AN ABSTRACT OF THE THESIS OF

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Title: TRACE METAL REDISTRIBUTION IN ARTIFICIAL ESTUARINE
SEDIMENTS

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The transfer of trace metals within an estuarine
system is a complex function of physical and chemical pro-
cesses unique to that system. Although interactions of
metals with individual components has been studied, there
has been little investigation of interactions with multi-
ple component systems. Thus to further understand these
processes, an artificial sediment was chosen which would
contain the major components of a natural estuarine sedi-
ment and would be simple enough to allow the analysis of
the quantity of metals within each separate component
using a relatively simple extraction technique. In this
way metals could be initially dosed on individual sedi-
ment components and the redistribution of the metals into
other components could be followed as a function of time.
The stoichiometry of the metal redistribution could then
be studied as well as a general determination made of the
rate at which the process could occur.

An artificial sediment containing sea water, humic
acid, montmorillonite clay, ferrous sulfide, and sand was

constructed. Metals were dosed only on one component. The metals chosen were copper, cadmium, lead, and zinc at concentrations of 0.2, 0.1, 0.2, and 0.4 mg/kg in the sediment respectively. The metal-dosed sediments were incubated in plastic bottles over a 44 day period under anaerobic conditions. Bottles were removed periodically for chemical analysis using atomic absorption spectroscopy.

Metals associated with each sediment component were stripped by a stepwise extraction procedure devised specifically for this sediment mixture. Pore water was removed by centrifugation, humic acid metals by 1% ammonium hydroide, clay metals with 1% nitric acid, and ferrous sulfide metals by hot concentrated nitric acid.

Results indicated that metals transfer occurs rapidly and equilibrium is established within five days. Equilibrium was assumed to exist during Days 5 through 14; concentrations of metals were then computed for each metal component and results were correlated with observations found in natural estuarine sediments. Copper was found associated primarily with ferrous sulfide, while cadmium, lead, and zinc were found with the clay fraction. The distribution was discussed in terms of the affinities of the pure sediment components for the individual metals. Anomalous scattering of data at longer incubation times were explained in terms of buffering changes and carryover of particulate matter.

The study concluded that metal transfer between sediment components occurs within a period of several days, that the rate of transfer and stoichiometry were the same for each metal regardless of the initial location, and the extraction technique provided a rapid method of determining the partitioning of metals between the sediment components.

Trace Metal Redistribution in
Artificial Estuarine Sediments

by

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INTRODUCTION

Initially pollution control research centered on the study of gross environmental contaminants such as air particulate matter or sewage. More recently concern has centered on many other more subtle pollutants, especially those present in trace amounts such as chlorinated hydrocarbons and heavy metals.

Heavy metals are particularly important. They are often required in minute quantities in metabolic processes, in which they function by complexing with important organic ligands. Certain metals, however, form such stable complexes that they may interfere with natural processes when present in excess amounts. It is this affinity for ligands that allows heavy metals to accumulate in the food chain. Higher animals and eventually man may then become susceptible to ingestion of toxic quantities of metals. Industrialization has led to release of large quantities of heavy metals and thus their impact on humans has become the focus of recent scientific investigations.

Metals, whether derived from geological processes or from industrial development, generally are transported to the sea in the sequence of rivers to estuaries to oceans.

The estuaries thus become exceedingly important, not solely because of its intermediacy in the transport system, but also because of its special physical and chemical properties which can allow it to act as a natural sink for various metals.

Transport or deposition of metals in an estuary involves the interrelationships of a large number of chemical species. Much work has been accomplished in chemically characterizing estuarine sediments, but few studies have correlated these characteristics with the potential for environmental damage.

Purpose

The purpose of this research was to determine the kinetics and stoichiometry of the redistribution of metals between five chemical components of estuarine sediments. It was attempted to model natural estuarine systems to describe processes that occur when metal-laden particulate matter are introduced into an estuarine environment.

Scope

A five component artificial sediment was chosen to simulate estuarine sediments. This artificial sediment would contain the major components found in natural systems, but would not be so complex as to preclude isolation of

metals associated with individual components. Suitable analytical methods were selected to determine the redistribution of the metals into the remaining sediment components as a function of time. This procedure allowed evaluation of the rates of redistribution and natural affinities of the metals for certain components.

Objectives

The objectives of this study were:

1. To determine the rates of metal redistribution in an artificial estuarine sediment;

2. To determine the stoichiometry of redistribution of each metal into the sediment components, and

3. To develop a practical, rapid analytical method for separating the metals associated with individual sediment components.

BACKGROUND

Introduction

The literature contains a substantial amount of material which covers the interaction of individual metal ions with various components of soil and sediments. Unfortunately studies of multicomponent systems generally are concerned with overall metal content rather than distribution through separate components. In lieu of such rigorous investigations, a review is provided that will assess the current knowledge of interactions of four metal cations - those of cadmium, copper, lead, and zinc - with sea water, humic acid, montmorillonite clay, and iron sulfide. In addition, the review will cover work concerning interactions of two sediment components in the presence of metals, as well as progress in perfecting extraction techniques used to separate metals from individual components of naturally occurring marine sediments.

Interaction of Trace Metals with Sea Water

It is well known that most metal ions in aqueous solution do not exist as distinct entities, but instead interact with water or ligand-forming species to form hydrated or complexed ions (Weber, 1972). In addition, a sphere of water molecules also solvates the ion or complex

to increase its effective diameter. This sphere of solvent is particularly important in the process of adsorption. Physical and chemical adsorption is a major pathway for the removal of trace metals from sea water and contributes substantially to observed low concentrations. Trace metal concentrations normally found in sea water are shown in Table 1. (Brewer and Spencer, 1975).

Table 1. Concentrations of metals in sea water (Brewer and Spencer, 1975)

Metal	Concentration (moles/l)
cadmium	1×10^{-9}
copper	8×10^{-9}
lead	1×10^{-10}
zinc	8×10^{-8}

Based on the normal levels found in sea water, Millero (1975) graphed the various chemical species of each of the four metals shown in Table 1 using the known formation constants of complexes and solubility products. The results are shown in Figure 1 indicate that for ionic species the chloride complexes are most important for cadmium, lead, and zinc, while hydroxy complexes predominate in copper species. Goldberg (1965) as well as Hahne and Kroontje (1973), however, found that hydroxy compounds of lead predominate over chloride complexes.
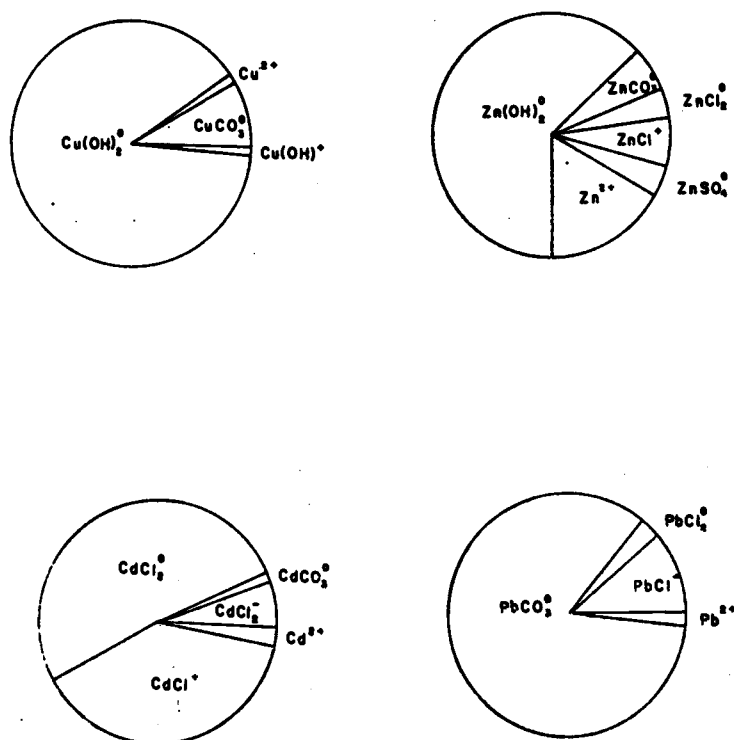
Figure 1. Metal species of copper, zinc, cadmium, and lead
in sea water at 25° C (Millero, 1975)

It thus seems apparent that, except for zinc, the divalent
cations are nearly nonexistent in the marine environment
and monovalent cation complexes will most likely be the
ionic species involved in interactions with other sedi-
ment components.

Interaction of Trace Metals with Humic Acid

Humic acids are a complex mixture of organic

compounds derived from the decomposition of plant and animal matter. Since living matter varies widely in composition, humic acids derived from this matter will also vary considerably. However, several distinct classes of compounds seem to predominate. These are phenols, aromatic carboxylic acids, quinones, polysaccharides, and nitrogenous material. (Flaig, et al., 1975). It is the organic functional groups that define these classes of compounds that are responsible for the interactions of humic acids with metal ions and complexes.

The carboxylic acid and phenolic hydroxyl groups, and to a much lesser extent the carbonyl and amino groups, are the most significant chelating functionalities. By blocking functional groups, several workers (Schnitzer, 1969; Schnitzer and Skinner, 1965; Rashid, 1971) found that metals were most probably chelated by phenolic and carboxylic groups simultaneously. since the dissociation of these acidic groups is pH dependent, it is likely that the binding stability of the metal humate is also pH dependent (Shapiro, 1964; Ghassemi and Christman, 1968). Other factors influencing the stability include the nature of the metal (Rashid, 1971; Schnitzer, 1969) as well as E_h and the nature of the humic acid (Jackson, 1975). Cation exchange capacities of humic acids have been found to be about three times that of an equivalent weight of clay in soils (Helling,

et al., 1964). However, its weight contribution in soil is significantly less than that of clay.

Most interest concerning organo-metal complexes was focused on determining the stability constants and competition of different metals for active sites. Stability constants are the result of two equilibria expressions (Bjerrum, 1941 as modified by Gregor et al., 1955),

$$HA + M^{+2} \xrightarrow{b_1} MA^+ + H^+$$

$$HA + MA^+ \xrightarrow{b_2} MA_2 + H^+$$
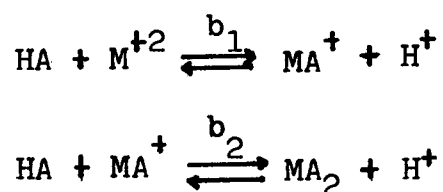
where HA humic acid, MA^+ and MA_2 are metal humate complexes, and M^{+2} and H^+ are free metal ion and hydrogen ion respectively.

The overall stability constant is given by:

$$B_2 = b_1 b_2 = \frac{[MA_2][H^+]^2}{[HA]^2[M^{+2}]} \quad .$$

Thus comparative complexing ability of metals can be quantitatively measured by comparison of stability constants. Stevenson (1976) applied potentiometric titration methods to determine the stability constants of humic acid complexes of copper, lead, and cadmium. The results are shown in Table 2, and were determined at a relatively low ionic strength (~ 0.1) and at pH 5. Thus the order of stabilities of the complexes is $Cu^{+2} > Pb^{+2} > Cd^{+2}$. This result

parrallels the stabilities found for various other metal complexes, which were summarized by the "Irving-Williams" series (Irving and Williams, 1948):

$$Cu^{+2} > Pb^{+2} > Ni^{+2} > Co^{+2} > Zn^{+2} > Cd^{+2} > Fe^{+2} > Mn^{+2} > Mg^{+2} > Ca^{+2}$$
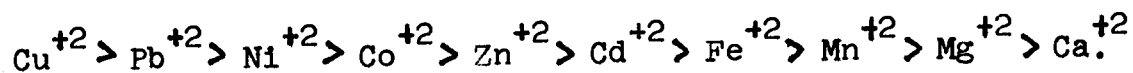
Table 2. Stability constants of humic acid complexes of copper, lead, and cadmium (Stevenson, 1976).

Metal	$\log B_2$
copper	- 1.3
lead	- 1.9
cadmium	- 4.2

Guy, et al. (1975) studied the sorption characteristics of metals with humic acid and found the limiting Langmuir adsorption concentrations shown in Table 3. Their experiments again indicated the strong preference of humic acid for copper. Zinc and cadmium have essentially identical affinity for the organic material.

Table 3. Limiting values for the adsorption of trace elements by humic acid (Guy, et al., 1975)

Metal	$\dfrac{\text{mmoles metal}}{\text{g humic acid}}$
copper	0.42
zinc	0.21
cadmium	0.22

The equilibria expressions for stability constant
calculation also illustrate why a decline in pH occurs dur-
ing the "binding" of metals to humic acids. By addition
of metal salts and subsequent titration of the released
protons an indication of the relative affinity of metals
for humic acids may be obtained. Van Dijk (1971) added
several metals to humic extracts and determined that copper
was most firmly bound, followed by lead and zinc (measured
at pH 5). At higher pH values he recognized the interfer-
ence caused by formation and bonding of hydroxy complexes
of the metals.

Khan (1969) measured the pH drop which occurred
upon the addition of metal ions and noted that the binding
strength of the complex diminished in the order $Fe^{+3} >$
$Al^{+3} > Cu^{+2} > Zn^{+2} > Ni^{+2} > Co^{+2} > Mn^{+2}$. Other researchers
(Khanna and Stevenson, 1962; Martin and Reeve, 1958; Basu,
et al., 1964) observed similar results and noted that cop-
per was bound much more firmly than zinc. Cadmium has
been found to complex with humic acids, but to a lesser ex-
tent than zinc (Levy and Francis, 1976).

In summary it appears likely that for the metals
of interest in the present work copper is bound most firmly
to humic acid, followed by lead, zinc, and cadmium. The
latter two elements appear to bind with nearly equal
strength. It must be noted that this generalization is

applicable to metal-humic acid systems only; interactions
involving the three component clay-humic acid-metal system
will be discussed later.

Interactions of Trace Metals with Montmorillonite

Montmorillonite (bentonite) is a crystalline smec-
tite group clay mineral primarily consisting of silica and
alumina. As shown in Figure 2, montmorillonite units con-
tain sheets of tetrahedral silica sandwiching the central
alumina octahedral sheets. Exchangeable cations and water
may penetrate between the tri-layers during the process of
adsorption (Grim, 1968).

Exchangeable Cations
nH$_2$O
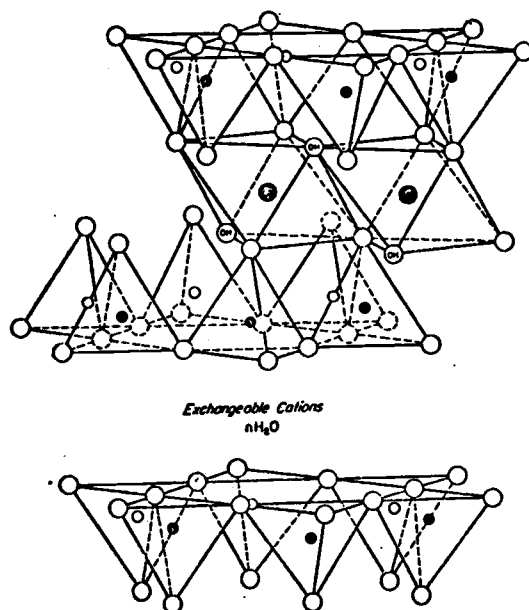
Figure 2. Crystalline structure of montmorillonite (Grim,
          1968).

A measure of the relative ability of exchangeable ions to adsorb to clay minerals is termed the cation exchange capacity (CEC) and is measured in milliequivalents of metal per 100 g at pH 7.0. Grim (1968) has determined that montmorillonite owes its relatively high CEC (80-150 meq/100 g) to two mechanisms: 1) broken bonds at the edges of the silica-alumina sandwich give rise to excess charges which must be satisfied by cation adsorption (20% of total CEC), and 2) substitution of trivalent aluminum for tetravalent silicon, or divalent magnesium for trivalent aluminum in the lattice structure which would again give rise to excess negative charge (80% of total CEC). It thus seems apparent that the two types of available sites will be of unequal energy and thus binding strength to cations will be variable.

The replaceability of one cation for another is a function of a number of factors including the relative concentrations of the competing ions, the nature of the ions, temperature, pH, and ionic strength. The relative ability of ions to displace other ions is quantitatively measured by the selectivity coefficient (SC), and is usually determined by the displacement of calcium ion.

$$SC = \frac{\left[\frac{[ion]}{[Ca]}\right]_{clay}}{\left[\frac{[ion]}{[Ca]}\right]_{solution}}$$

Although selectivity coefficients for the four trace metals used in the present work have not been studied simultaneously by one investigator to minimize differences in experimental conditions, relative adsorptions have been determined for isolated groups of ions. Lead and cadmium selectivity coefficients have been determined on montmorillonite (Bittel and Miller, 1974) using the calcium ion displacement method and were found to be 1.7 and 1.0, respectively. These results indicate that lead is preferentially retained over cadmium by a factor of 2 to 1, and cadmium is about equally competitive with calcium for adsorption sites. The solution pH varied between 4.8 and 6.5, and the metal salt solutions were 2-3 times the CEC of the clay. It should be noted that the selectivity coefficient has been reported as 3-4 at a pH of 7.8 (Bondietti, et al., 1974) on montmorillonite. It is of course difficult to assess the significance of these relatively small differences since the pH as well as the nature of the clay were different.

Studies of copper and zinc on H-montmorillonite (Bingham, et al., 1964) indicated that pH was extremely important, since precipitation of the metal hydroxides appeared to occur as the pH increased. At lower pH ranges (2-5) copper and zinc were found to be essentially equally adsorbed. Basu et al. (1962), however, found that at pH 4 montmorillonite was more selective toward copper than

zinc. Bingham (1964) was using extremely high concentrations of saturating metal salts (up to 3500 meq/100g clay), and his observation that metal retention was approximately equal to the CEC at low pH is certainly not unexpected.

Other workers studied the distribution coefficient of trace metals at concentrations which approach those of natural waters (Guy, et al., 1974). At a pH of 5 and ionic strength of 0.001, the distribution coefficients of copper, cadmium, and zinc were 9.0, 4.8, and 4.3 respectively on montmorillonite. This result affirms the relative affinities of these metals for clay as cited previously.

The effect of ionic strength on the adsorption of cadmium has also been investigated (Garcia-Miragaya and Page, 1976). Studies indicated that increasing ionic strength (0.01 to 1.00) resulted in decreased adsorption. Results with the chloride and perchlorate salts showed that 25-50% less adsorption took place with chloride salts at equivalent ionic strength. The authors suggested that negatively charged complexes ($CdCl_3^-$ and $CdCl_4^{-2}$) and uncharged $CdCl_2$ might explain the diminished adsorption. All adsorption experiments were carried out at a pH of 6.5 - 7.0.

In summary, it is difficult to accurately judge the relative adsorptions of the four metals considered in this paper. Clearly there is a pH dependence operating. Studies at the lower pH ranges however seem to indicate

that lead is probably adsorbed to the greatest extent, but it seems likely that there are no great differences between the ions. It is quite possible that solubility considerations dictate the degree of adsorption since hydroxy complexes would predominate at higher pH.

Interaction of Trace Metals with Ferrous Sulfide

Experimental work concerning the interaction of trace metal ions with ferrous sulfide seems to be absent from the literature, although it is expected that simple replacement reactions occur readily and chemical reaction would predominate over adsorption.

Interaction of Trace Metals in Mixed Systems

An important consituent of many soils is the clay-organic complex, a surprising entity considering that clays are known to possess a negative charge, as do dissociated humic acids. Ordinarily repulsion occurs, but in the presence of metal ions a "bridge" between the two anionic groups is possible through the mutual attraction for the cation. Although strong bridges may result for aluminum (III) and iron (III) cations, divalent ions can be readily displaced from the clay-organic complex by leaching (Greenland, 1971). In any event, the adsorption of the metal ion in a mixed system may be modified relative to pure

systems of clay and humic acid. However, cadmium adsorption on montmorillonite was unaffected by the additional adsorption of humic acid on the clay (Levy and Francis, 1976). This result may be misleading since cadmium was found to be weakly adsorbed by humic acid anyway (Stevenson, 1976). It seems likely that clay-humic acid complexes probably behave as if the two species were simply separated. Schnitzer and Kodama (1966) found that a humic material (fulvic acid) was adsorbed only on the external montmorillonite surface and failed to penetrate the clay matrix at pH 7. Thus only a slight reduction of the CEC of the clay and humic acid would be expected since 80% of the CEC is due to ions penetrating the matrix sheets (Grim, 1968).

The powerful role that humic material may play in the transfer of metals was clearly demonstrated by Pauli (1975). Reaction of heavy metal humates (copper, zinc, lead, and cadmium) suspended in water saturated with hydrogen sulfide for two days gave only 60% conversion to the corresponding metal sulfide. The solution pH was not stated nor was the contribution of the individual metal humates to the total conversion. It was significant, however, that despite the marked insolubility of heavy metal sulfides the extreme conditions were insufficient to liberate all the metals from their humates. In a related work, Rashid and Leonard (1973) approached the study from the

opposite direction. Their investigation of the solubiliz-
ing effect of humic acid on precipitated metal sulfides
indicated that solubilization can occur even with very in-
soluble sulfides (CuS). Their results for this experiment
are shown in Table 4. Reaction times were three days.
Table 5 indicates the effect of humic acids in preventing
the precipitation of metal sulfides. It is again evident
that the organic complexes apparently suppress the process
by effectively lowering the concentration of free ions in
solution to a value below that required for the precipi-
tation.

Table 4. Quantity of metal solubilized per gram of humic
acid at pH 7. (Rashid and Leonard, 1973)

Metal sulfide	mg solubilized
CoS	90
CuS	36
MnS	338
Nis	0
Zns	23

Table 5. Quantities of metals (μmoles) required to cause
precipitation in a solution with $[S^=] = 100$
μmoles/50 ml, $[HA]=6.2$ mg/50 ml, pH $= 8.5$
(Rashid and Leonard, 1973)

	Mn	Ni	Cu	Fe
Sulfide alone	2.7	5.1	3.2	1.4
Sulfide + humic acid	50.6	40.9	37.0	60.0

A related investigation (Baker, 1973) examined the dissolution of both sulfide minerals and precipitated metal sulfides with a podzolic humic acid solution (0.1%, pH 3-3.4). His work indicated solubilization of the sulfides decreased in the order CuS > PbS > ZnS, exactly the opposite predicted by the solubility products of the respective sulfides. The results also indicated that appreciable solubilization occurred after only 24 hours. Interestingly, extremely large quantities of pure metals could also be extracted with the humic acids, which might be the result of relatively low pH and strong complexing ability of the humic substances.

In summary it appears that humic acid is capable of binding clay minerals through a metal bridge, but this bridge is probably relatively labile toward extracting agents. Most importantly, it appears that metal sulfides may be significantly solubilized by the action of humic acids, and this action may occur over a wide pH range in very short periods of time.

Extraction Techniques for Selective Solubilization of Metals in Sediment Fractions

Although a great deal of interest has been directed toward studying the relative strength of adsorption on one particular sediment component, the problem becomes more

complex in multicomponent systems. Ideally reagents are required which specifically release metals from one soil component without simultaneously interacting with another. Several methods described in the literature are summarized in this section.

Presley, et al. (1972) described a method in which soluble salts were initially removed. The sediment was then treated with hydroxylamine hydrochloride-acetic acid to remove metals associated with carbonates, some sulfides, and oxides of iron and manganese. A third leaching with hydrogen peroxide removed the remaining metals from sulfides and organic matter. A final dissolution of the sediment in a mixture of hydrofluoric, nitric, and perchloric acids completed the procedure.

Nissenbaum (1972) using an alternate approach to the previous work, leached sediments successively with boiling water, alkaline hydrogen peroxide, 2N acetic acid, and 6 N hydrochloric acid. The acetic acid fraction was acknowledged to contain metals leached from calcium carbonate, iron and manganese oxides, and most (if not all) clay lattice sites. The subsequent leaching with hydrochloric acid to dissolve remaining oxides of iron and manganese also resulted in the decomposition of some clay lattice sites.

Another method (Mercer and Swift, 1974) called first for the removal of interstitial water. Soluble ions

and weakly adsorbed ions were removed from the sediment by washing with distilled water and 1 $\underline{N}$ ammonium acetate solution. Organics and metal sulfides were then removed by oxidation with sodium hypochlorite. A fifth fraction was produced by treating the leached sediment with 25% acetic acid to remove metals from carbonates and acid soluble iron oxide minerals. A buffered mixture of sodium citrate and sodium dithionite removed metals from remaining hydrous oxides. After leaching with 6 $\underline{N}$ hydrochloric acid to remove other metals in mineral lattices the residual sediment was totally digested to remove all remaining metals.

Several workers have examined the distribution of copper in soil fractions. Grimme (1967) separated five soil fractions chemically. Organically bound copper was first extracted with a 0.5 $\underline{N}$ sodium hydroxide -0.01 $\underline{M}$ EDTA mixture. Extraction of the residue with ammonium oxalate-metallic zinc combination (reducing conditions) released copper bound in iron oxide lattices. Treatment of this residue with perchloric acid freed the metal from silicate minerals; final treatment with perchloric-hydrofluoric acid dissolved the remaining solids. A more refined method, provided by McClaren and Crawford (1973), is summarized in Figure 3. Organically bound copper was separated by extraction with potassium pyrophosphate, while copper occluded in oxides was removed by treatment with acidic ammonium

oxalate. Sorption of copper on inorganic sites (specific adsorption) was determined by extraction with 2.5% acetic acid solution. The investigators recognized that interferences might result from incomplete solubilization of one fraction with subsequent carryover to the next. Copper present on readily exchangeable sites and in pore water was leached with 0.05 M calcium chloride using untreated soil samples.
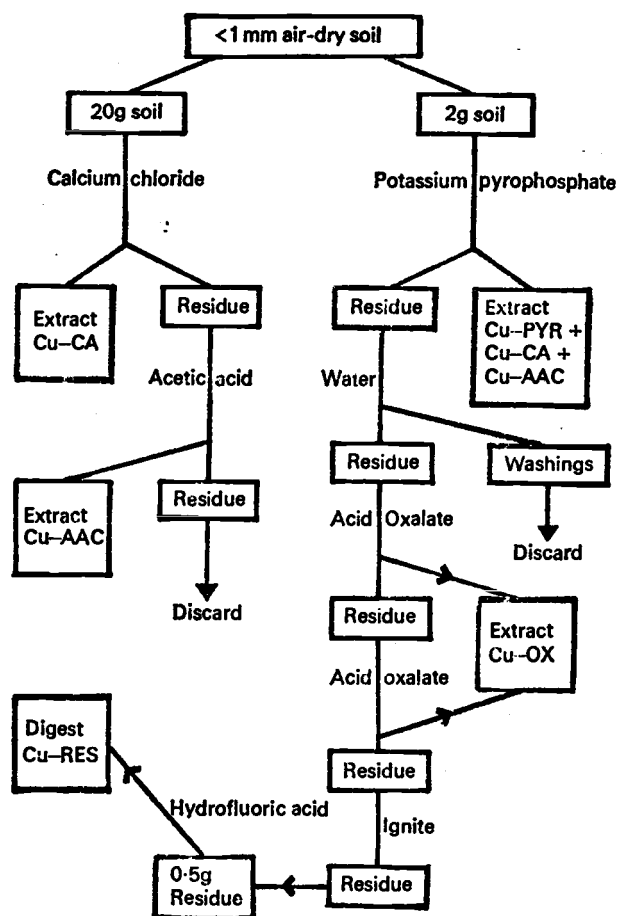
Figure 3. Flow diagram for separation of copper in soil fractions (from McClaren and Crawford, 1973).

More recently, chemical extractions were performed on freshwater, marine, and estuary sediments Brannon, et al., 1976). Interstitial water was removed by centrifugation. A second sediment sample was treated with 1 $\underline{N}$ ammonium acetate to remove readily exchangeable ions. The residue was leached with 0.1 $\underline{M}$ hydroxylamine hydrochloride-0.01 $\underline{M}$ nitric acid to remove primarily metals associated with hydrous oxides of manganese, although hydrous iron oxides probably also contribute. A subsequent extraction with acidic hydrogen peroxide to remove metals bound to organics and sulfides was followed with a citrate-dithionite leaching to remove metals in the remaining hydrous iron and manganese oxides. A final total digestion with nitric and hydrofluoric acids completed the procedure.

In summary, extraction procedures vary considerably and it is difficult to judge the effectiveness of any one technique. There is also no criteria to judge how specific a given extractant is for a definite sediment component, and extracts can only be defined in such terms as "easily reducible" or "acid leachable". In addition, since oxidative workup with hydrogen peroxide or sodium hypochlorite results in removing metals in both organic and sulfide sediment components, there is no way to further partition this fraction into their component subgroups. It is apparent that a great deal of work remains to be done to

refine the methods of sediment metal classification.

EXPERIMENTAL

Materials

Solutions and Reagents

Nitric and hydrochloric acids were distilled prior to use. All other materials were reagent grade unless specified otherwise.

Stock metal solutions were prepared by dissolving 1.000 g of pure metal in acid and diluting each to 1.0 liter. The standard lead solution was prepared by dissolving 1.598 g of lead (II) nitrate in dilute nitric acid. All metal solutions contained 1000 mg/1 of metal.

Standard metal colutions were prepared by dilution of the stock solutions with the appropriate amount of double distilled water. Standards contained 1, 5, 10, and 20 mg/1 of metals.

Sea Water

Sea water was obtained from Oregon coastal waters, filtered through a 0.45 μ Millipore filter, and stored in Nalgene bottles.

Humic Acid

Humic acid (Aldrich Chemical, technical grade) was

found to contain 13% inorganic material after combustion at 550° C. It was thus repurified in the following manner. A 100 g sample was dissolved in 1.0 liter of dilute ammonium hydroxide solution and the pH adjusted to 10.5-11 by addition of concentrated NH_4 OH. The resultant slurry was transferred to centrifuge bottles and centrifuged for 15 minutes. The residue was discarded and the solution filtered twice through GF-A glass filters using a Millipore "sterifil" filtration apparatus. The filtrate was acidified to pH 1 with hydrochloric acid, centrifuged, and the supernate discarded. The solid resiude was washed twice with distilled water, dried in an oven at 80-90° C, and crushed to a fine powder to give 46.3 g of dark brown solid.

Montmorillonite

Montmorillonite clay (Cameron, Arizona; API Standard No. 31) was suspended in distilled water, centrifuged, and dried at 50-60° C. The dry solid was then powdered with a mortar and pestle.

Sand

Reagent sand (Mallinkrodt #7062) was used without modification. Analysis of samples showed no leaching of metals occurred into a solution of nitric acid.

Ferric Hydroxide

Stock ferric hydroxide suspension was prepared by dissolving 8.44 g of ferric chloride hexahydrate in 100 ml of sea water and adjusting the pH to 7 with NH_4 OH. The suspension was then diluted to 1.0 liter with sea water.

Ferrous Sulfide

A suspension of ferrous sulfide was obtained by diluting 500 ml of stock ferric hydroxide suspension with an equal volume of sea water. The diluted slurry was treated with excess hydrogen sulfide gas and gave a black suspension having a pH of 4-4.5. The suspension was then swept with prepurified nitrogen until a moistened lead acetate paper strip failed to give a positive test for H_2S. The final pH was 6.8 - 7.0. The suspension was stored in a glass container until ready for use. A 10 ml sample would produce the equivalent of 500 mg/kg of FeS-sulfur in the final sediment sample.

Dosing of Metals

Sea water was dosed with metals using the following method. A mixture containing the following volumes of stock metal solutions (1.00 ml 1.00 mg metal) was prepared:

10 ml Zn^{+2}, 5.0 ml Cu^{+2}, 5.0 ml Pb^{+2}, and 2.5 ml of Cd^{+2}.
The pH was adjusted to 7.5 with NH_4OH and diluted to 1.0
liter with sea water.

Individual metal humates were prepared by treating
a humic acid sample with a single metal solution using the
following procedure. Separate 3 g samples (5 g for zinc)
of purified humic acid were treated with 100 ml portions
of each stock solution of metal and the pH adjusted to 7
with NH_4OH. After initial swirling, the flasks were al-
lowed to stand 1 to 2 hours. The contents were filtered
through GF-A glass fiber filters, the residues dried at
100-105° C, and the solid powdered using a mortar and pes-
tle. Yield of metal humates were: Zn-HA (3.0 g), Cu-HA
(1.3 g) Cd-HA (1.2 g), and Pb-HA (1.2 g). Analysis of the
humates by atomic absorption showed they contained, res-
pectively, 10 mg Zn/g, 14 mg Cu/g, 18 mg Pb/g, and 4.3 mg
Cd/g.

Individual 100 g samples of montmorillonite clay
were treated with 100 ml of the appropriate stock solutions
of metals and 100 ml of distilled water, and the pH was
adjusted to 7 with NH_4OH. After standing several hours
the suspensions were centrifuged, the supernatant liquid
discarded, and the residue dried in an oven at 50-20° C.
The dry residue was powdered using a mortar and pestle.
Yield of metal-clay were: Zn-clay (90.5 g), Cu-clay

(90.0 g), Cd-clay (90.0 g), and Pb-clay (89.3 g). Analysis by atomic absorption on 1.0 g samples extracted with 1% HNO_3 showed the metal clays contained respectively 0.79 mg Zn/g, 0.64 mg Cu/g, 0.50 mg Cd/g, and 0.98 mg Pb/g.

Metal-dosed ferrous sulfide was prepared by treating 250 ml of stock ferric hydroxide suspension with a solution containing 40 ml Zn^{+2}, 20 ml Cu^{+2}, 20 ml Pb^{+2}, and 10 ml Cd^{+2}. The solution had been prepared from the stock metal solutions and had been adjusted to a pH of 7 with NH_4OH. After diluting to 500 ml with sea water, the mixture of ferric hydroxide and metals was treated with excess gaseous hydrogen sulfide, then swept with prepurified nitrogen until a moistened strip of lead acetate paper indicated the absence of H_2S. The suspension was stored in a stoppered glass container until ready for use.

Preparation of Incubation Bottles

A mixture of 1.2g of Zn-humate, 0.33 g of Pb-humate, 0.42 g of Cu-humate, 0.69 g of Cd-humate, and 3.36 g of untreated humic acid was thoroughly mixed to give a powder, a 0.2 g sample of which would contain 0.4 mg Zn, 0.2 mg Pb, 0.2 mg Cu, and 0.1 mg Cd.

In addition, a mixture of metal-dosed clays, containing 15.0 g Zn-clay, 6.0 g Pb-clay, 9.0 g Cu-clay, 6.0 g Cd-clay, and 24.0 g of undosed clay, was also prepared.

A 2.0 g sample of the mixture contained 0.4 mg Zn, 0.2 mg Pb, 0.2 mg Cu, and 0.1 mg Cd. Both these metal humate mixture and clay-metal mixtures were used for dosing.

Forty nalgene bottles (60 ml) were filled with 7.8 g of reagent sand. The bottles were dosed with metals by introducing the elements in one of four separate components, i.e. sea water, humic acid, montmorillonite, or ferrous sulfide. Ten bottles were allocated for metal dosing by each one of the four components. The following amounts of sediment components were used in each bottle: clay (or clay-metal mixture) 2.0 g, humic acid (or metal humate mixture) 0.2 g, ferrous sulfide (or metal-dosed ferrous sulfide) 10 ml, and sea water (or metal-dosed sea water 40 ml). After the contents were added, the bottle was swept with prepurified nitrogen and the pH was adjusted to 7.5-8 with 5 $\underline{M}$ sodium hydroxide solution. The bottles were sealed, placed in glass jars under a positive pressure of nitrogen, and the jars placed on a mechanical shaker. The bottles were shaken continuously during the incubation and maintained at room temperature. Periodically four bottles representing each one of the four metal-dosed components was withdrawn for analysis. The remaining bottles were readjusted to pH 7.5-8 if necessary by periodic addition of 4 drops of saturated sodium bicarbonate and 1 drop of 5 $\underline{M}$ sodium hydroxide solution. The bottle was then purged with prepurified nitrogen and resealed for incubation.

Analysis

The analyses of separate sediment components were done in the following manner. The contents of the bottle were poured into a 50 ml glass centrifuge tube and centrifuged 3 minutes at 3100 rpm. The supernate containing interstitial water ("IW") was decanted into a Nalgene bottle and the remaining solid treated with three separate 15 ml portions of 1% ammonium hydroxide solution. The slurry was centrifuged between washes and the supernate separated. The combined liquids contained dissolved humic acid ("HA"). The solid was then extracted with two 20 ml portions of 1% nitric acid, the slurry centrifuged between washes, and the washes combined to give the clay extracted metals ("clay"). Finally the solid residue was treated with 25 ml of concentrated nitric acid for 15 minutes and the resulting hot mixture was centrifuged to give a supernate liquid which contained the ferrous sulfide extracted metals ("FeS"). Each extract was diluted to 50 ml with distilled water and analyzed on a Perkin-Elmer 360 atomic absorption spectrophotometer using flame techniques and single element lamps. Concentrations were obtained using standard calibration curves. The concentration of each metal in each of the extracts is shown in Appendix 1.

Methods

Heavy metals may be transported into an estuarine
system by a number of pathways, principally as dissolved
material in the water column or as adsorbed species on
suspended matters such as organics, weathered mineral mat-
ter, and hydrous metal oxide coatings. Suspended matter
may interact with estuarine systems in such a manner that
adsorbed metals may be incorporated into sediments, leading
to an enrichment of these potentially toxic elements. In
order to develop an understanding of the rate at which me-
tals may be transported from one component to another, a
model estuary sediment was chosen and a method developed
which would allow isolation and determination of metal
loading on each sediment component. Metals were then arti-
ficially incorporated into different sediment components
and the progress of metal migration followed by incubating
the sediments and determining sediment component metal con-
centrations as a function of time until equilibrium was
established.

Sediment

A model sediment was required which would contain
the major components found in an estuary, yet would not be

so complex as to preclude relatively clean isolation of
component metals. The system which was finally chosen con-
tained organic matter, clay, sand, iron sulfide, and sea
water in a proportion that approximated that found in an
estuary. The organic matter found in estuarine systems is
a complex mixture of compounds; humic acid, the product of
decomposition of plant and animal matter, probably most
closely resembles the organic material found in natural
systems. The material used in this study was commercial
humic acid, purified to remove inorganic material by alter-
nate extraction with base, centrifugation to remove solids,
and reprecipitation at pH 1. In order to assess transport
rates, a clay with low cation exchange capacity (CEC) would
appear essentially inert in this system. Thus, a clay with
a high CEC, such as montmorillonite (bentonite) or vermicu-
lite, would be more desirable. Montmorillonite was chosen
since it is found in greater abundance in sediments (Grim,
1968). Sand, with a low CEC and chemically inert, served
only to aid in proportioning the other components. Iron
sulfide was synthesized in a manner which would resemble
the processes active in an anoxic estuarine system. Iron
(III) hydroxide was first produced by combining ferric
chloride and ammonium hydroxide. The floc was then satur-
ated with gaseous hydrogen sulfide and excess H_2S removed
by sweeping with nitrogen. This ensured the complete

conversion of the ferric hydroxide to ferrous sulfide as
well as the complete absence of excess sulfide which would
likely precipitate free metals during the course of the in-
cubation. Finally, the sea water utilized as pore water
was filtered through a 0.45 μ Millipore filter to remove
suspended and colloidal material which also might inter-
fere with the experiment. The relative proportion of each
component was chosen to approximate an average anaerobic
system, and is outlined in Table 6.

Table 6. Abundance of each component in model sediment.

Component	Per cent
Humic acid	2
Clay	20
Sand	78
Ferrous sulfide-S	0.05[a]

a. 500 mg/kg as FeS-S

Introduction of Metals

In order to study metal migration, different sediment com-
ponents were dosed with metals and the uptake of these ele-
ments in the remaining components was measured as a func-
tion of time. The metals chosen were cadmium, copper, lead,
and zinc. These elements represent species of particular
interest since they are frequently associated with human

industrialization. Standard solutions of the elements
were prepared by dissolving the pure metal in acid solu-
tion (lead solutions were prepared from the nitrate salt).
These standard solutions were then used to treat each of
the sediment components. Examination of studies carried
out by others (Mercer and Swift, 1974; Posner and Weber,
1975) indicated a wide range of metal concentrations exist
in estuary and harbor sediments, as shown in Table 7. Since
the upper region of these concentration ranges represent
values for sediments in highly industrialized areas it
seemed prudent to select more conservative values that
would reflect a more generalized estuary. Thus in this
study the dosages were adjusted to give cadmium, 10 mg/kg;
copper, 20 mg/kg; lead, 20 mg/kg; and zinc, 40 mg/kg.
Cadmium was given a relatively high dosage in order to
facilitate measurements by atomic absorption.

Sediment components were dosed in the following
manner. Pore water was prepared by mixing the appropriate
amounts of stock metal solution, adjusting to pH 7, and
diluting with sea water. The humic acid was dosed by add-
ing each of the metal solutions to separate portions of
purified humic acid. The suspensions were then neutralized,
allowed to mix for 1-2 hours, filtered, dried, and powdered.
Samples were then dissolved in dilute base and analyzed for
metal content by atomic absorption. From these data the

Table 7. Range of trace metal concentrations in estuary
          and harbor sediments (Mercer and Swift, 1974;
          Posner and Weber, 1975).

Metal	Range (mg/kg)
cadmium	0.21 - 5.2
copper	11 - 121
lead	17 - 131
zinc	42 - 314

appropriate amount of each metal humate was added to a
known amount of purified humic acid. A 0.2 g samples of
this final mixture of powders contained the requisite a-
mount of each metal. Montmorillonite clay was dosed in
much the same manner. Separate portions of clay were
treated with each of the standard metal solutions. The
solid was then separated by centrifugation and dried.
Analysis of known amounts of each clay-metal were performed
by stripping the clay with dilute nitric acid and measuring
the concentration in the eluate by atomic absorption. A
mixture of untreated clay and each of the clay-metals was
prepared in auch a manner that a 2.0 g sample contained
the requisite amount of each metal. The ferrous sulfide
fraction was prepared by treating ferric hydroxide with
a solution of all four metals which had previously been
adjusted to pH 7. The floc was then treated with excess
hydrogen sulfide; excess sulfide was then removed by sweep-
ing with nitrogen. A 10 ml smaple of this suspension pro-
vided the requisite amount of each metal. The sand was not
treated with metals.

The incubation vessels were Nalgene bottles with
plastic caps containing Nalgene liners. Ten bottles were
assigned to each of the following metal-dosed components
respectively: sea water, humic acid, clay, and ferrous
sulfide. All other components in each series were undosed.

After mixing the components in each bottle, the mixture was purged with nitrogen, adjusted to pH 7.5-8, and sealed. Substantial transfer of oxygen through Nalgene was found to occur in preliminary trials. This was corrected by placing the bottles in glass jars and maintaining a positive pressure of nitrogen in the jars. The pH was maintained at 7.8 by periodic checks and addition of a sodium bicarbonate-sodium hydroxide buffer. The bottles were shaken continually and maintained at room temperature.

Metal Analysis

The most difficult task in this investigation was to obtain a clear separation of the metals associated with each sediment component. Separation of the sea water (pore or interstitial) fraction was easily accomplished by centrifuging the bottle contents and decanting the supernatant liquid. Most partitioning schemes generally ignore or discard this fraction. Mercer and Swift (1974) also carried out an additional rinse with distilled water. Preliminary studies here indicated only trace amounts of metals in this rinse cycle, with the disadvantage of loss of colloidal material from the remaining sediment due to the greatly decreased ionic strength of the wash. The rinse step was thus discarded.

After the removal of the interstitial water, the major step is accomplishing the separation of the humic acid,

clay, and ferrous sulfide fractions cleanly. Several ap-
proaches were attempted in this work before a final selec-
tion was made. Two methods are outlined in Figure 4.
Scheme 1 involves a preliminary stripping of metals off the
clay fraction with 1 $\underline{N}$ ammonium acetate solution, a techni-
que often used for determining adsorbed metals in soils,
and used by Mercer and Swift (1974) and Brannon, et al.
(1976) in their studies of bay and harbor sediments. How-
ever, investigations here with clay containing adsorbed
zinc indicated that only two-thirds of the zinc could be
removed with one washing of ammonium acetate, and three
washings would likely be required. Copper and lead, more
tightly bound than zinc, would likely be even more difficult
to remove. It seemed likely that carryover of metals into
the ferrous sulfide fraction would probably occur, and this
route was abandoned. Scheme 2 leaves the clay stripping
step until last. However, the initial step of removing
metals associated with the iron sulfide again causes diffi-
culty. Ferrous sulfide is soluble in acetic acid solutions,
but sulfides of the other trace metals, formed by the re-
action of the metals with FeS, are highly insoluble in a-
cetic acid. For example, ferrous sulfide, which was dosed
with the mixture of metals then treated with acetic acid,
gave an insoluble precipitate even though the FeS had
dissolved. The suspension, when filtered, showed no copper

in the filtrate. Use of more acidic stripping reagents would clearly cause loss of metals from the clay fraction, since tests with acetic acid alone indicated about 10% of both cadmium and zinc were dexorbed under these conditions.

Humic Acid-Clay-FeS

Scheme 1   Scheme 2

$1 N$
NH_4 Ac^- Acetic
                                                                   Acid

Soluble   Insoluble   Soluble   Insoluble

Clay   Humic Acid,   FeS   Humic acid,
               FeS   Clay

NH_4 OH NH_4 OH

Soluble   Insoluble   Soluble   Insoluble

Humic acid   FeS   Humic acid   Clay

HNO_3 | dilute |
               | HNO_3 |
               ↓   ↓

               Soluble   .Soluble

               FeS   Clay
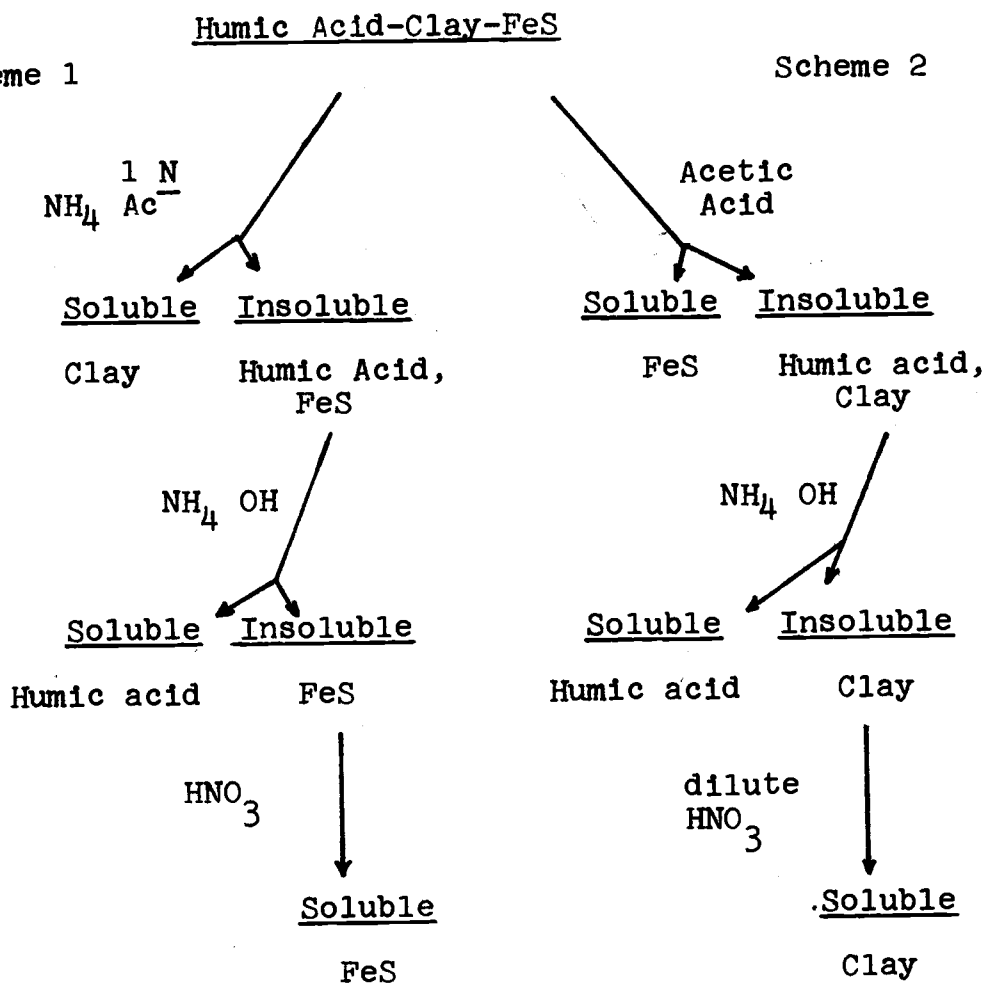
Figure 4.   Proposed methods to separate metals associated
             with humic acid clay, and ferrous sulfide frac-
             tions.

A more favorable scheme, shown in Figure 5, was adopted for use in this work. The humic material could be easily solublized in 1% ammonium hydroxide solution and separated by centrifugation. Treatment of the remaining clay and ferrous sulfide solids with 1% nitric acid would

result in stripping the clays of their metals as well as
dissolving the ferrous sulfide. Tests indicated that, ex-
cept for some solubilization of zinc sulfide, the nitric
acid would not effectively dissolve the trace metal sul-
fides. By centrifuging the mixture, the solid fraction
could be isolated with only the metal sulfides associated
with the FeS fraction remaining. This fraction, leached
with heated concentrated nitric acid, was then freed of its
metals. The only inherent problem in this method would
occur during treatment with dilute nitric acid, since re-
latively high concentrations of hydrogen sulfide are pro-
duced during the dissolution of ferrous sulfide. This might
result in some precipitation of metal released from the clay
fractions, with an accompanying high result in the values
obtained for the succeeding hot nitric acid leaching. A
further examination of this possibility will be included
later in the discussion of results. This scheme does
offer the advantage that, unlike other proposed methods
(Mercer and Swift, 1974; Nissenbaum, 1972; Presley, et al.,
1972) which oxidatively degrade the sulfides and organics
together, metals in the sulfide and organic fractions may
be determined separately.

Using the optimized extraction technique, the ex-
periment was carried out over the 44 day period. It was
found, after periodic extraction of samples, that concentra-
tions of metals in the interstitial water were near the

lower detection limits of the atomic absorption analysis, all values being about 0.1 mg/l, which corresponds to a sediment concentration of 0.5 mg/kg. The low concentrations in the pore water are in accord with the findings of other workers using natural sediments (Posner and Weber, 1975; Nissenbaum, 1972). For example, Posner and Weber (1975) found the ranges shown in Table 8. Although the interstitial water is likely the media responsible for the transport of metals between sediment components, it is clear that equilibrium levels of these metals within the sediment are very low. It is also apparent that although some humic acid material is undoubtedly solubilized and some inorganic colloids are present, these contribute very little to increasing the concentration of metals in the aquescus phase. Equilibrium concentrations are also established rapidly in the water as evidenced by little overall change after the first day of the incubation.

Table 8. Metals in harbor sediment pore water (Posner and Weber, 1975)

Metal	Concentration, mg/kg
Copper	0.4 - 7.3
Cadmium	0.0 - 0.04
Lead	0.01 - 0.32
Zinc	0.11 - 0.71

Humic Acid-Clay-FeS

NH_4OH

Soluble ← → Insoluble

Humic Acid   Clay-FeS

dilute | HNO_3

Soluble   Insoluble

Clay   FeS

conc. | HNO_3

Soluble

FeS
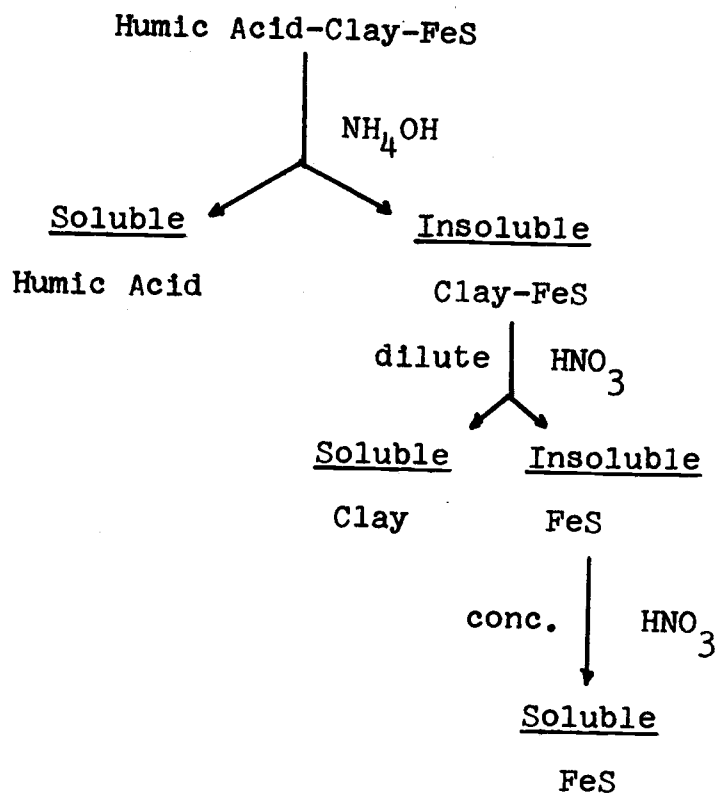
Figure 5. Method adopted to remove metals associated
with humic acid, clay, and ferrous sulfide frac-
tions.

RESULTS

Results of tests with forty bottles containing metals dosed is separate sediment components are summarized in Appendix 1 and in Figures 6 - 9. All results are reported in terms of mg/l in each extract. All data were calculated by diluting the leachate to 50 ml and determining the metal concentrations by atomic absorption spectroscopy. The mean values were computed by averaging data obtained from Days 5 through 14. Standard deviations from the mean are also indicated, with all data points found within two standard deviations of the mean. The results are shown graphically in Figures 6 through 9. Examination of the data indicated that apparently equilibrium was established during days 5, 8, and 14. The mean and standard deviation for this "steady-state" period are tabulated in Appendix 1. In several instances, mainly in the case of metals dosed initially in the interstitial water and clay phases, some substantial changes from the "steady-state" occurred at longer incubation periods. It appears that the humic acid phase increased its metal capacity at the expense of metals retained by the ferrous sulfide (and sometimes clay) fraction. Whether this trend is indicative of changes in the system or is merely an artifact from extraction or analytical procedures is not entirely clear.

During the incubation period the pH was maintained by addi-
tion of bicarbonate buffer. The increased buffering was
found to affect the solubilization of humic acid in the
aqueous ammonia extract. More extractions with smaller
portions of base were required, and this may have caused
some alteration in the metal distribution. In conjunction
with the use of more extracts, the carryover of additional
particulate matter into the humic acid phase may also have
contributed to the increase of metals associated with that
phase. Aspiration of particulate matter during atomic ab-
sorption analysis could then contribute to anomalously high
metals content associated with a particular fraction due to
the "fogging" effect of the solids. This might explain why
values for concentrations for all metals seemed to be in-
ordinately high in certain fractions (most notably metals
originally introduced in the clay fraction and found in
the humic acid fraction were all anomalously high on days
28 and 44). In any event, the cause of the "nonsteady-
state" beyond Day 14 is unknown at the present time.

Table 9 is derived from the data contained in Appen-
dix 1 and shows the relative per cent of each metal asso-
ciated with each of the sediment phases. The distribution
was calculated by assuming that "steady state" conditions
had been reached during Day 5 through 14. Each metal was
considered separately. For each location of the initial
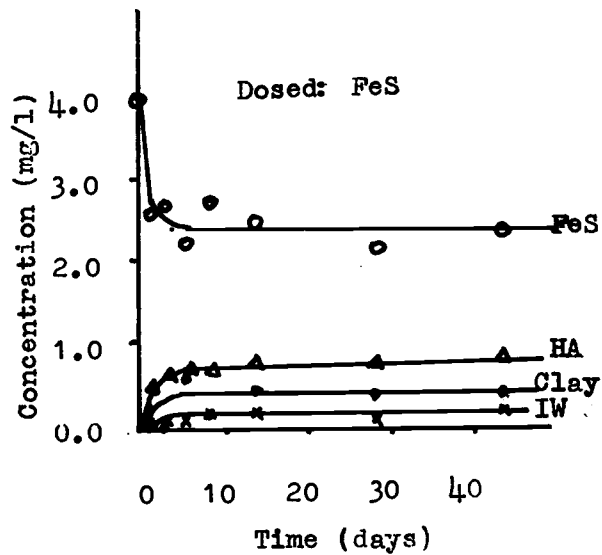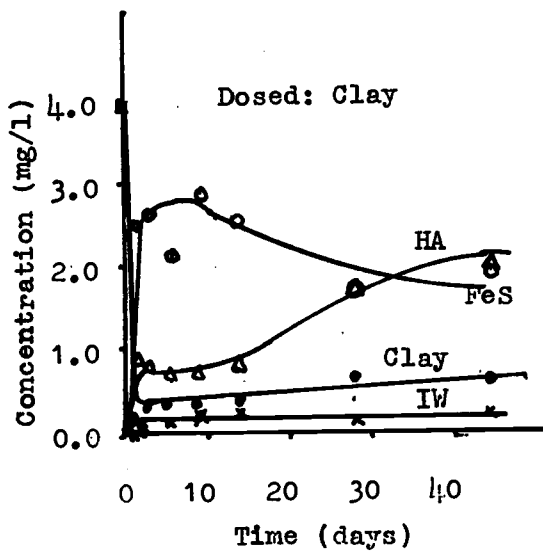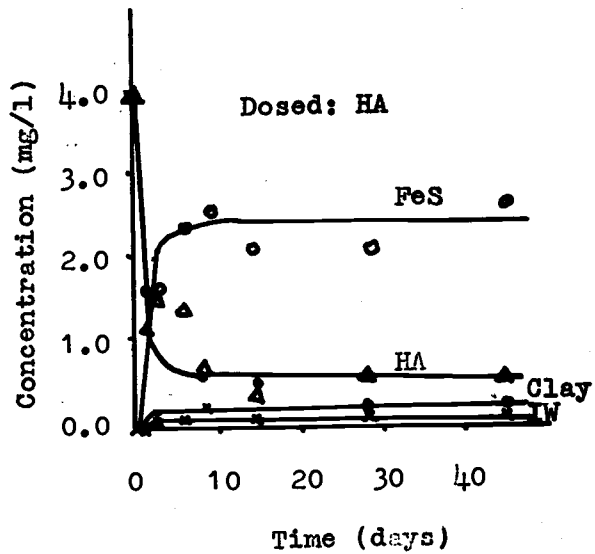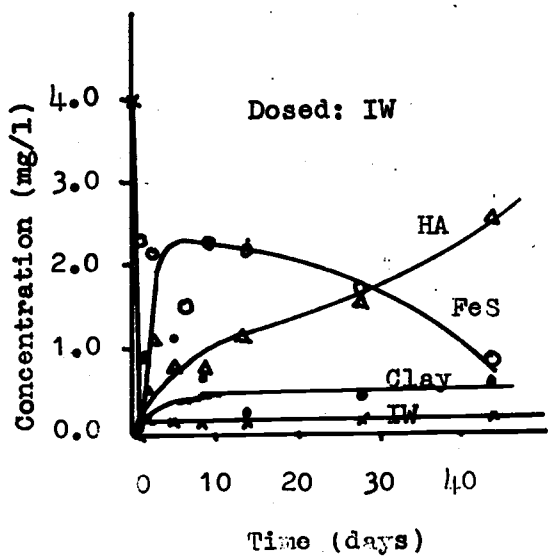
Figure 6. Redistribution of copper during incubation.
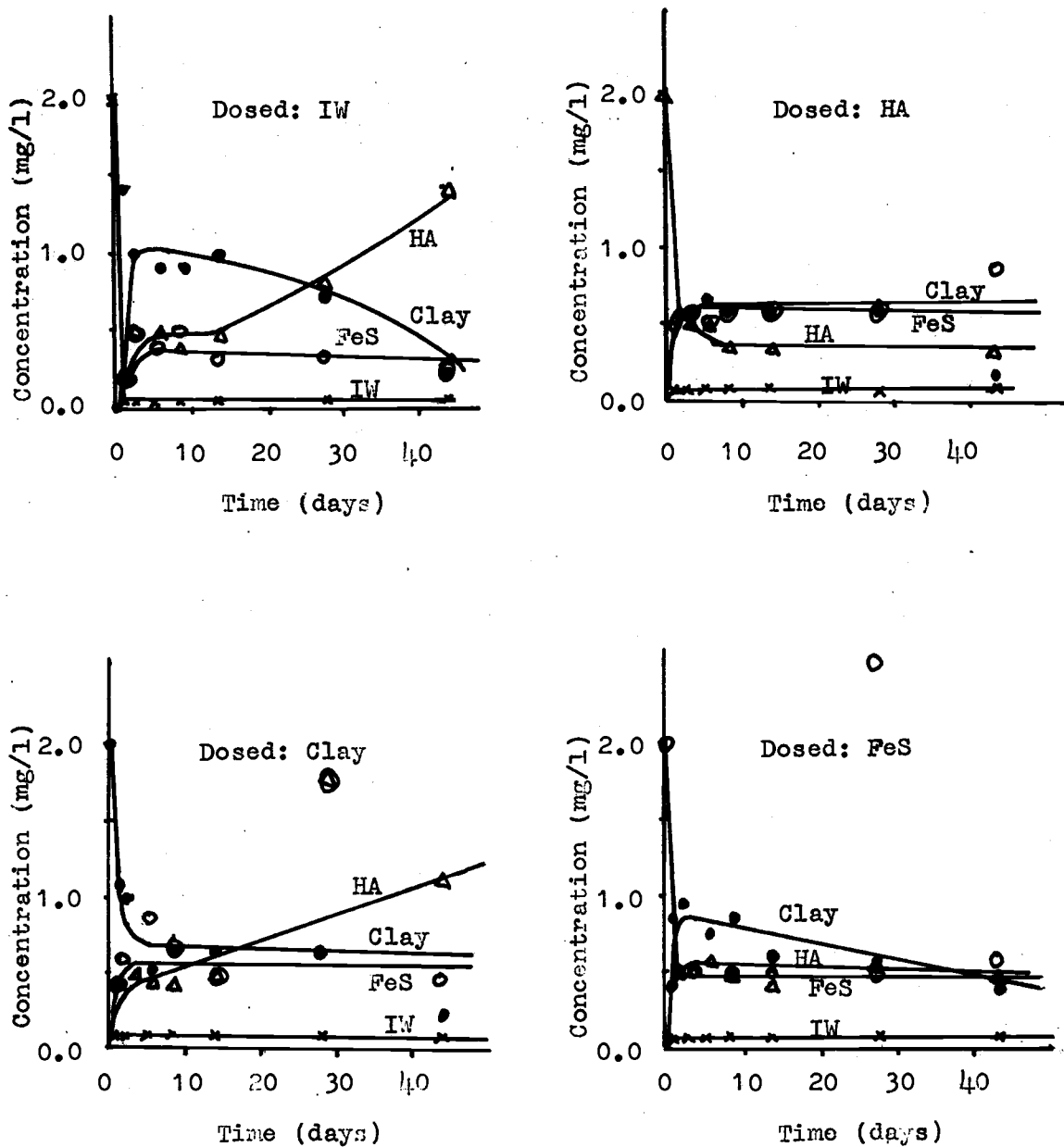
Figure 7. Redistribution of cadmium during incubation.
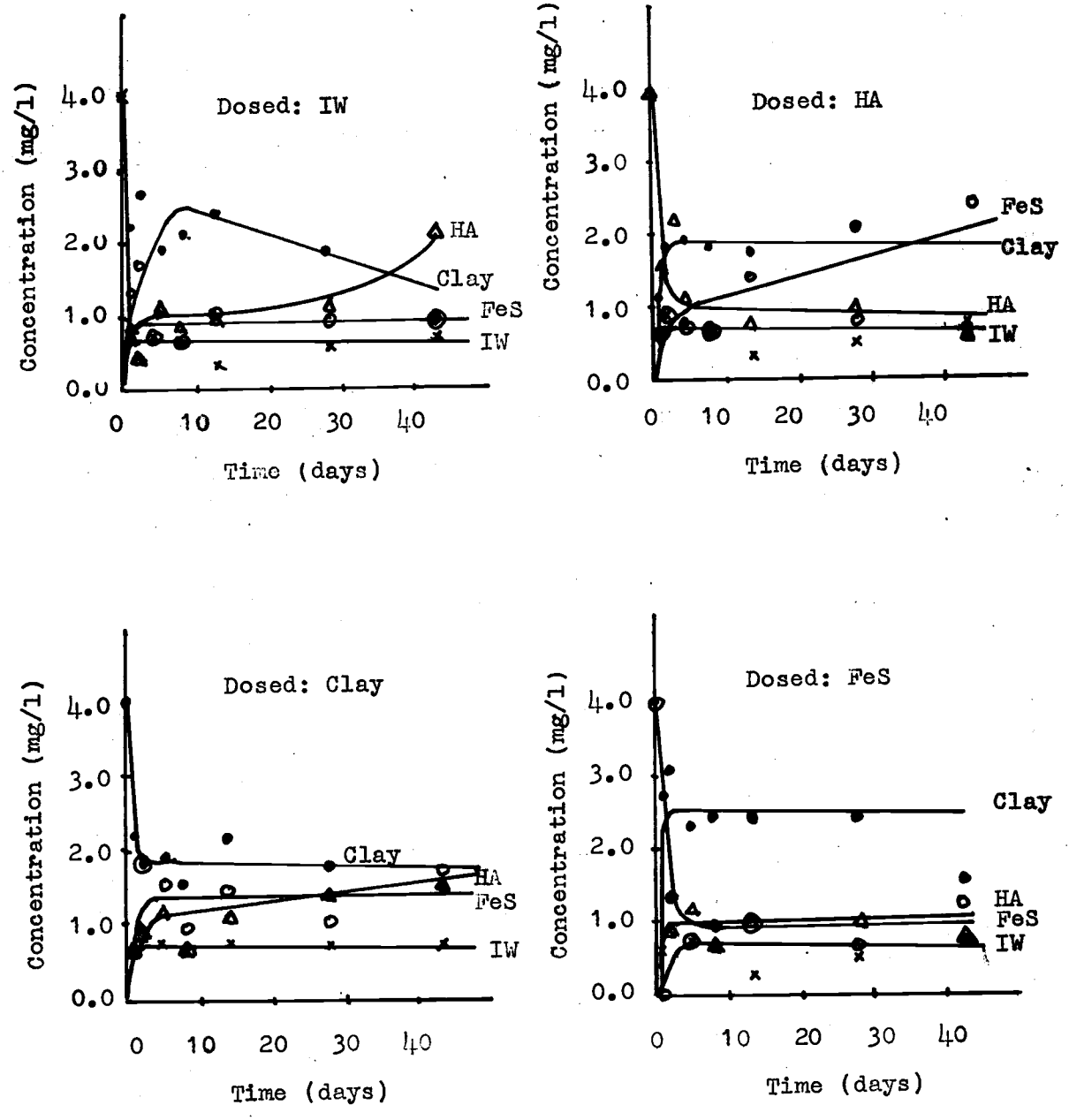
Figure 8. Redistribution of lead during incubation.
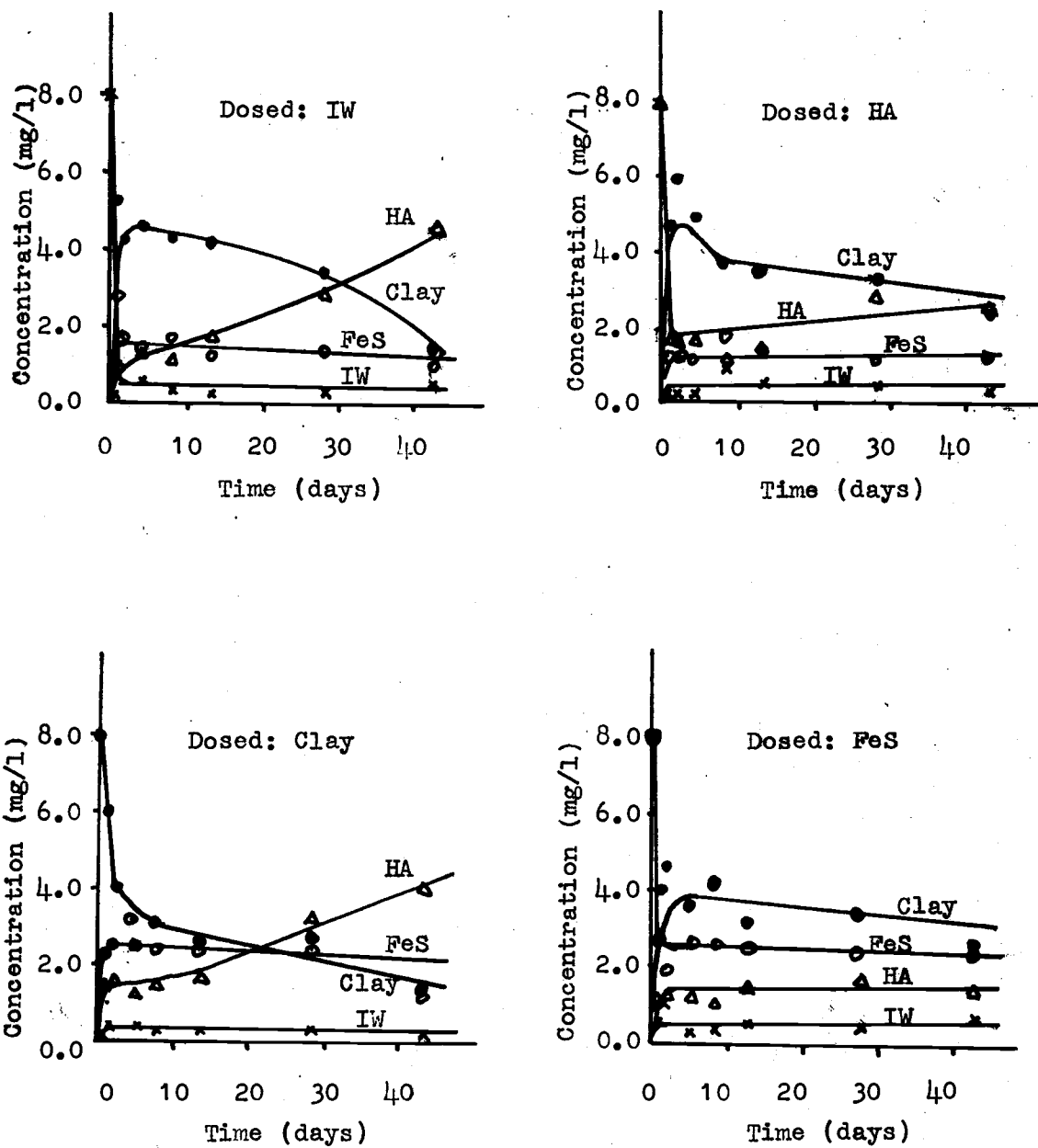
Figure 9. Redistribution of zinc during incubation.

dose a value at equilibrium was obtained by averaging Days 5 through 14 for each of the phases. These mean values were then converted to per cent, and the per cent values were averaged to give a distribution of the metal through all phases regardless of the location of the initial dosing. The standard deviations in per cent are also shown.

Table 9. Average distribution of metals through all phases in per cent, with corresponding standard deviations shown in parenthesis.

	Copper	Zinc	Cadmium	Lead
Interstitial Water	3.6 (.82)	5.1 (.77)	5.6 (.29)	13 (1.3)
Humic Acid	21 (3.3)	19 (1.5)	25 (2.6)	20 (1.9)
Clay	12 (4.3)	49 (7.1)	40 (6.4)	46 (5.1)
Ferrous Sulfide	63 (6.4)	27 (7.8)	30 (7.0)	21 (4.3)

Figure 10 graphically shows the final distribution of each metal in its sediment matrix.

A brief overview of the data indicates that mass conservation is good, within 10% of the dosed value. This indicates that the fractionation procedure appears to leach all metals from the sediment and that extraneous material is not introduced from the decomposition of the clay or sand.

The data clearly indicate that interstitial water

generally contributes little to the overall metal capacity
of the sediment-water system. In all cases the concentra-
tion of metals is near the lower detection limit of the
spectrometer, and values obtained may be high due to back-
ground noise.
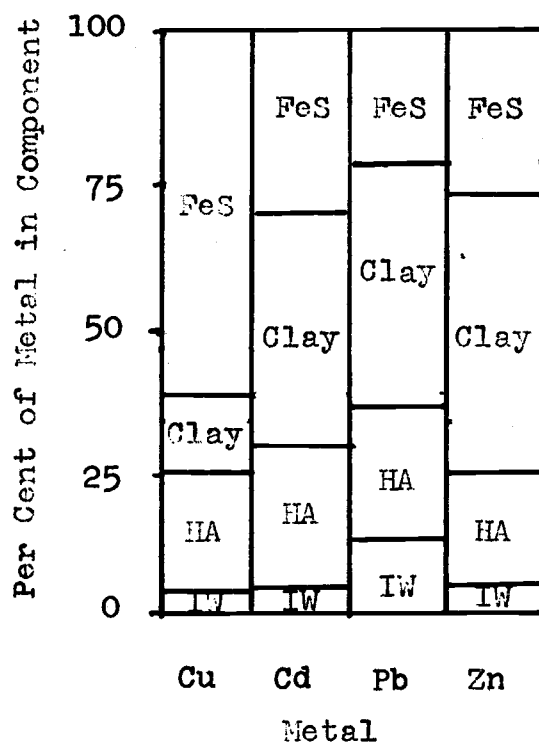
Figure 10. Per cent of metal associated with each sediment
component.

In contrast to the aqueous phase, the metals asso-
ciated with the remaining phases are variable in their be-
havior. Copper shows a strong preference for the ferrous
sulfide fraction (58%), with a secondary preference for
humic acid over clay. Other workers (Presley et al., 1972)

also found copper significantly associated with the combined sulfide and organic fraction (52%) of an anoxic fjord. Significantly, in a study off the coast of Siberia, Nissenbaum (1972) found no copper in this same fraction, but in contrast about 88% on exchangeable and hydrous oxide sites. This may indicate a preference by copper for hydrous oxide sites, a component absent from the present study. The partitioning of copper between FeS and humic acid is also in accord with the work of Pauli (1975), who noted only 60% conversion of metal humates to sulfides when treated with hydrogen sulfide.

The distribution of zinc and cadmium differs significantly from copper. Zinc and cadmium both appear to favor the clay fraction over the sulfide and organic fractions. This is somewhat surprising since, according to the literature review, the weakest bonding by clays occurs with these two metals. However, extraction data of Mercer and Swift (1974) in two San Francisco Bay harbors indicated a strong preference by cadmium for the exchangeable (clay) fraction (~45% of total) over the combined organic-sulfide fraction (~20% of total). In marked contrast, other workers (Brannon, et al., 1976) found no cadmium in the exchangeable sites of sediments from three harbors. However, the latter workers did find zinc in significant amounts in all fractions with only a variable preference for any one

fraction. This latter result is in accord with the results of the present study. Presley, et al. (1972) also found zinc in all fractions, but another investigation (Nissenbaum, 1972) found most zinc associated with clays and some hydrous oxides (acetic acid soluble fraction). It is thus clear that in natural systems zinc is apparently ubiquitous in all eluates of extractions, while cadmium may be quite variable. It is also highly probable that the amount of metal associated with the clay fraction is a function of the relative amounts and types of individual clay minerals, and drawing conclusions from natural systems and applying them to model systems is highly presumptuous.

Lead also shows the strongest tendency to associate with the clay fraction, with secondary, nearly equal preferences for the humic acid and ferrous slufide fractions. Mercer and Swift (1974) found the combined sulfide and organic fractions were slightly greater in lead content than the exchangeable (clay) fractions, in agreement with the results of the present study.

It is also instructive to examine the apparent equilibrium concentrations of each metal in the different components of the artificial sediment, to correlate the relative affinities of each metal for an individual component. Table 8 showed the amounts of each metal, converted to per cent to allow quantitative comparisons, in each sediment

fraction. It is important to consider that dosages were un-
equal, zinc being the most abundant in terms of equivalents,
followed by copper, lead, and cadmium in the approximate
ratio of 6:3:1:1. It is clear that of the four metals, cop-
per contributes by the far the greatest percentage of its
total content to the sulfide fraction (58%), not unsurpris-
ing since the solubility of copper sulfide is several orders
of magnitude below the other metal sulfides. Table 10 shows
the solubility products of the metal sulfides (Sillen and
Martell, 1964). Zinc, lead, and cadmium contribute nearly
equally (27, 21, and 30% respectively) of their metal con-
tent to their sulfide fraction, not unexpected due to the
similarity of their K_{sp} values.

Table 10. Solubility products of metal sulfides (Sillen and
Martell, 1964).

Metal sulfide	K_{sp}
CdS	9.2×10^{-27}
CuS	3.9×10^{-36}
PbS	7.0×10^{-28}
ZnS	1.5×10^{-24}

In the clay fraction, lead seems to parallel the
affinity cited in the literature, with 46% of its total
metal content located in that component. Zinc also con-

tributes a significant portion of its content to clay, which may in part be due to its known weak association with the humic acid and sulfide ion.

The humic acid fractions contain essentially the same amount of each metal, with cadmium relatively higher than the others. Studies previously mentioned have indicated that zinc and cadmium have less of an affinity for humic acid; the seemingly high value of cadmium is without explanation.

Table 9 also suggests that a possible vexing problem, discussed earlier with respect to the selection of the extraction method, did not materialize. This was the possibility that hydrogen sulfide, liberated by the acidification of ferrous sulfide during the clay stripping phase, might react with the metals released from the clay. It could thus be envisioned that a colloidal suspension or precipitate of metal sulfides might be produced. In both cases a carryover into the next extraction would result, with very low values for clay-held metals and high values for the FeS extract. Except for copper, all clay concentrations were found to be higher than the ferrous sulfide values and carryover does not seem to be a problem. There was no visible colloidal suspension in the dilute acid extract after acidification and centrifugation. The apparent absence of carryover may be due to oxidation of the sulfides by nitric acid.

Kinetics of Partitioning

In addition to the interest in discerning the relative affinities of the metals for various sediment components, it is importnat to determine the rate at which metals may be transferred from one particulate component to another. In an estuarine systems it is possible to measure the trace metal concentrations in each of several sediment components using the procedures outlined in this work. However, the results of these measurements give only the instantaneous values at a given time and no clue is provided as to the origin of the metal. As an example, if a large fraction of a metal were found in one sediment component, two conclusions may be drawn. If the rate of metal transfer between components is small (i.e. years or centuries) then it would be possible to conclude that the metal arrived on the sediment component at the time of deposition in the estuary. However, if the rate of metal transfer is relatively rapid (i.e. hours or days) then the large quantity of metal may only be attributed to the natural affinity of the metal for the sediment component, and no indication of the original mode of transport of the metal into the estuary may be deduced. Until the present study no investigation into the rates of migration of metals between components had been carried out.

The results obtained in this study indicate that transfer of metals between components is indeed rapid, with a majority of the transfer occurring within the first few days, and equilibrium apparently being reached within one week. There appears to be a few anomalous changes oc-curing after that period but these may be due in part to the addition of buffering reagents or the possible oxida-tion of some sulfides by oxygen that may have entered the system during the buffering procedure. The system was swept with nitrogen during these periods to minimize this effect.

Although the transfer rates are relatively fast, there is some indication from the literature that this is not too surprising a result. For example, humic acid solu-bilization of metal sulfides has been found to be well ad-vanced after only a three day contact time (Rashid and Leonard, 1973). Baker (1973) also extracted relatively large quantities of metals from their sulfides in a matter of several hours. In addition, sorption and desorption of metals from clays and humic acids are also very rapid.

Conclusions

1. Transfer of metals between sediment components was a rapid process occurring within a matter of days.

2. The kinetics and stoichiometry of the metal transfer

were the same regardless of the initial location of the metal.

3. The extraction method outlined provided a rapid analysis of the partitioning of metals between artificial sediment components of interstitial water, humic acid, clay, and ferrous sulfide.

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APPENDIX

Appendix 1. Concentration of metals in extracts from sediments dosed initially in sea water, humic acid, clay, and ferrous sulfide, amount of metal recovered, amount of metal applied (all in mg/l). Mean and standard deviations are for Days 5 through 14.

Copper Initially in Sea Water

Day

	0	1	2	5	8	14	28	44	$\bar{X}$	s
IW	4.0	0.0	2.2	0.1	0.1	0.1	0.1	0.2	0.10	0.00
HA	0.0	0.9	1.1	0.8	0.8	1.2	o.5	2.6	0.92	0.23
Clay	0.0	0.0	0.5	1.1	0.7	0.2	0.4	0.5	0.67	0.45
FeS	0.0	2.3	2.1	1.4	2.3	2.2	1.7	1.0	1.97	0.49
Recovered Cu	4.0	3.2	3.9	3.4	3.9	3.7	3.7	4.3		

Copper Initially in Humic Acid

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	S
IW	0.0	0.0	0.1	0.1	0.2	0.1	0.1	0.1	0.12	0.06
HA	4.0	1.1	1.5	1.4	0.7	0.3	0.7	0.7	0.80	0.56
Clay	0.0	0.1	0.2	0.1	0.6	0.4	0.2	0.2	0.37	0.25
FeS	0.0	1.6	o.6	2.3	2.5	2.1	2.1	2.7	2.30	0.20
Recovered Cu	4.0	2.8	3.4	3.9	4.0	2.9	3.1	3.7		

Copper Initially in Clay

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	s
IW	0.0	0.0	0.1	0.1	0.2	0.1	0.1	0.2	0.13	0.06
HA	0.0	0.9	0.8	0.7	0.7	0.9	1.8	2.1	0.77	0.11
Clay	4.0	0.1	0.3	0.4	0.4	0.4	0.7	0.6	0.30	0.00
FeS	0.0	2.5	2.6	2.1	2.9	2.5	1.8	2.0	2.50	0.40
Recovered Cu	4.0	3.5	3.7	3.2	4.1	3.8	4.4	4.9		

Copper Initially in Ferrous Sulfide

Day

	0	1	2	5	8	14	28	44	$\bar{X}$	S
IW	0.0	0.0	0.1	0.1	0.2	0.2	0.1	0.2	0.17	0.06
HA	0.0	0.4	0.5	0.6	0.6	0.7	0.7	0.8	0.63	0.06
Clay	0.0	0.2	0.0	0.6	0.2	0.4	0.4	0.4	0.40	0.20
FeS	4.0	2.5	2.6	2.2	2.7	2.4	2.2	2.4	2.43	0.25
Recovered Cu	4.0	3.1	3.2	3.5	3.7	3.7	3.4	3.8		

Cadmium Initially in Sea Water

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	S
IW	2.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.10	0.00
HA	0.0	0.2	0.5	0.5	0.4	0.5	0.8	1.4	0.47	0.06
Clay	0.0	1.4	1.0	0.9	0.9	1.0	0.7	0.2	0.93	0.06
FeS	0.0	0.2	0.5	0.4	0.5	0.3	0.3	0.2	0.40	0.10
Recov-ered Cd	2.0	1.9	2.1	1.9	1.9	1.9	1.9	1.9		

Cadmium Initially in Humic Acid.

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	S
IW	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.10	0.00
HA	2.0	0.6	0.5	0.5	0.3	0.3	0.6	0.3	0.37	0.12
Clay	0.0	0.6	0.6	0.7	0.6	0.6	0.6	0.2	0.63	0.06
FeS	0.0	0.5	0.6	0.5	0.6	0.6	0.6	0.8	0.57	0.06
Recovered Cd	2.0	1.8	1.8	1.8	1.6	1.6	1.9	1.4		

Cadmium Initially in Clay

Day

	0	1	2	5	8	14	28	44	$\overline{x}$	s
IW	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.10	0.00
HA	0.0	0.4	0.5	0.4	0.4	0.5	1.8	1.2	0.43	0.06
Clay	2.0	1.1	1.0	0.5	0.5	0.5	0.5	0.2	0.63	0.12
FeS	0.0	0.4	0.6	0.8	0.7	0.5	1.8	0.5	0.67	0.15
Recov-ered Cd	2.0	2.0	2.2	1.8	1.9	1.3	4.4	2.0		

Cadmium Initially in Ferrous Sulfide

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	s
IW	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.10	0.00
HA	0.0	0.5	0.5	0.6	0.5	0.4	0.6	0.5	0.50	0.10
Clay	0.0	0.8	0.9	0.7	0.8	0.6	0.6	0.4	0.70	0.10
FeS	2.0	0.4	0.5	0.5	0.5	0.5	2.5	0.6	0.50	0.00
Recovered Cd	2.0	1.8	2.0	1.9	1.9	1.6	3.8	1.6		

Lead Initially in Sea Water

Day

	0	1	2	5	8	14	28	44	$\bar{X}$	s
IW	4.0	0.6	0.4	0.7	0.6	0.3	0.6	0.8	0.53	0.21
HA	0.0	0.8	0.4	101	0.9	1.0	1.3	2.2	1.00	0.10
Clay	0.0	2.2	2.7	1.9	2.1	2.4	1.9	1.0	2.13	0.25
FeS	0.0	1.3	1.8	0.7	0.6	1.0	1.0	1.0	0.77	0.21
Revovered Pb	4.0	4.9	5.3	4.4	4.2	4.7	4.8	5.0		

Lead Initially in Humic Acid

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	s
IW	0.0	0.6	0.9	0.7	0.6	0.3	0.5	0.8	0.53	0.21
HA	4.0	1.6	2.2	1.1	0.6	0.7	1.0	0.6	0.80	0.26
Clay	0.0	1.1	1.8	1.9	1.8	1.7	2.1	0.8	1.80	0.10
FeS	0.0	0.6	0.9	0.7	0.6	1.4	0.8	2.4	0.90	0.44
Recovered Pb	4.0	3.9	5.8	4.4	3.6	4.1	4.4	4.6		

Lead Initially in Clay

Day

	0	1	2	5	8	14	28	44	$\bar{X}$	S
IW	0.0	0.6	0.9	0.7	0.6	0.7	0.6	0.6	0.67	0.06
HA	0.0	0.6	0.9	1.1	0.6	1.0	1.3	1.5	0.90	0.26
Clay	4.0	2.2	1.8	1.9	1.5	2.1	1.8	1.5	1.83	0.31
FeS	0.0	0.6	1.8	1.5	0.9	1.4	1.0	1.7	1.27	0.32
Recov-erec Pb	4.0	4.0	5.4	5.2	3.6	5.2	4.7	5.3		

Lead Initially in Ferrous Sulfide

Day

	0	1	2	5	8	14	28	44	$\bar{X}$	s
IW	0.0	0.6	0.9	0.7	0.6	0.3	0.5	0.8	0.53	0.21
HA	0.0	0.0	0.9	1.1	0.6	1.0	1.0	0.8	0.90	0.26
Clay	0.0	2.7	3.1	2.3	2.4	2.4	2.4	1.5	2.37	0.06
FeS	4.0	0.0	1.3	0.7	0.9	1.0	0.6	1.3	0.87	0.15
Recovered Pb	4.0	3.3	6.2	4.8	4.5	4.7	4.5	4.4		

Zinc Initially in Sea Water

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	S
IW	8.0	0.1	0.8	0.6	0.3	0.2	0.3	0.6	0.37	0.21
HA	0.0	0.9	1.7	1.4	1.3	1.9	2.8	4.5	1.53	0.32
Clay	0.0	5.3	4.2	4.5	4.2	4.1	3.5	1.4	4.27	0.21
FeS	0.0	2.7	1.7	1.6	1.8	1.3	1.5	1.1	1.57	0.25
Recovered Zn	8.0	9.0	7.4	8.1	7.6	7.5	8.1	7.6		

Zinc Initially in Humic Acid

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	s
IW	0.0	0.2	0.2	0.2	0.7	0.5	0.4	0.3	0.47	0.25
HA	8.0	1.8	1.7	1.8	1.0	1.6	2.8	2.6	1.47	0.42
Clay	0.0	4.5	6.0	4.7	3.8	3.6	3.4	2.5	4.03	0.59
FeS	0.0	1.2	1.3	1.2	1.9	1.6	1.5	1.6	1.57	0.35
Recovered Zn	8.0	7.7	9.2	7.9	7.4	7.3	8.1	7.0		

Zinc Initially in Clay

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	S
IW	0.0	0.1	0.4	0.4	0.3	0.3	0.3	0.2	0.33	0.06
HA	0.0	1.5	1.7	1.3	1.5	1.8	3.7	4.1	1.53	0.25
Clay	8.0	6.0	4.0	2.5	3.4	3.0	2.8	1.7	2.97	0.45
FeS	0.0	2.1	2.3	3.1	2.5	2.5	2.2	1.5	2.70	0.35
Recovered Zn	8.0	9.7	8.4	7.3	7.7	7.6	9.0	7.5		

Zinc Initially in Ferrous Sulfide

Day

	0	1	2	5	8	14	28	44	$\overline{X}$	S
IW	0.0	0.5	0.9	0.3	0.4	0.5	0.5	0.6	0.40	0.10
HA	0.0	1.1	1.3	1.3	1.2	1.5	1.7	1.5	1.33	0.15
Clay	0.0	4.0	4.5	3.7	4.1	3.6	3.7	2.7	3.80	0.26
FeS	8.0	2.5	1.9	2.4	2.5	2.5	2.3	2.5	2.47	0.06
Recovered Zn	8.0	8.1	8.6	7.7	8.2	8.1	8.2	7.3		