO_3 in sediments (due to the poor buffering capacity of 0.01N nitric acid). Neutralization dramatically affected extraction of at least Cu, Zn, and Fe (Luoma, unpublished data); thus our hydroxylamine data was meaningful only at stations where carbonates were present in very low concentrations.

1N ammonium acetate at pH 7. Subsamples (2 ml) of wet sediment were extracted for 2 h. The filtrate was preserved for analysis with 25 μ l concentrated HNO_3 .

0.1N sodium pyrophosphate. Subsamples (2 ml) were extracted for 2 h.

1N ammonia and 0.1N sodium hydroxide (NaOH). Subsamples (4 ml) were extracted for 1 week in 20 ml (~15:1 extractant/dry solid) of extractant. The time of extraction was determined from preliminary experiments which indicated very slow metal and organic matter removal by both methods. The normalities of the two extractants were chosen to maximize the extraction of Cu and organic materials (Fig. 1).

The concentration of organic materials extracted (which we will operationally define as humic substances) was measured by light absorbance at 460 nm in a 1-cm cell. This wavelength was within a broad band of absorbance observed in the extracts. In sediments from the Looe estuary 1 unit of absorbance/g sediment equalled 0.0005 g humic acid/g sediment (determined by repeated precipitation of the organics at pH < 2 and weighing the residue). Addition of FeCl_2 up to twice the highest Fe concentration found in any extract did not affect absorbance, suggesting all the absorbance was due to organic materials.

Carbon determination. Total organic carbon (TOC) was determined on a carbon analyzer by the difference between total carbon and inorganic carbon. Inorganic carbon was dissolved in boiling phosphoric acid and the evolved CO_2 was detected by the carbon analyzer. The TOC results were compared with concentrations of organic materials determined from either ashing at 400°C for 6 h (Jaffe and Walter, 1974) or ashing for 1 h at 500°C (Dean, 1974). The comparison indicated the former method is a satisfactory

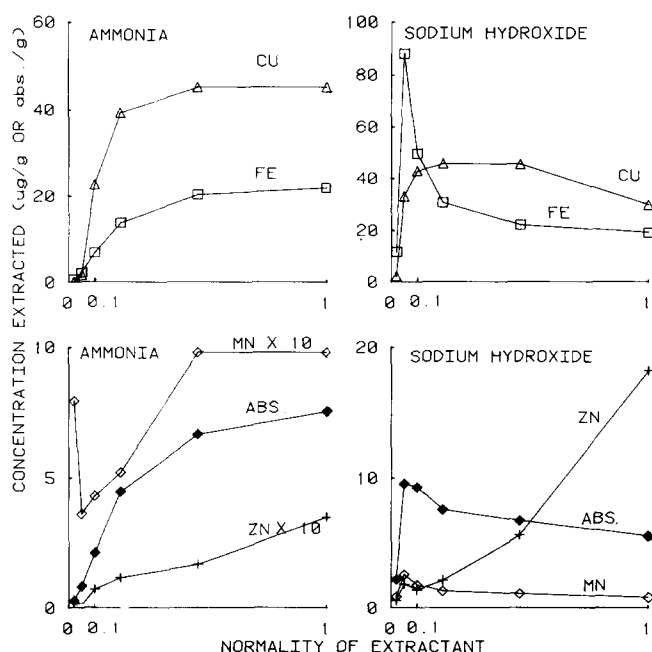


Fig. 1. Extraction of Cu, Zn, Fe, Mn and humic substances by ammonia and sodium hydroxide as a function of the strength of the extractant. Sediment from Tamar estuary.

substitute for TOC analyses when an organic carbon analyzer is not available (Fig. 2). The latter method removes approximately 3 per cent of the sediment weight that is not organic carbon.

Particle size. The proportion of fine particles in the sieved sediments was estimated from the percent particles less than $14\ \mu\text{m}$, as determined by the proportion of the sediment mass which did not settle after 15 min in an Andreasen's pipette apparatus.

STATISTICAL APPROACH

All data were transformed to logarithms for the statistical analyses. Linear regressions compared all combinations of extractable metals and extractable substrates. The unique nature of the data set (comparing a number of estuaries which vary widely in their physical and chemical characteristics) greatly helped circumvent the limitations of conducting statistical studies either over narrow data ranges or within single water bodies.

A statistical filtering technique was designed to test if substrates competed for the partitioning of a metal, and if that competition was influenced by substrate concentrations in the sediment. It was assumed that, if two substrates were competing for binding a metal, a stronger statistical correlation between the metal and the first substrate would be observed among sediments

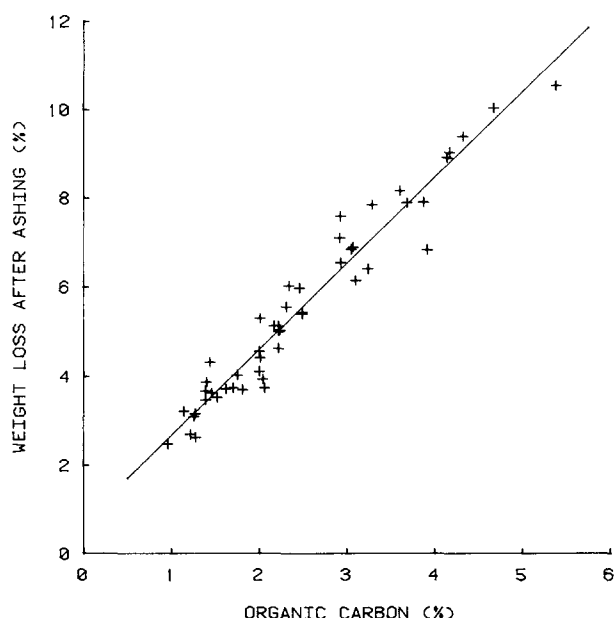


Fig. 2. A comparison of the concentration of organics determined by ashing at 400°C for 6 h (Jaffe and Walter, 1974) versus organic carbon determined on a carbon analyzer. Solid line shows least squares best fit by equation $y = 1.84x + 0.484$. Weight loss during ashing was corrected for weight loss due to salt in sediment.

with low concentrations of the competing substrate than would be observed if the competing substrate occurred in a range of concentrations in the data set. The statistical filter isolated subsets of data with low concentrations of one substrate. Correlations were then calculated between metals and all other substrates within that data set. If a metal and a substrate showed a progressively stronger correlation as the calculation was restricted to stations with progressively lower concentrations of the "competing" substrate, then it was concluded that competition was occurring between the two substrates. For example, if Fe and Mn oxides were competing for the binding of a metal, statistical correlations between Fe and the metal (signifying a partitioning of the metal to Fe oxide) would be weakened if stations occurred in the data set where the metal was predominantly partitioned to Mn. Since our objective is to test if the ability of Mn to compete with Fe for the metal was dependent upon the concentration of Mn, we: (1) calculate the correlation between Fe and the metal among all stations; (2) eliminate those stations with very high Mn concentrations from the data set (this becomes subset 1) and recalculate the Fe-metal correlation; (3) eliminate the stations with the highest Mn concentrations in subset 1, and recalculate the Fe-metal correlation in subset 2; and (4) progressively continue to eliminate high Mn stations until we reach a minimum of 12–16 data points (this resulted in 3–5 subsets, depending upon the range of data available for the substrate chosen as the competitor, Table 2). If the correlation between Fe and metal

TABLE 2

SAMPLES WITH HIGHER SUBSTRATE CONCENTRATIONS THAN SHOWN HERE WERE EXCLUDED (FILTERED OUT) FROM THE REGRESSION CALCULATION FOR EACH RESPECTIVE SUBSET

The correlation of each metal-substrate combination was calculated within each subset shown here. Numbers in parentheses are the sample sizes (*n*) in each calculation. Total sample size was 50. The concentrations of substrate which defined the different subsets were chosen on the basis of a maximum change in sample size between subsets for the same substrate.

Competing substrate	Fraction	Subset ₁ (less than)	Subset ₂ (less than)	Subset ₃ (less than)	Subset ₄ (less than)	Subset ₅ (less than)
Fe	oxalate (μg/g)	10,000 (37)	7,000 (27)	4,000 (16)		
Fe	total (μg/g)	35,000 (37)	30,000 (27)	26,000 (16)		
Mn	acetic acid (μg/g)	600 (41)	400 (38)	300 (32)	200 (27)	120 (17)
Mn	total (μg/g)	900 (41)	500 (24)	400 (16)		
Humic substances (absorbance/g)		15 (36)	9 (27)	6 (20)	5 (14)	
Organic carbon (percent)		4.0 (42)	3.5 (35)	2.5 (26)	2.0 (12)	
Carbonate carbon (percent)		2.0 (42)	1.0 (33)	0.5 (28)	0.1 (20)	
Fe/Mn	acetic acid	150 (40)	50 (30)	30 (21)	22 (15)	

improved progressively as we eliminated stations with high Mn from the data set, we concluded that Mn competed with Fe in a concentration-dependent manner for partitioning of the metal. Furthermore, if the correlation between Mn and the same metal improved progressively as we eliminated stations with high Fe concentrations, the evidence for concentration-dependent competition between Fe and Mn was even stronger. By including different forms of substrates (as operationally-defined by the extracts) as either a correlating variable or a competing substrate, we could also test which operationally-defined forms were (statistically) most important in the partitioning process.

The statistical filter requires a large data base with a wide range of values. However, where adequate data is available, it provides an orderly, objective method for study of interactions within specific subsets of data, which cannot be obtained from more conventional techniques (i.e., multiple regression). Because of the number of regressions calculated ($> 15,000$) only statistically significant results are reported here. Although filtering reduced the overall variance in the data set in some cases by progressively reducing the number of estuaries included in the calculation, the overwhelming majority of the correlations remained insignificant.

RESULTS

Sample collection

Three lines of evidence indicated that sediments collected from the thin surface layer on the mud flats were predominantly oxidized in character: (1) Surface sediments were obviously lighter in color than were subsurface sediments. (2) "In situ" measurements of Eh in light-colored surface sediments of estuarine mudflats consistently yield positive values (Luoma, unpublished data); and (3) Significantly higher concentrations of Cu, Pb, Zn and Co (Ag and Cd were not measured) were extracted from the surface sediments than from the subsurface sediments by all extractants (exemplified by acetic acid extractions in Table 3). Metal sulfides should be of lower extractability in most extractants than oxidized forms of sediment-bound metals. The difference between extractions from surface and subsurface were greater for Cu and Pb than for Zn and Co. These differences followed the solubility of the sulfides of the metals (Krauskopf, 1956), consistent with a predominantly oxidized form of metals in surface sediments and a domination of metal forms characteristic of a reducing environment in subsurface sediments. The following discussion relates only to extractions of the surficial oxidized sediments.

Substrate characterization

Humic substances. Ammonia and NaOH removed similar quantities of humic substances and trace metals. In the Looe estuary the humic substances extracted by ammonia constituted 23 percent of the total organic

TABLE 3

A COMPARISON OF Cu, Zn, Co AND Fe EXTRACTION FROM SURFACE SEDIMENTS AND SUBSURFACE SEDIMENTS IN THREE ESTUARIES WITH VARYING METAL ENRICHMENT

	Total metal		Acetic acid metal	
	Surface sediment	Subsurface sediment	Surface sediment	Subsurface sediment
<i>Copper</i>				
Restronguet	3052	3648	1638	10
Tamar	282	306	95	0.04
Looe	36	49	5	0.19
<i>Lead</i>				
Restronguet	323	385	126	2.0
Tamar	179	222	97	7.5
Looe	78	117	48	8
<i>Zinc</i>				
Restronguet	3544	3110	2627	901
Tamar	363	386	222	101
Looe	115	137	40	25
<i>Cobalt</i>				
Restronguet	23.2	27.3	12.6	8.0
Tamar	18.0	16.5	6.3	3.1
Looe	11.1	11.1	0.8	0.3
<i>Iron</i>				
Restronguet	48,383	46,531	10,802	12,096
Tamar	36,330	37,031	3,869	6,438
Looe	27,739	28,000	919	1,086

material in the sediments. If the calibration for the Looe sediments held throughout the study area, the humic materials varied from 1.0 per cent (Bristol Channel; Restronguet Creek) to 23 per cent (East Looe) of the organic matter among the different stations.

A single 1-week extraction did not remove all the humic substances from the sediments. Pretreatment of sediments with acid ammonium oxalate resulted in a substantial increase in the extraction of organic matter, Fe, and Cu by ammonia, compared to subsamples extracted without pretreatment (Table 4). In at least some sediments, a fraction of the humic substance is strongly enough associated with substances solubilized by acid ammonium oxalate (most likely Fe oxides — Sholkovitz, 1976), to prevent total extraction of the humic substance by ammonia.

Fe oxides. A variety of extractants have been used to operationally characterize the concentrations of different forms of Fe in sediments. In the sediments we considered, acid ammonium oxalate and 1N NCl removed

TABLE 4

A COMPARISON OF THE EXTRACTION OF HUMIC SUBSTANCES, Cu AND Fe BY AMMONIA FROM SEDIMENTS PRE-TREATED WITH AMMONIUM OXALATE TO REMOVE AMORPHIC Fe, AND FROM UNTREATED SEDIMENTS

Station	Concentration of humic substance (abs./g)		Ammonia-extractable metal conc.			
			Cu ($\mu\text{g/g}$)		Fe ($\mu\text{g/g}$)	
	Untreated	After pre-treatment	Untreated	After pre-treatment	Untreated	After pre-treatment
Poole Harbor	6.85	36.6	19.9	46.7	10	246
Beaulieu R.	22.3	31.1	13.0	7.3	156	313
Looe I	4.8	11.3	4.9	5.4	26	149
Looe II	3.6	8.7	4.2	8.1	19	126

a similar proportion of the total Fe (Table 5). Acetic acid removed less than half of the quantity of Fe removed by oxalate. Earlier work using only sediments from the Tamar estuary (Bryan, unpublished data) indicated adding 0.1N hydroxylamine to 25 percent acetic acid (Chester and Hughes, 1967) extracted only slightly more Fe from oxidized sediments than did acetic acid alone (19.8 percent vs. 11.6 percent, respectively). Hydroxylamine alone (in nitric acid) extracted 7.6 percent of the total Fe from sediments where carbonates did not interfere with the extraction. The neutralization of the hydroxylamine extract by carbonates greatly reduced the extraction of Fe.

The differences among stations in the concentrations of extractable Fe were substantially greater than the interstation differences in total Fe. The wide variations in Fe extractability suggest processes independent of total concentration (such as those governing the crystallinity of the Fe oxide) play an important role in determining the quantity of Fe removed by each extractant. Laboratory experiments with pure Fe oxides also show that Fe extractability with acetic acid and with hydroxylamine decline with the age (and thus crystallinity) of the precipitate (Luoma and Bryan, 1979). If crystallinity governs extractability, then increasingly crystalline forms of Fe are removed by extractants in the order oxalate = 1NHCl > acetic acid + hydroxylamine > acetic acid > hydroxylamine.

The concentration of Fe removed by NaOH or ammonia correlated very strongly with the concentration of humic substance in the extracts (Fig. 3). Ammonia or NaOH may not quantitatively remove the organically-complexed Fe in the sediment (at high pH weakly complexed Fe may precipitate) but the concentrations which are removed by these techniques are controlled by the quantity of extractable organic materials in the sediment.

Mn oxides. The 10 different chemical treatments separated only 4 fractions of Mn: total Mn, a fraction of Mn (40–50 percent) similarly soluble in most acids and reducing agents, a smaller fraction (2.4–21.6 percent) soluble in

TABLE 5
THE RANGE OF METAL CONCENTRATIONS AND THE PERCENT OF TOTAL METAL EXTRACTED BY VARIOUS EXTRACTANTS

Extractants	Ag	Co	Cu	Fe	Mn	Pb	Zn
Concentrated nitric acid range of concentrations ($\mu\text{g/g}$) proportion of total (%)	<0.2–10.0 100	3.1–36.1 100	17–3079 100	2.00 ^d –4.84 100	138–1448 100	41–6006 100	95–3544 100
Hydrochloric acid range of concentrations (%) proportion of total: range (%) medial %	0.10–1.69 6.8–100 63.4	1.4–14.9 9.3–65.6 37.5	8–1860 38.1–91.0 64.6	0.16 ^d –1.73 7.5–39.6 23.6	58–1013 15.3–78.1 46.7	22–4760 51.9–92.0 72.0	43–2656 35.1–92.3 63.7
Acetic acid range of concentrations ($\mu\text{g/g}$) proportion of total: range (%) medial %		0.3–12.6 1.0–64.0 32.6	3–1638 5.5–90.0 47.8	0.10 ^d –1.08 3.9–25.3 14.2	40–1092 10.7–100 55.4	13–4291 20.0–73.6 46.8	40–2627 29.0–91.1 60.1
Acid ammonium oxalate range of concentrations ($\mu\text{g/g}$) proportion of total: range (%) medial %		0.7–15.9 9.5–63.6 37.0	<0.2–619 0.1–62.5 31.3	0.20 ^d –279 7.9–63.9 35.9	47–958 14.1–67.7 40.9	1–505 0.7–42.5 21.6	30–2786 24.1–83.4 53.8
Hydroxylamine hydrochloride–nitric acid ^a range of concentrations ($\mu\text{g/g}$) proportion of total: range (%) medial %		0.3–13.4 6.1–77.6 41.9	0.2–379 0.1–48.8 24.4	180–2185 0.70–14.4 7.6	37–958 8.3–66.5 37.4	1–120 0.8–70.8 35.8	15–1555 10.6–70.1 40.4
Ammonium acetate range of concentrations ($\mu\text{g/g}$) proportion of total: range (%) medial %		<0.1–2.6 1.2–3.2 4.2	<0.1–131 0.4–4.9 2.5	<1–347 0.005–0.40 0.03	3–245 2.4–21.6 12.0	<0.8–443 0.4–7.3 3.8	0.7–295 1.0–10.7 5.9
Pyrophosphate ^b range of concentrations ($\mu\text{g/g}$) proportion of total: range (%) medial %		<0.1–9.3 0.8–44.1 22.5	0.8–202 0.4–9.7 5.1	109–1618 0.4–4.5 2.5	14–159 3.5–27.2 15.6	1–13 0.8–11.7 6.3	5–753 3.8–27.2 15.5

TABLE 5 (continued)

<i>Extractants</i>	<i>Ag</i>	<i>Co</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>
Ammonia					
range of concentrations ($\mu\text{g/g}$)	<0.02–0.77	1–399	0.5–642	0.1–17.5	0.2–137
proportion of total: range (%)	9.0–45.0	7.1–33.3	0.02–0.9	0.1–1.2	0.1–7.6
medial %	27.0	20.2	0.46	0.61	3.8
Sodium hydroxide					
range of concentrations ($\mu\text{g/g}$)	0.07–0.51	6.2–360	1.0–286	0.3–6.8	0.33–11.5
proportion of total: range (%)	8.0–41.4	8.9–54.2	0.004–1.27	0.05–1.04	0.17–2.30
medial %	24.7	31.6	0.64	0.55	1.24

^aHydroxylamine data includes 18 samples unaffected by carbonates^bPyrophosphate extractions were conducted on 17 samples.^cSodium hydroxide extractions were conducted on 27 samples.^dConcentration in percent.

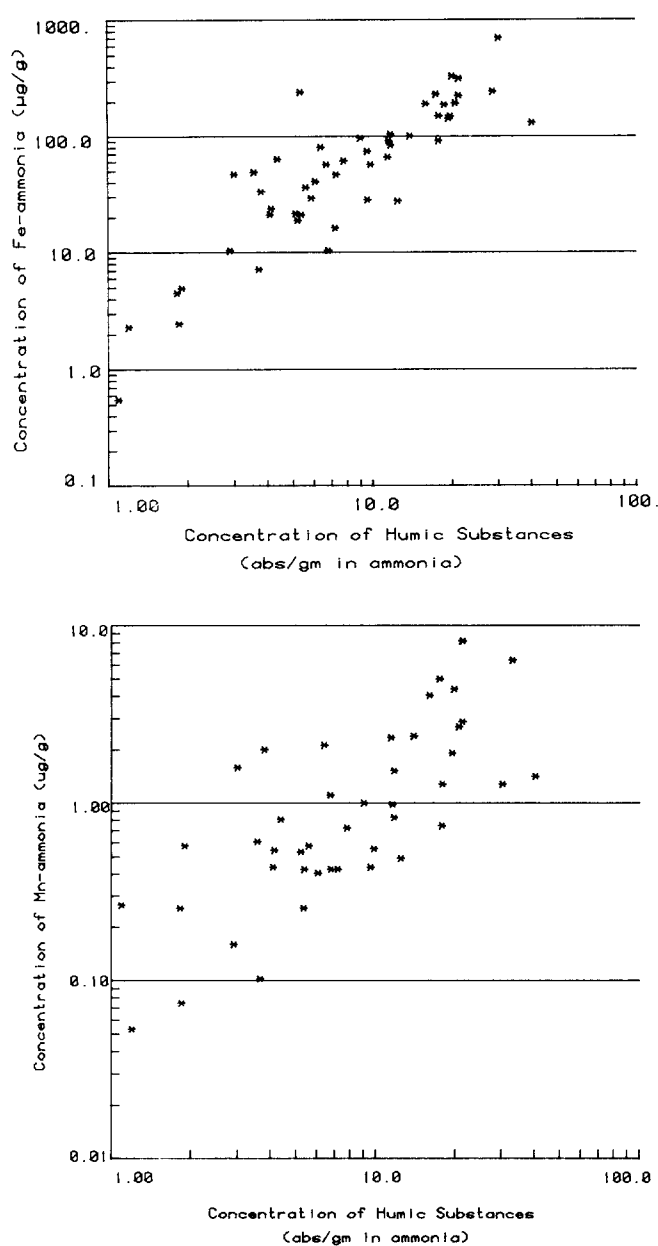


Fig. 3(a). Iron concentrations extracted by ammonia as a function of humic substance concentrations extracted by ammonia. (b). Manganese concentrations extracted by ammonia as a function of humic substance concentrations extracted by ammonia.

ammonium acetate, and a very small fraction soluble in ammonia or NaOH (Table 5). The fraction of Mn dissolved by weak acids correlated strongly with total Mn among all stations ($r = 0.81$ for oxalate to $r = 0.88$ for acetic acid). The concentration of Mn extracted by ammonium acetate was

controlled by processes largely independent of total Mn concentrations ($r = 0.45$ for correlation of ammonium acetate—Mn and total—Mn). Concentrations in ammonia and NaOH (as with Fe) were controlled by the quantity of humic substance extracted (Fig. 3).

Extraction of trace metals

Hydrochloric acid removed a greater concentration of trace metal from the sediments than other extractants (Table 5). Greater than 60 percent of the Ag, Cu, Pb and Zn in the oxidized sediments was removed by HCl, although only 39 percent of the Co was HCl-soluble. Acetic acid extracted substantially more Cu and Pb than acid ammonium oxalate, but the two extractants removed roughly similar concentrations of Co and Zn. In the Tamar sediments (Bryan, unpublished data) the mixture of hydroxylamine with acetic acid resulted in an extraction similar to acetic acid alone for Cu and Zn (34 vs. 44 percent and 70 vs. 66 percent, respectively), but extracted more Pb than acetic acid (68 vs. 42 percent). Concentrations of most metals in the three acids were strongly correlated with the total metal concentrations in the sediment (Table 6), indicating extractability was largely dependent upon total concentration.

A high proportion, relative to other metals, of total Cu and Ag was removed from the sediments by NaOH and ammonia (Table 5), indicating the relative importance of humic substances as a substrate for binding Cu and Ag. Interestingly, the sum of acetic acid—Cu and ammonia—Cu was similar to the concentrations of Cu extracted by HCl at most stations (Table 7). Strong deviations from this relationship were observed only at 2 stations

TABLE 6
CORRELATION OF EXTRACTABLE METAL CONCENTRATION WITH TOTAL METAL CONCENTRATION

r = Correlation coefficient. b = Slope of regression. $n = 45$ for all except pyrophosphate where $n = 17$ and Ag—ammonia, were $n = 21$. a = Insignificant correlation, $p > 0.05$. nd = Not determined

Extractant		Ag	Co	Cu	Fe	Mn	Pb	Zn
Hydrochloric acid	r	0.70	0.77	0.88	0.62	0.84	1.00	1.00
	b	0.53	1.66	1.08	1.38	1.39	1.06	1.16
Acetic acid	r	nd	0.81	1.00	0.67	0.88	1.00	1.00
	b		2.04	1.11	1.61	1.43	1.12	1.21
Oxalate	r	nd	0.86	0.52	0.69	0.81	0.69	1.00
	b		1.68	0.80	1.68	1.35	1.04	1.24
Ammonium acetate	r	nd	0.33	0.55	0.40	0.45	0.62	0.90
	b		0.86	0.81	2.08	0.87	1.09	1.49
Pyrophosphate	r	nd	0.11 ^a	0.90	0.22 ^a	0.48	0.67	0.95
	b		0.23	0.96	0.41	0.89	0.82	1.17

TABLE 7

A COMPARISON OF HCl—Cu WITH THE SUM OF (ACETIC ACID—Cu) + (AMMONIA—Cu) AT SELECTED STATIONS AND ALONG THE SALINITY GRADIENT OF 4 ESTUARIES

Estuary	A Acetic acid—Cu ($\mu\text{g/g}$)	B Ammonia—Cu ($\mu\text{g/g}$)	(A) + (B) ($\mu\text{g/g}$)	HCl—Cu ($\mu\text{g/g}$)
Plym	25.1	23.7	48.8	49.1
Erme	9.3	8.2	17.5	14.5
W. Looe	13.7	12.6	26.3	27.8
Fal (mouth)	1423	367	1790	1770
	1638	399	2037	1823
(head)	426	240	666	1860 ^a
Tamar (mouth)	154	59	213	194
	95	50	145	168
	154	55	209	233
	127	53	180	253
	165	60	225	260
	149	47	196	250
(head)	700	237	937	605 ^a
Fowey (mouth)	26	13	39	49
	22	15	37	44
	23	17	37	50
	33	20	53	50
	35	24	59	65
(head)	11	18	29	55 ^a
Gannel (mouth)	28	11	39	41
	35	11	46	41
	71	30	101	87
(head)	135	49	184	197
Beaulieu	10	7	17	12
Poole	16	23	39	90 ^a
Hayle	493	121	614	645
Bristol Channel	17	5	22	23

^aStations with substantial deviations between HCl—Cu and acetic acid Cu + ammonia—Cu.

where the samples included some reduced sediments due to sampling difficulties (thus inhibiting the extraction of Cu by acetic acid) and three stations near the freshwater—seawater interface. Excluding the anomalous stations the regression of HCl—Cu vs. (acetic acid—Cu) + (ammonia—Cu) had a correlation coefficient of 0.98, a slope of 0.98 and an intercept of $1.07 \mu\text{g/g}$ Cu. These results suggested ammonia extracted roughly the same organically complexed Cu as HCl, but that this form of Cu was not extracted by acetic acid. Extraction schemes which employ acetic acid to determine “non-detrital” trace metals (Loring, 1976) may miss at least some organically complexed forms of Cu.

The concentrations of Ag, Cu and Zn extracted by the alkaline extractants

TABLE 8
A MATRIX OF CORRELATION COEFFICIENTS, SHOWING INTERRELATIONSHIPS AMONG SEDIMENTARY SUBSTRATES
Sample size (n) = 50. (—) indicates a negatively sloped relationship.

	Fe _{Acet.ac.}	Fe _{HCl}	Fe _{Total}	Mn _{AmAc}	Mn _{Acet.ac.}	Mn _{Total}	Particle size	Humic substances	Organic carbon
Mn _{AmAc}	0.12	0.15	0.13						
Mn _{HAc}	0.00	0.20	0.26						
Mn _{Total}	0.19	0.34	0.43 ^a						
Particle size	0.47 ^a	0.39 ^b	0.09	(—)0.05	0.01	0.08			
Humic substances	0.15	0.06	0.12	0.06	(—)0.23	(—)0.19	0.29		
Organic carbon	0.72 ^c	0.64 ^c	0.35	0.05	0.07	0.10	0.65 ^c	0.46 ^a	
Carbonate carbon	0.01	(—)0.04	(—)0.09	0.01	0.16	0.15	0.15	(—)0.56 ^c	(—)0.19

^a $p < 0.005$. ^b $p < 0.01$. ^c $p < 0.001$.

TABLE 9

CORRELATION OF EXTRACTABLE FRACTIONS OF Co, Zn, Pb, Cu, Ag AND Cd WITH ORGANIC CARBON AND SELECTED FRACTIONS OF Fe AND Mn

Numbers are correlation coefficients (*r*). Extractants shown are those which gave strongest correlations. Correlations with oxalate—Fe are shown in Tables 12–15.

Metal Extraction	Mn _{AmAc}	Mn _{oxal.}	Mn _{total}	Fe _{HCl}	Fe _{total}	Organic carbon
<i>Co</i>						
Acetic acid	0.42 ^a	0.63 ^b	0.55 ^b	0.46 ^b	0.56 ^b	0.12
HCl	0.40 ^a	0.67 ^b	0.60 ^b	0.48 ^b	0.43 ^a	0.23
Oxalate	0.43 ^a	0.75 ^b	0.75 ^b	0.54 ^b	0.51 ^b	0.18
Total	0.41 ^a	0.71 ^b	0.75 ^b	0.58 ^b	0.70 ^b	0.19
<i>Zn</i>						
Ammonium acetate	0.30 ^c	0.21	0.38 ^d	0.64 ^b	0.41 ^a	0.19
Acetic acid	0.30 ^c	0.15	0.36 ^d	0.79 ^b	0.52 ^b	0.41 ^a
HCl	0.25	0.10	0.35 ^c	0.82 ^b	0.52 ^b	0.44 ^a
Oxalate	0.27	0.15	0.38 ^d	0.80 ^b	0.50 ^b	0.42 ^a
Total	0.26	0.14	0.37 ^d	0.79 ^b	0.58 ^b	0.36 ^c
<i>Pb</i>						
Acetic acid	0.35 ^c	0.31 ^c	0.37 ^d	0.35 ^d	0.37 ^c	0.03
HCl	0.36 ^c	0.33 ^c	0.40 ^d	0.46 ^b	0.42 ^a	0.07
Oxalate	0.32 ^c	0.35 ^c	0.22	0.30 ^a	0.27	0.06
Total	0.38 ^d	0.31 ^c	0.30 ^c	0.48 ^b	0.40 ^d	0.05
<i>Cu</i>						
Acetic acid	0.36 ^c	0.40 ^a	0.41 ^a	0.49 ^b	0.41 ^a	0.13
HCl	0.28 ^c	0.13	0.27	0.71 ^b	0.54 ^b	0.39 ^a
Oxalate	0.25	0.59 ^b	0.50 ^b	0.28 ^c	0.29	(-)0.10
Total	0.29 ^c	0.10	0.30 ^c	0.69 ^b	0.52 ^b	0.33 ^c
<i>Ag</i>						
HCl	0.01	-0.12	0.17	0.29 ^c	0.49 ^b	-0.07
Total	0.12	-0.05	0.09	0.57 ^b	0.47 ^b	0.21
<i>Cd</i>						
HCl	0.10	-0.21	-0.21	0.50 ^b	0.15	0.49 ^b

^a*p* < 0.005. ^b*p* < 0.001. ^c*p* < 0.05. ^d*p* < 0.01.

were strongly correlated with total Ag, Cu and Zn in the sediments, but not with the abundance of humic substances.

Statistical analyses

Substrates. Among substrates, the strongest correlations were observed between total organic carbon and extractable Fe (Table 6). This relationship was at least partly due to a similar dependence of extractable Fe and organic

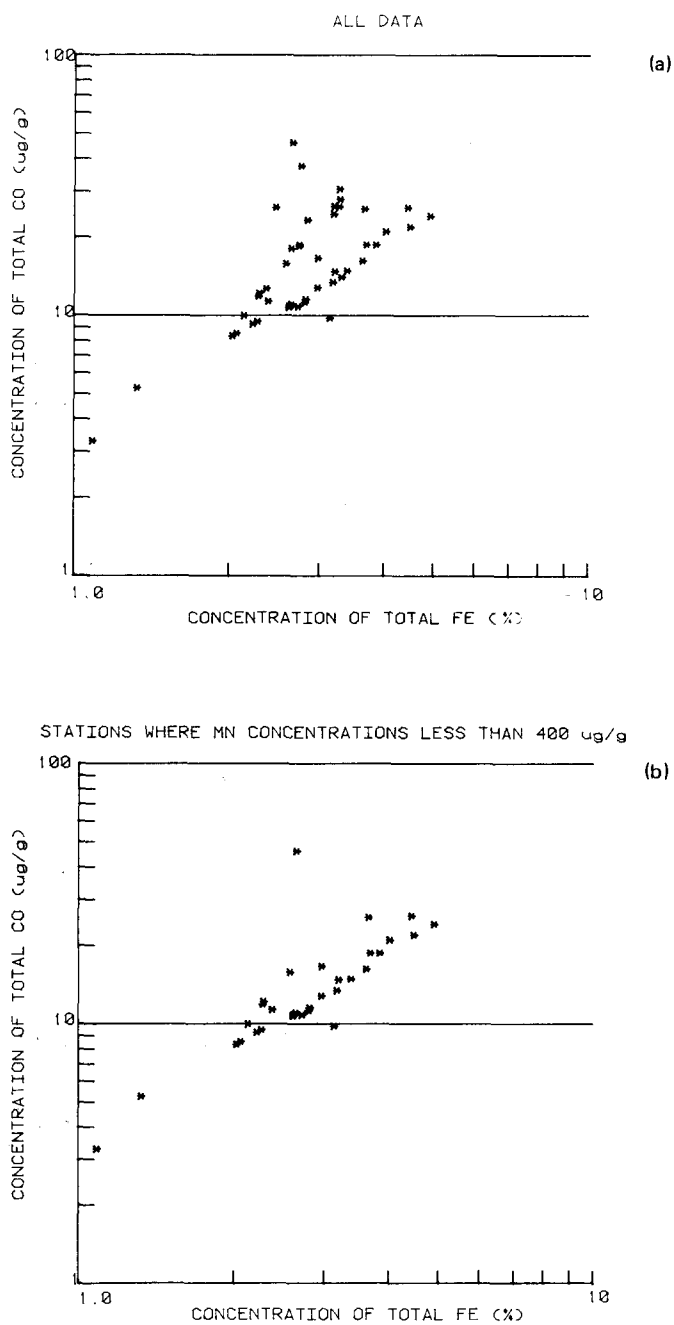


Fig. 4.

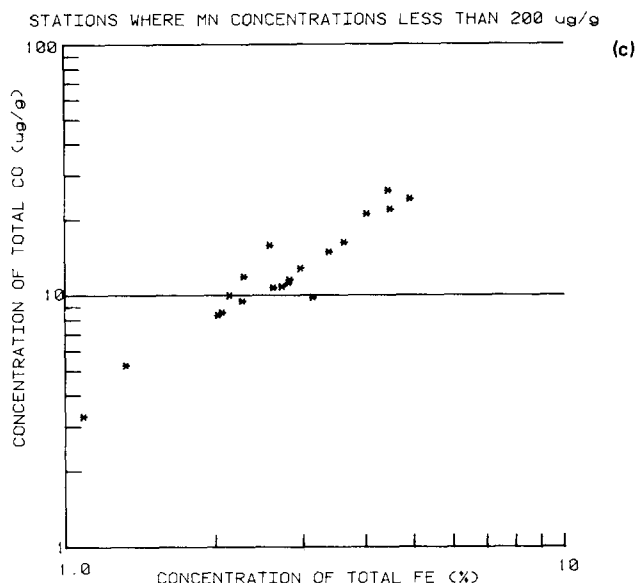


Fig. 4. Correlation of total Co in sediment with total Fe in sediment (a) among all stations; (b) among stations with concentrations of extractable Mn less than 400 $\mu\text{g/g}$; and (c) among stations where concentrations of extractable Mn were less than 200 $\mu\text{g/g}$.

materials upon particle size distributions, since concentrations of both correlated significantly with the proportion of fine particles in the sediments. The significant, negative relationship between carbonates and humic substances reflected physical rather than chemical processes. Humic substances declined in concentration from the head to the mouth of most estuaries and occurred in low concentrations at stations heavily influenced by marine processes. Carbonates occurred in high concentrations where marine influences were greatest, and increased from the head to the mouth of most estuaries.

Cobalt. Among all samples, Co correlated most strongly with total Fe, total Mn and oxalate-soluble Mn (Table 9). A multiple regression calculation indicated total Fe and total Mn together explained 88 percent of the variance in concentrations of Co in the sediments.

Out statistical filtering method was used to test whether Fe and Mn competed for the binding of Co at different stations. The correlation between total Fe and total Co became progressively stronger when stations with high Mn concentrations were eliminated from the calculation (Fig. 4). Thus, stations where concentrations of Mn were high ($>300 \mu\text{g/g}$) tended not to fit the Fe—Co relationship, indicating a partitioning of Co away from Fe where competition from Mn might be most effective. Similarly, the correlation of Co and Mn was strongest among subsets of samples with low concentrations of Fe (Table 10). Stations with high concentrations of Fe did not fit well in the Co—Mn relationship. These results suggest Co was

TABLE 10

CORRELATION OF Co WITH Fe AND Mn WITHIN SUBSETS OF DATA WHICH EXCLUDE THE SAMPLES FROM THE PREVIOUS SUBSET WITH THE HIGHEST CONCENTRATIONS OF THE SPECIFIED COMPETING SUBSTRATES.^a

Filter		Correlation of coefficients (<i>r</i>)					
Competing substrate	Fraction	All samples	Subset ₁	Subset ₂	Subset ₃	Subset ₄	Subset ₅
		$\text{Fe}_{\text{total}} \text{ vs } \text{CO}_{\text{total}}^b$					
Mn	acetic acid	0.71 ^c	0.81 ^d	0.83 ^d	0.97 ^d	0.99 ^d	1.00 ^d
		$\text{Mn}_{\text{total}} \text{ vs } \text{CO}_{\text{total}}^b$					
Fe	oxalate	0.75 ^d	0.80 ^d	0.98 ^d	0.97 ^d		
Fe	total	0.75 ^d	0.82 ^d	0.82 ^d	0.90 ^d		

^a Filter levels and sample sizes for each subset of data are shown in Table 2.

^b Similar results were obtained with all forms of acid extractable Co.

^c $p < 0.005$.

^d $p < 0.001$.

dominantly partitioned to Mn oxides where concentrations of Fe oxide were low, and where concentrations of Mn oxide were low, Co was dominantly partitioned to Fe oxide.

Zinc. Both acid-soluble and total Zn correlated very strongly with concentrations of Fe in the sediments, and correlations with extractable Fe were substantially stronger than correlations with total Fe (Table 9). A very strong correlation of Zn with Fe occurred among stations low in Mn, total organic carbon or humic substances (Table 11), suggesting partitioning of Zn away from Fe where these substrates were in high concentration. Moreover, Zn correlated only weakly with organic materials and with Mn among all samples; but where Fe or Fe/Mn were low, both correlations were greatly improved.

If the statistical relationships result from the mechanism we have postulated, then extractable forms of Fe dominated the partitioning of Zn in most sediments; but where Fe concentrations were low and/or the concentrations of either Mn or organic materials were high, the latter two substrates were also important in binding Zn.

Lead. Concentrations of Pb in sediments correlated weakly, but significantly, with Fe and Mn among all samples (Table 9). Similar to Zn, a very strong correlation of Pb with extractable-Fe (but not total Fe) was observed among stations where either Mn or organic carbon were low in concentration (Table 12). A strong correlation of Pb with Mn was also observed where Fe/Mn was low, suggesting strong competition between at least extractable Fe and Mn for the binding of Pb in the sediments. The correlation of Pb with

TABLE 11

CORRELATION OF Zn WITH Mn, ORGANIC CARBON AND EXTRACTABLE Fe WITHIN SUBSETS OF DATA WHICH EXCLUDE THE SAMPLES FROM THE PREVIOUS SUBSET WITH THE HIGHEST CONCENTRATIONS OF THE SPECIFIED COMPETING SUBSTRATES^a

Filter		Correlation coefficients (r)					
Competing substrate	Fraction	All samples	Subset ₁	Subset ₂	Subset ₃	Subset ₄	Subset ₅
		Zn_{HCl}^b vs. Fe_{oxal}					
Mn	acetic acid	0.82 ^c	0.84 ^c	0.85 ^c	0.91 ^c	0.94 ^c	0.92 ^c
Organic carbon		0.82 ^c	0.81 ^c	0.80 ^c	0.83 ^c	0.95 ^c	
Humic substances		0.82 ^c	0.85 ^c	0.89 ^c	0.93 ^c	0.91 ^c	
		Zn_{HCl}^b vs. Organic carbon					
Fe	oxalate	0.44 ^d	0.47 ^d	0.33	0.81 ^c		
Mn	total	0.44 ^d	0.47 ^d	0.77 ^c	0.92 ^c		
Mn	acetic acid	0.44 ^d	0.50 ^d	0.53 ^c	0.63 ^c	0.60 ^c	0.79 ^c
		Zn_{HCl}^b vs. Mn_{total}					
Fe/Mn	0.35 ^e	0.49 ^d	0.74 ^c	0.84 ^c	0.92 ^c		

^a Filter levels and sample sizes for each subset of data are shown in Table 2.

^b Similar results obtained with total Zn.

^c $p < 0.001$.

^d $p < 0.005$.

^e $p < 0.05$.

organic carbon where Mn was low may reflect either a role for organic materials in Pb partitioning which was not statistically evident among all samples; or a secondary effect of the correlation between organic carbon and extractable Fe.

Copper. Statistical correlations among all samples were consistent with previous conclusions that HCl extracted both organically and inorganically-bound forms of Cu, but acetic acid only extracted Cu from inorganic substrates (Table 9). Extractable Fe also showed a stronger relationship with Cu than did total Fe.

A very strong relationship between Cu and extractable Fe was found where humic substances, Mn or total organic carbon were low in concentration (Table 13). The deviations from the Fe—Cu relationship which occurred at high humic substance concentrations, and the high proportion of Cu soluble in ammonia, both indicated the importance of humic substances in the partitioning of Cu. The correlation of Cu with Mn, organic

TABLE 12

CORRELATION OF Pb WITH Mn, ORGANIC CARBON AND EXTRACTABLE Fe WITHIN SUBSETS OF DATA WHICH EXCLUDE THE SAMPLES IN THE PREVIOUS SUBSET WITH THE HIGHEST CONCENTRATIONS OF THE SPECIFIED COMPETING SUBSTRATES^a

Filter		Correlation coefficients (<i>r</i>)					
Substrate	Fraction	All samples	Subset ₁	Subset ₂	Subset ₃	Subset ₄	Subset ₅
		<u>Pb_{total}^b vs. Fe_{oxal}</u>					
Mn	acetic acid ^c	0.48 ^d	0.56 ^d	0.56 ^d	0.91 ^d	0.99 ^d	1.00 ^d
Organic carbon		0.48 ^d	0.46 ^e	0.46 ^f	0.48 ^f	0.91 ^d	
		<u>Pb_{total}^b vs. Mn_{total}</u>					
Fe/Mn	acetic acid	0.38 ^f	0.43 ^f	0.50 ^e	0.76 ^d	0.75 ^e	
		<u>Pb_{total}^b vs. organic carbon</u>					
Mn	total	0.05	0.19	0.64 ^e	0.78 ^d		

^a Filter levels and sample sizes for each subset of data are shown in Table 2.

^b Slightly weaker but similar responses were observed with HCl-soluble Pb.

^c A slightly weaker but similar response was observed to the total Mn filter.

^d $p < 0.001$.

^e $p < 0.005$.

^f $p < 0.01$.

carbon or humic substances was not progressively or substantially improved where Fe concentrations were low. Extractable forms of Fe appeared to dominate the partitioning of Cu, but the relationship of Cu with the other substrates was difficult to clearly resolve from statistical comparisons.

Silver. Hydrochloric acid extracts Ag as a soluble Ag-chloro complex. HCl-Ag correlated relatively weakly with total Ag ($r = 0.70$). The proportion of Ag solubilized by HCl was lowest in sediments characterized by either high concentrations of Fe (Fal, Tamar estuaries) or high concentrations of Mn (Gannel estuary). HCl-Ag also correlated more weakly with extractable-Fe than did total Ag (Table 9); and the improvement in the correlation of extractable Fe and Ag which occurred among stations with low Mn concentrations was greater for total than for HCl-soluble Ag (Table 14). Both fractions of Ag showed a similar correlation with Fe where humic substances were low, however. The correlations suggest (1) Ag is primarily partitioned among extractable forms of Fe, humic substances (as also suggested by NaOH and ammonia extractions) and perhaps Mn oxides in oxidized

TABLE 13

CORRELATION OF Cu WITH EXTRACTABLE Fe WITHIN SUBSETS OF DATA WHICH EXCLUDE THE SAMPLES FROM THE PREVIOUS SUBSET WITH THE HIGHEST CONCENTRATIONS OF THE SPECIFIED COMPETING SUBSTRATES^a

Filters		Correlation Coefficients (r)					
Competing substrate	Fraction	All samples	Subset ₁	Subset ₂	Subset ₃	Subset ₄	Subset ₅
		<u>Cu_{total}^b vs. Fe_{oxal}</u>					
Humic substances		0.69 ^c	0.78 ^c	0.84 ^c	0.95 ^c	0.96 ^c	
Mn	acetic acid	0.69 ^c	0.71 ^c	0.72 ^c	0.81 ^c	0.89 ^c	0.77 ^c
Organic carbon		0.69 ^c	0.72 ^c	0.71 ^c	0.75 ^c	0.80 ^c	

^a Filter levels and sample sizes for each subset of data are shown in Table 2.

^b HCl-soluble Cu shows a slightly weaker but similar trend.

^c $p < 0.001$.

TABLE 14

CORRELATION OF Ag WITH EXTRACTABLE Fe AND HUMIC SUBSTANCES WITHIN SUBSETS OF DATA WHICH EXCLUDE THE SAMPLES FROM THE PREVIOUS SUBSET WITH THE HIGHEST CONCENTRATIONS OF THE SPECIFIED COMPETING SUBSTRATES^a

Filter		Correlation coefficients (r)					
Competing substrate	Fraction	All samples	Subset ₁	Subset ₂	Subset ₃	Subset ₄	Subset ₅
		<u>AgHCl vs. Fe_{oxal}</u>					
Humic substances		0.31 ^b	0.51 ^c	0.63 ^d	0.67 ^d	0.77 ^c	
Mn	acetic acid	0.31 ^b	0.31 ^b	0.35 ^b	0.43 ^b	0.54 ^c	0.50 ^b
		<u>Ag_{total} vs. Fe_{oxal}</u>					
Humic substances		0.58 ^d	0.67 ^d	0.74 ^d	0.79 ^d	0.75 ^c	
Mn	acetic acid	0.58 ^d	0.58 ^d	0.60 ^d	0.73 ^d	0.84 ^d	0.94 ^d
		<u>Ag_{total} vs. humic substance</u>					
Fe	oxalate	0.08	0.16	0.37	0.57 ^b		

^a Filter levels and sample sizes for each subset of data are shown in Table 2.

^b $p < 0.05$. ^c $p < 0.005$. ^d $p < 0.001$.

TABLE 15

CORRELATION OF Cd WITH ORGANIC CARBON AND EXTRACTABLE Fe WITHIN SUBSETS OF DATA WHICH EXCLUDE THE SAMPLES FROM THE PREVIOUS SUBSET WITH THE HIGHEST CONCENTRATIONS OF THE SPECIFIED COMPETING SUBSTRATES^a

Filter		Correlation Coefficients (r)					
Competing substrate		All samples	Subset ₁	Subset ₂	Subset ₃	Subset ₄	Subset ₅
<u>Cd_{HCl} vs. organic carbon</u>							
Mn	acetic acid	0.49 ^b	0.51 ^b	0.58 ^b	0.68 ^b	0.67 ^b	0.68 ^b
Humic substances		0.49 ^b	0.50 ^c	0.44 ^d	0.30	0.09	
<u>Cd_{HCl} vs. Fe_{oxal}</u>							
Mn	acetic acid	0.49 ^b	0.47 ^c	0.47 ^c	0.60 ^b	0.63 ^b	0.66 ^b
Organic carbon		0.49 ^b	0.45 ^c	0.41 ^d	0.51 ^e	0.65 ^d	

^a Filter levels and sample sizes for each subset of data are shown in Table 2.

^b $p < 0.001$.

^c $p < 0.005$.

^d $p < 0.05$.

^e $p < 0.01$.

sediments; and (2) HCl extracts Ag bound to humic substances, but does not extract a proportion of the Ag associated with Fe and/or Mn oxides.

Cadmium. Among all samples, Cd correlated significantly with amorphous Fe, organic carbon and particle size (Table 9); and among sediments low in Mn the correlations of Cd with all three variables were enhanced (Table 15). However, amorphous Fe, organic carbon and particle size are intercorrelated (Table 8), thus the relative importance of the three variables in Cd partitioning could not be separated.

Manganese. Manganese may occur in oxidized sediments as Mn carbonate, Mn oxide or Mn bound to other substrates. Strong correlations between Mn and carbonate occurred in sediments low in either organic materials or total Fe (Table 16), suggesting Mn carbonate was more common where substrates which bind Mn were in low concentration. Similarly, the strong correlation of Mn with organic materials in sediment low in carbonates indicated complexation of Mn was important where Mn carbonate was least likely to form in abundance. Manganese also correlated significantly with particle size (increasing in concentration in finer grained sediments) in low carbonate sediments. Such a correlation could be a secondary result of complexation with organic materials in environments where Mn carbonate was less abundant, since Mn oxides tend to occur as discrete particles (Jenne, 1968; 1977).

TABLE 16

CORRELATION OF Mn WITH CARBONATE, PARTICLE SIZE AND ORGANIC CARBON WITHIN SUBSETS OF DATA WHICH EXCLUDE THE SAMPLES FROM THE PREVIOUS SUBSET WITH THE HIGHEST CONCENTRATIONS OF THE SPECIFIED COMPETING SUBSTRATES^a

Filters		Correlation of coefficients (r)				
Competing substrate	Fraction	All samples	Subset ₁	Subset ₂	Subset ₃	Subset ₄
		<u>Mn_{HCl}^b vs. carbonate</u>				
Fe	Total	0.15	0.34 ^c	0.67 ^d	0.72 ^d	
Total organic carbon		0.15	0.35 ^c	0.37 ^c	0.59 ^d	0.81 ^d
		<u>Mn_{HCl}^b vs. particle size</u>				
Carbonate		0.06	0.14	0.18	0.34	0.52 ^c
		<u>Mn_{HCl}^b vs. TOC</u>				
Carbonate		0.09	0.18	0.27	0.49 ^e	0.62 ^f

^a Filter levels and sample sizes for each subset of data are shown in Table 2.

^b Similar effects, but weaker correlations were observed with total and oxalate-Mn.

^c $p < 0.05$.

^d $p < 0.001$.

^e $p < 0.01$.

^f $p < 0.005$.

Acidic extractions (HCl, acetic acid, acid ammonium oxalate, hydroxylamine—nitric acid) appeared to solubilize all three forms of Mn, since no correlation of Mn with any substrate was evident in acid extractants when all samples were considered.

Evidence from calculations with Co, Zn, Pb, Cu and Cd indicated ammonium acetate selectively extracted Mn oxide in low carbon sediments. Correlations of all five metals with ammonium acetate—Mn were weak among all sediments but very strong among sediments low in organic carbon. Hydrous oxide is the form of Mn which binds metals most strongly in sediments. Where little Mn was expected in complexed form (sediments low in organic carbon) the association of metals with ammonium acetate-soluble Mn was strong. Metal correlations with acid-soluble Mn also improved slightly in low carbon sediments (since less organically complexed Mn would be extracted from such sediments the association of the trace metals with the form of Mn involved in binding may have been more evident), but the improvements were not as dramatic as with ammonium acetate—Mn (since the acids extract both Mn carbonate and Mn oxide).

Common effects among metals

Several observations common among a number of metals were also evident

in the calculations. No metal except Cd correlated significantly with the proportion of fine particles in the sediments, either among all samples or in any subset of samples. Particle size is well established as an important variable affecting trace metal concentrations within samples or over narrow concentration ranges (Bryan and Hummerstone, 1977). Through a wide data range, however, anthropogenic/geologic enrichment and chemical associations may swamp out statistically detectable particle size effects among samples.

All metals except Co, correlated negatively with carbonates in sediments which were low in humic substances (i.e., sediments most influence by marine processes). Such correlations could reflect a substantial dilution of metal concentrations where carbonates occur in abundance, or a net desorption of metals with increasing marine influence in seaward estuarine reaches. The former explanation seems most likely, since calcium carbonates constituted up to 30 percent of the sediment weight in some areas. If so, comparisons of trace metal enrichments within and among estuarine stations should be calculated on a carbonate-free basis.

DISCUSSION

Extracting oxidized sediments

Chemical characterization of the sediments in estuaries will be grossly affected by procedures used to collect and store sediments, prior to extraction. Since the oxidized sediments in most estuaries lie in a thin layer at the sediment-water interface, samples collected by procedures (grabs, mixed cores, etc.) which do not include subsurface sediments may show substantially different extractability of metals and substrates than would be observed if only surface sediments were collected. Storage procedures which allow sediments to become anoxic will yield similar results (Thomson et al., in press). A comparison with our results indicate that most studies which have attempted, to date, to characterize sediment-bound metal forms with chemical extractants have considered anoxic sediments (Gupta and Chen, 1976; Serne, 1977; Brannon et al., 1976), despite the chemical and biological importance of the predominantly oxidized sediments at the sediment-water interface.

The extractions were quite useful in describing the fractions of substrates which reacted most strongly with trace metals. Both direct extractions and statistical relationships indicated that the alkali-soluble fraction of the organic substrate was very important in the organic complexation of at least Cu and Ag. The extractable fraction of Fe in the sediment showed a stronger association with Ag, Cd, Cu, Pb and Zn (but not Co) than did total Fe, reflecting the higher density of sorption sites in the amorphous Fe phases removed by extractants (Jenne, 1977). The fraction of Fe extracted by acid ammonium oxalate or IN HCl correlated more strongly with trace metals than did the smaller quantity of Fe removed by acetic acid. The low solubility in acid extracts of both Co and Fe, substantiated the statistical inference

that Co associated with a more crystalline fraction of Fe than did other metals. The association of Co with total Fe indicated either: (1) specific sorption sites of low density, but with a high affinity for Co, may occur in crystalline Fe forms; or (2) much of the Co in these estuaries originated in geologic association with some crystalline Fe mineral. The latter would suggest that nearly all the non-detrital Co was partitioned to Mn.

The extractants operationally defined 3 fractions of Mn, but did not clearly resolve the partitioning of Mn in the sediments. Among all stations, Co, Zn, Pb and Cu generally correlated more strongly with total Mn than with any of the extractable fractions. If we assume Mn oxides are more important in metal partitioning than Mn carbonates or sorbed Mn, the strong correlations of metals with total Mn suggested most extractants contain proportionately more Mn carbonate or bound Mn, and less Mn oxide than does the concentrated nitric acid digest (i.e., much of the trace metal-reactive Mn oxide in sediments is not solubilized by weak acid extraction). The presence of Mn carbonates in the sediments is evidenced by the correlations of Mn and carbonate. However, the improvement of correlations between metals and extractable Mn at stations where concentrations of organic carbon were low rather than in sediments low in carbonates, suggested complexed forms of Mn made up a larger fraction of the Mn extracted by acids than did Mn carbonates.

The extractions were of minimal value in directly removing specific metal forms, as expected (Guy et al., 1977; Luoma and Jenne, 1976). Concentrations of acid-soluble metal correlated strongly with total metal in most instances; thus the fraction of metal involved in partitioning could not be determined from the statistical relationships within the extraction data. The strongest metal-substrate correlations were observed with either HCl-soluble or total metal, suggesting HCl would be the preferred method for an operational definition of "extractable" metal concentration in sediments (as also concluded by Malo, 1977, and Agemian and Chau, 1977). Eaton (1978) recently employed acid ammonium oxalate to assess extractable metal in San Francisco Bay sediments. This method extracted low and highly variable quantities of Pb and Cu from the sediment we studied. Either desorption of Cu and Pb is ineffective at pH 3.3, or some resorption of metals to undissolved substrates (or precipitation in the case of Pb) occurs during the extraction. Acetic acid has also been used to describe extractable and biologically available metals (Loring, 1976); however, in some sediments acetic acid does not extract organically complexed Cu removed by HCl.

The fraction of metal removed from sediments by most weak acid extractants was a constant function of the total metal in the sediment. Although the proportion of weak acid-soluble metal increased with enrichment (except for Ag), the correlation with total metal suggested no acid extractant successfully removed all the non-lithogenic metal. The formation of sedimentary particles by successive layering of adsorption substrates (Jenne, 1977), the solid state diffusion of metals into the interstices of substrates such as manganese oxides (Jenne, 1977), and the movement of metals into lattices

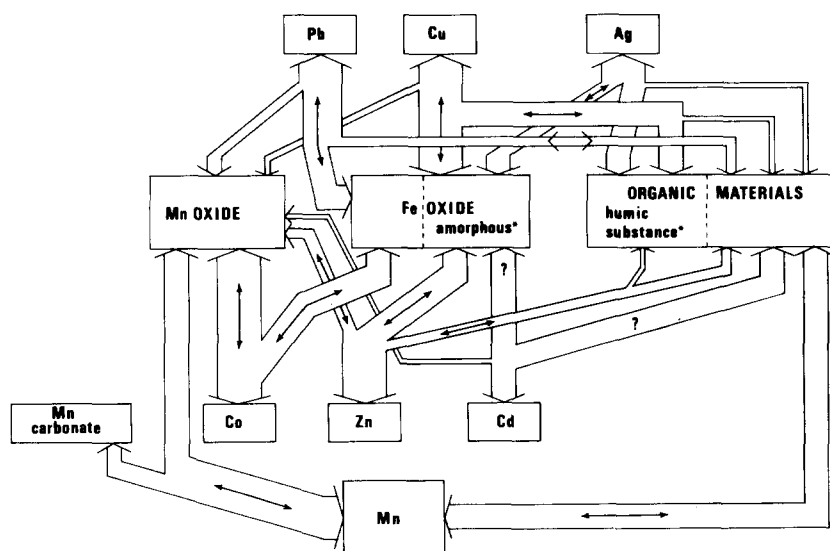
after adsorption (Farrah and Pickering, 1978) may limit the efficiency of acid extractions. A single extraction with a weak acid may aid in assessing the biological availability of some metals from sediments (Luoma and Bryan, 1978; 1979) but our data suggest no extractant will satisfactorily define the anthropogenically-derived metal in a sediment (as proposed, for example, by Agemian and Chau, 1977).

Useful information on metal partitioning in oxidized sediments may be optimally obtained from simple partial extraction schemes which:

- (1) Employ HCl of sufficient acidity to buffer carbonate neutralization;
- (2) Employ an alkaline extractant to characterize concentrations of humic substances; and
- (3) Characterize extractable Fe and Mn oxides with acid ammonium oxalate.

Correlations suggest 1N HCl may be employed in place of acid ammonium oxalate with only a small loss of information. An additional extraction with ammonium acetate could be added to gain information about partitioning to Mn oxides.

The information obtained from such extractions may be useful in statistically illustrating metal-substrate associations, defining the relative abundance of different substrate forms for use in partitioning or bioavailability models, or empirically defining a less-than-total, "extractable phase" of metals in sediments.



* Operationally-defined

Fig. 5. A flow diagram of metal partitioning in oxidized sediments. The width of the arrows roughly signifies partitioning in most sediments in south and west England estuaries; however, in any given sediment partitioning may vary with concentrations of substrates.

Partitioning

Statistical evidence indicated Ag, Cd, Co, Cu, Pb and Zn were all partitioned among a variety of competing substrates in these oxidized estuarine sediments (Fig. 5). The relationships indicated partitioning was characterized by competition between substrates. The outcome of the competition was influenced by substrate concentrations. Hydrous oxides of Fe appeared to dominate the partitioning of Zn, Pb and, possibly, Cd in most sediments; oxides of Fe and humic substances were both generally important in the partitioning of Cu and Ag; and Co appeared to be equally partitioned between hydrous oxides of Fe and Mn. However, organic materials and oxides of Mn were also important in partitioning where sediments contained low concentrations of Fe, except in the case of Co.

Generalizations which infer metal associations with one type of substrate may be overly simplistic. Metal partitioning in sediments is a dynamic process, subject to influence by the physicochemical environment. Metals may be partitioned among several forms simultaneously. The dominant form of any metal may differ substantially among chemically different sediments or within sediments over time.

We have used statistical relationships to test the postulated existence of mechanisms such as concentration-dependent competition among substrates for metal partitioning. Statistical relationships do not prove cause and effect, nor does the existence of correlations predicted from our hypotheses irrefutably prove the postulated mechanisms exist. A statistical approach may be necessary to help identify the important variables in complex natural systems, however, and may be most useful in pointing to specific studies which more directly test the existence of such mechanisms.

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