Estuarine Sediment Controls on Trace Metal Distributions

by

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ABSTRACT

Sediments are the major compartment for many materials of toxic or nutrient concern in aquatic environments. The lack of knowledge of the phase associations of toxic metals in sediments is the largest deficiency in our understanding of the environmental hazard posed by metal contamination. In this study, the sedimentary partitioning of copper and cadmium were examined with the goal of predicting the environmental fate of these metals in estuaries.

Five solid phases were chosen to simulate components responsible for trace metal binding in oxidized sediments: synthetic hydrous oxides of iron and manganese, montmorillonite clay, a synthetic aluminosilicate gel, and estuarine humic substances (EHS) extracted from a natural sediment. The uptake of copper and cadmium by these model phases in artificial seawater was measure as a function of pH and salinity.

The affinity of the model phases for cadmium, as measured by the slope K_p of the linear absorption isotherm, was found to be in the following order: manganese > iron > EHS > aluminosilicates > montmorillonite. Copper binding affinities were much higher than those of cadmium. The relative order of affinity of the phases was similar except for copper binding by EHS, for which K_p was relatively higher (exceeding that of iron). Metal binding was not influenced by interactions involved in three types of phase complex: iron-clay, iron-humic and clay-iron-humic. This suggests that experiments with isolated phases are adequate to predict partitioning.

The measured K_p values were used to calibrate a simple model for predicting partitioning and total metal uptake by sediments. This model, which is analogous to speciation in a solution of competing ligands, predicts that cadmium uptake by estuarine sediments is dominated by iron while both iron and organics are important for copper. Results of selective extraction studies and studies of cadmium uptake by natural estuarine sediments are in semiquantitative agreement with these predictions. In anerobic sediments, thermodynamic caluculations suggest that copper and cadmium concentrations are determined by equilibria involving solid sulphides and bisulphide and polysulphide complexes.

It is expected that the results of this investigation will aid in assessing the environmental significance of metal-contaminated estuaries.

FOREWORD

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NOMENCLATURE

A	Surface area; Absorbance
abs.	Absorbance
C	Concentration; Constant
E	Energy; Electrical Potential
F_n	Phase concentration, nth phase
f	Fractional Adsorption
f	"Function of"
G	Gibbs free energy
I	Ionic strength
IR	Infrared
K	Equilibrium Constant
K_p	Linear partition coefficient
k	Density of adsorption sites
L	Ligand
M	Metal
m	Stoichiometric coefficient
N	Number of phases; Radioactivity
n	Stoichiometric coefficient; Density of binding sites
P_n	Partition coefficient
PZC	pH of the point of zero charge
p	-log base 10
R	Gas Constant
r	Ionic radius
S	Solid (adsorbent); Electrode slope
T	Temperature; Total
TOC	Total organic carbon
TS	Total solids; Total sulphides
UV	Ultraviolet
VS	Volatile solids
XRD	X-ray diffraction
x	Apparent stoichiometric coefficient
z	Ionic charge

Greek

α	Distribution coefficient
β	Formation constant (equilibrium constant)
Γ	Adsorption density
γ	Activity coefficient
γ_b	Bulk density
Δ	"Change in"
ε	Electron activity
θ	Porosity
λ	Wavelength
μ	Micro (prefix)
$\bar{\nu}$	Binding density, analogous to Γ
Π	"Product of"
ρ	Density
Σ	"Sum of"
σ	Surface charge
ψ	Electrical Potential

Other

( )	Parentheses. In normal use these function as delimiters but in this study where they occur in equilibrium expressions they denote activity of chemical species.
[ ]	Brackets. Denote concentration of chemical species.
{ }	Braces. Denote mass or areal concentration of solid phases.
$^{o}/oo$	Parts per thousand (salinity).

ESTUARINE SEDIMENT CONTROLS ON TRACE METAL DISTRIBUTIONS

1. GOAL AND OBJECTIVES

Estuaries are unique in the hydrological cycle in containing the brackish mix of fresh and saline waters where rivers meet the sea. Estuaries are of great ecological importance because of the uniqueness of their environmental conditions and because of their very high biological productivity (Odum, 1970). Estuaries are also the focus of human "ecosystems" being centres of industry and commerce. The ecological importance of estuaries is well documented but so is their vulnerability to adverse impact from the activities of man (Odum, 1970).

It is now increasingly being recognized that problems of adverse impact on aquatic environments are not merely a problem of *water* quality, although this is frequently a major component of the total environmental problem. The boundaries of the "aquatic environment" that need to be considered may include the whole watershed and certainly do not coincide with the solid/water interface but extend some depth into the sediments (Bella, 1975). That "environmental quality" is more than merely "water quality" is nowhere more true than in estuarine environments in which sediments dominate the hydraulic, chemical and biological processes (Lauff, 1967; McDowell and O'Conner, 1977).

It is also increasingly being recognized that many of the chemical reactions of importance in aquatic environments are heterogeneous reactions, that is, they involve phases other than the aqueous solution phase (Feltz, 1980). In estuarine waters and sediments a number of different solid phases are present whose chemical or biochemical reactivity, and thus environmental significance, vary greatly (Serne and Mercer, 1975; Engler *et al*, 1977). The sediments often act as the major reservoirs for nutrient or toxic materials in the estuarine environment (Aston and Chester, 1973) and to a large extent may buffer against concentration changes in the overlying water column by acting alternatively as sources and sinks. These attitudes: (a) that the

sediments are a dominant influence on estuarine quality and (b) that heterogeneous chemical and biochemical reactions are of similar importance or greater importance in estuaries than aqueous reactions, have determined the focus of the present research.

Heavy metals were chosen for study from an environmental perspective. The study focus was further narrowed down to the metals copper and cadmium which have a demonstrated high toxicity to estuarine flora and fauna (Bryan, 1976). The choice of copper and cadmium was somewhat arbitrary in that a number of other metals (mercury, lead, zinc, chromium, nickel, cobalt, iron and manganese) and many nonmetal and organic compounds (notably the persistent organo-chlorine biocides and the PCB's) (Duke, 1970; Hammond, 1972) are of environmental significance in estuaries from a toxic or nutrient standpoint and are known to associate strongly with the sediments.

The goal of the present research then was to understand the partitioning of trace metals among phases of estuarine sediments under different conditions in order to predict the role of such sediments as sources or sinks and thus the environmental hazard associated with contaminated estuaries.

The broad objectives can be stated as follows:

(1) To select experimental solid phases that are a reasonable model for natural sediment phases and to characterize these solids sufficiently well to ensure reproducibility of metal uptake studies.

(2) To determine equilibrium partitioning of metals between isolated solid phases and the solution phase under a range of conditions as are encountered in estuarine environments.

(3) To study the equilibrium partitioning of metals between combined solid phases and solution and thus gain insight into the effect of phase interactions on metal binding capacity of sediments.

(4) To determine the equilibrium metal binding capacity of natural sediments and examine the relative importance of solid phases in these sediments.

(5) To attempt to model the partitioning of metals between solid phases and the solution phase in sediments and thus improve the basis for predicting mobilization or uptake of metals in estuaries.

The following chapter presents a literature review by way of background to the conceptualization of the problem and an outline of the study plan is presented in Chapter 3. The above objectives form the subject matter of Chapters 4 - 7 of this thesis.

2. BACKGROUND AND LITERATURE REVIEW

The following review presents a survey of studies pertinent to understanding the functioning of sediments as sinks and sources of metals of environmental concern. This topic is necessarily "interdisciplinary" in nature thus a diversity of literature sources have been drawn upon including the areas of soil science, sedimentology, colloid chemistry, geochemistry, environmental science and engineering and chemical and geological oceanography.

2.1 ESTUARINE SEDIMENTS

The bulk of the sediment deposited in present day estuaries is of Holocene (recent) age (Curry, 1967; Lauff, 1967; Allen, 1970) thus the mineralogy of estuarine sediments largely reflects that of watershed soils from which the terrigenous components have been eroded. There has been little opportunity on a geological time scale for extensive diagenetic change. However, those changes which have occurred and have endowed estuarine sediments with a different character from watershed soils, are of great environmental importance.

For the present purposes we may consider estuarine sediments to be composed of the constituents listed in Table 2.1. This table was constructed from a review of diverse literature sources including Trask (1968), Folger (1972), Jenne (1968, 1977), Leckie and Nelson (1975), Serne and Mercer (1975), Engler *et al* (1977), Lindsay (1979), Nelson (1980) and Luoma and Bryan (1981) and the author's own experience with estuarine sediments (Davies-Colley, 1978).

The interstitial water of estuarine sediments is usually very similar to that of overlying water as regards the major cations and chloride (Table 2.2). However, early diagenetic changes (Berner, 1971; Nissenbaum *et al*, 1972; Troup *et al*, 1974) may greatly change the concentration and/or the speciation of the biochemically active elements sulphur, nitrogen, phosphorous and carbon in estuarine sediments. Bacteriologically-mediated oxidation of organic matter consumes dissolved oxygen which is only transferred very slowly in

Table 2.1

CLASSIFICATION OF ESTUARINE SEDIMENT CONSTITUENTS

Constituents	Common Range in Estuarine Sediments (Wet Wt %)	
	Range	"Typical" Sediment
1. interstitial water	10 - 50%	25%
2. silicates and aluminosilicates (other than clays)	"remainder"	65%
3. clays	0 - 25%	5%
4. metal oxides	1 - 5%	2%
5. metal carbonates	0 - 30%	3%
6. metal sulphides (anaerobic sediments)	0 - 1%	0.05%
7. organic matter	0 - 10%	4%

Table 2.2

COMPOSITION OF INTERSTITIAL ESTUARINE WATER COMPARED WITH SEAWATER AND AVERAGE RIVER WATER

	Molar Concentrations		Interstitial Estuarine Water
Constituent	Riverwater[a]	Seawater[a]	(Reducing Sediments)[b]
Na^+	2.7×10^{-4}	0.47	4.1×10^{-1}
K^+	5.9×10^{-5}	1.0×10^{-2}	1.2×10^{-2}
Ca^{2+}	3.8×10^{-4}	1.0×10^{-2}	6.2×10^{-3}
Mg^{2+}	3.4×10^{-4}	5.4×10^{-2}	5.4×10^{-2}
Cl^-	2.2×10^{-4}	0.55	5.1×10^{-1}
$SO_4^=$	1.2×10^{-4}	3.8×10^{-2}	1×10^{-3}
Σ S(-II)	---	---	1×10^{-3} (variable)
Σ P	---	1.5×10^{-6}	1×10^{-4}
Alkalinity (N)	9.6×10^{-4}	2.3×10^{-3}	3×10^{-2}
Σ N(-III)	---	---	5×10^{-3}
pH	---	7.9	7.7
Ionic Strength	---	0.67	0.67

(a) Adapted slightly after Stumm and Morgan (1970, p385).
(b) Adapted slightly after Leckie and Nelson (1975).

NB Interstitial water composition is for overlying water of 35% salinity (i.e., substantially undiluted seawater).

sediments (by molecular diffusion, except for intermittent bioturbation or hydrodynamic erosion). Thus the P_{O_2} at a small depth into the sediment falls to extremely low values and anaerobic processes using SO_4^{2-} and, to a lesser extent, NO_3^- as terminal election acceptors begin to dominate (Berner, 1971) and produce sulphides and ammonia respectively. Total sulphur in the pore water may drop due to loss of $H_2S_{(g)}$ by vertical diffusion out of the sediments and by precipitation of metal sulphides (Bella, 1975). In some cases the SO_4^{2-} may be so depleted in pore water (especially in low salinity upper estuaries) that the redox potential falls to a level where methane production becomes thermodynamically favorable. Phosphate concentration increases due to decomposition of organic matter which may be represented overall by the Redfield *et al* (1963) equation:

$$(CH_2O)_{106}(NH_3)_{16}\ H_3PO_4 + 138O_2 =$$

$$106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4 \qquad (2.1)$$

Phosphate sometimes reaches sufficiently high levels to precipitate vivianite ($Fe_3(PO_4)_2$) (Holdren and Bricker, 1977).

The pH of the pore water falls slightly, sometimes below 7.0 due to release of CO_2 on oxidation of organics. Berner (1971) has shown that the pH in seawater and, presumably, estuarine sediments, should be approximately proportional to log P_{CO_2} (which may rise as high as -1.5). Since Ca^{2+} is in equilibrium with $CaCO_{3(s)}$:

$$CO_{2(g)} + H_2O + Ca^{2+} = CaCO_3 + 2H^+ \qquad (2.2)$$

$$K = \frac{(H^+)^2}{P_{CO_2}\ (Ca^{2+})} = 10^{-9.75} \qquad (2.3)$$

the pH is given:

$$pH = 4.88 - \frac{1}{2}\log\ (Ca^{2+}) - \frac{1}{2}\log P_{CO_2} \qquad (2.4)$$

(which predicts a pH of 7.93 for seawater with $(Ca^{2+}) = 10^{-2.6}$ and $P_{CO_2} = 10^{-3.5}$).

The bulk of the solid fraction of estuarine sediment is allochthonous; that is, it has been formed outside the basin and then deposited in the estuary at a later stage (Postma, 1967). However, carbonates, sulphides and some fraction of the silica and organic matter are autochthonous, being produced within the basin.

Carbonates in estuarine sediments are mostly shell fragments and a minor contribution to the silicate fraction is also biogenic (e.g., diatom frustules). Ferrous carbonate (siderite) and manganous carbonate (rhodochrosite) may be of local importance as shown by Holdren and Bricker (1977). Solid sulphides are derived from the most important diagenic process in estuarine sediments; that in which abundant sulphate is used as a terminal electron acceptor and is itself reduced to sulphides once oxygen is depleted in the estuarine water (Berner, 1969, 1971). Many heavy metal sulphides are extremely insoluble and iron and manganese, while more soluble than the trace metals in the presence of sulphide (Smith and Martell, 1976), precipitate and give reduced estuarine sediment its characteristic black color (Berner, 1971).

Organic matter in estuarine sediments represents a mixture of allochthonous and autochthonous contributions (Jackson, 1975). Estuarine organic contributions, humified to varying degrees, are mainly from algal and saltmarsh flora and the fecal deposits of estuarine fauna (Johnson, 1974) while terrestial contributions include particularly, soil humic material, often coflocculated with iron and aluminum (Picard and Felbeck, 1976; Sholkovitz, 1976, 1978). Commonly 50% or more of sediment organic matter is humic material (Nissenbaum and Swaine, 1976; Knezevic and Chen, 1977).

The silicates and aluminosilicates, metal oxides and (generally) the clays are detrital in origin. The silicates and aluminosilicates other than clays are mostly present as sand or silt-sized grains which are generally considered to have minor chemical significance because of their relatively low specific surfaces. However, in as much as these minerals determine grain size distribution (being the largest single constituent in Table 2.1) they are extremely important in providing the macroporosity which in turn influences diffusion of solutes and the rapidity of approach to equilibrium in sediments.

Grain size is the single most important environmental parameter characterizing estuarine sediments (Trask, 1968) and very often parameters of geochemical interest with respect to estuarine sediments (such as iron or organic carbon concentration) are strongly related to grain size within a basin (for example, Luoma and Bryan, 1981).

The metal oxides, particularly of iron, manganese and aluminum are of major environmental significance, particularly because of their high specific surface areas and their tendency to form coatings on silicate and clay particles (Jenne, 1968, 1977) and complexes with organics (Schnitzer and Khan, 1972). The strong association of iron and manganese with clays and with humic materials may derive from the co-flocculation of these materials that occurs when river water is mixed with saline water in estuaries (Scholkovitz *et al*, 1978). The clay minerals or phyllosilicates are composed of alternating layers of alumina (gibbsite structure) and silica (Grim, 1968; Van Olphen, 1977). These minerals have fairly high specific surfaces and may provide the bulk of the cation exchange capacity in estuarine sediments.

2.2 COPPER AND CADMIUM

A number of reviews are available on the environmental role and significance of heavy metals including copper and cadmium (e.g., Bowen, 1966; Leckie and James, 1974; Parks, 1975; Davey and Phelps, 1975; Millero, 1975; Bryan, 1976; Chen and Lockwood, 1976; Vigon, 1977; Schmidt, 1978).

Copper and cadmium, while similar in many ways, also provide an interesting contrast. Copper is an essential micronutrient (Bowen, 1966) and occurs in the haemocyanin complex in the blood of certain estuarine invertebrates (Bryan, 1976). It also has a high "sublethal" toxicity (e.g., phytotoxicity to marine algae at around 1-2 ppb). (It may well be argued that, in the long term, exposures causing "sublethal" toxic responses are just as "lethal" as those causing death of test organisms in standard 96 hour bioassay studies.) Cadmium has no known physiological function (Bowen, 1966) and has a "sublethal" toxicity (to estuarine organisms) of a similar order to that of copper (Bryan, 1976). Cadmium is highly toxic to man (EPA, 1973) and is of

concern in estuarine food webs, from a human health standpoint, while copper is not considered toxic to man and indeed is only listed in potable water standards (W.H.O., 1970; EPA, 1973) because of its astringent taste. According to Bryan (1976) "sublethal" toxic responses to both copper and cadmium occur with the most sensitive organisms (particularly egg and larval life stages of invertebrates) at about ten times the background levels in seawater, that is at a few ppb. However, short-term lethal affects may not be detected until concentrations reach two orders of magnitude higher than the "sublethal" threshold. The mechanism of toxicity, as with the other toxic metals is probably enzyme inhibition (Bryan, 1976) thus it is not surprising that many complex interactive responses are observed with copper and cadmium and other pollutants and environmental stresses. Generally copper and cadmium are not ecologically magnified in food chains so that water exposure, and direct ingestion of sediment in the case of benthic feeders, are the important mechanisms of uptake (Bryan, 1976).

The mode of entry of anthropogenic cadmium and copper to the marine environment may be similar. Cadmium occurs as a natural contaminant of zinc thus corrosion of zinc plated or zinc-alloy fittings results in cadmium mobilization. Copper can also be corroded from metallic fittings, thus both metals may enter estuaries from municipal wastewaters and urban drainage as well as from electroplating and other industrial sources. Surprisingly, even in the highly industrial New York area, municipal sources of both metals contributed greater mass-flows than industrial sources (Klein, 1974). It is also surprising that the NAS (1975) study found that the major source of copper to the ocean was the weathering of anti-fouling paint used extensively in estuarine areas, although it is uncertain whether the physico-chemical form of the element in this case is as environmentally significant as copper from other sources.

The above discussion suggests that knowledge of the partitioning of toxic metals in sediments (as the major metal reservoir) is the critical requirement in understanding their biogeochemical cycling in estuaries. The uptake and release by sediments is seen to be yet more important when it is considered that chronic low-level ("sublethal")

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exposures to metal contamination are of more concern generally than gross chemical pollution as with spillage of metal wastes.

2.3 ADSORPTION OF METALS ON SOLIDS

The concentration of metals in solution may conceivably be controlled by two main categories of process: precipitation/coprecipitation and adsorption/ion exchange. Krauskopf (1956) has shown that in ocean water the concentration of heavy metals is unlikely to be controlled by precipitation reactions since seawater is greatly undersaturated with respect to conceivable solid phases although *coprecipitation* can in principle reduce concentrations to low levels. Sulphide precipitation may control concentrations in anoxic basins and reduced sediments (Krauskopf, 1956). However, it is generally agreed that sorption reactions are the most important control in marine environments (Parks, 1975).

Leckie and James (1974) and MacNaughton and James (1977) have summarized interfacial phenomena which must be explained by any comprehensive model of metal adsorption on solid surfaces:

1) There is a critical pH range called the "adsorption edge" over which fractional adsorption increases from nearly zero to almost unity.
2) The pH of the adsorption edge is often close to that where metal hydrolysis species become significant but is rather insensitive to the nature of the adsorbent while it does depend on the concentration of the adsorbent.
3) The adsorption edge shifts to higher pHs as total metal concentration increases.
4) H^+ ions are released during sorption.
5) If the adsorbent is negatively charged the zeta potential ψ_z (determined by electrophoretic observations) may reverse in sign.
6) Concurrent with change in sign of ψ_z the adsorbent may coagulate.

The shift of the adsorption edge to higher pHs at higher concentrations suggests *non-linear* partitioning of metal between solid and solution phases. Plots of adsorption density Γ versus solution phase activity at constant pH yield *adsorption isotherms* that can be fitted to standard curves such as the Langmuir or Freundlich isotherms (Parks, 1975). Usually the Freundlich isotherm gives a better fit to metal adsorption data since, unlike the Langmuir isotherm, it does not require that only one site be present (i.e., that free energy of adsorption ΔG^o_{ads} be independent of adsorption density) (Stumm and Morgan, 1970) but can allow for the empirical fact that ΔG^o_{ads} decreases as Γ increases (Benjamin, 1978).

The classic theory of adsorption is the Stern-Grahame theory (Parks, 1975) which explains adsorption in terms of electrostatic interaction of the metal ion with the electric double layer (EDL) (Stumm and Morgan, 1970) present near charged solid surfaces. Specific adsorption (chemical binding) is allowed for by adding a term, $\emptyset$, to the EDL potential ψ_d at the distance of approach of the ion, thus the free energy of adsorption is:

$$\Delta G^o_{ads} = -z\ F\ (\psi_d + \emptyset) \tag{2.5}$$

where z is ion charge and F is the Faraday. The isotherm takes the form:

$$\Gamma = 2rC\ \exp(-\frac{\Delta G^o_{ads}}{RT}) \tag{2.6}$$

where Γ is sorption density, r is ion radius and C is concentration and R and T have their usual meanings. As shown by James and Healy (1972 a,b,c) this isotherm often gives poor data fits.

More recent models of adsorption can be considered in three general categories (James and MacNaughton, 1977):

1) ion exchange,
2) surface complexation, and
3) physical models.

Ion exchange models view solid surfaces as exchanging one metal ion for another (or hydrogen). Thus selectivity coefficients can be

written to quantify the relative preference of the surface for different ions. Dugger *et al* (1964) applied an ion exchange model to metal adsorption on silica gel and were able to calculate the energy of specific adsorption of heavy metals by assuming that this quantity was negligible for Na^+ and K^+ which have little tendency to form covalent bonds.

Avotins (1975) studied interaction of Hg(II) with hydrous ferric oxide and interpreted the results in terms of an ion exchange model. Coprecipitation (Hg present during precipitation of the ion) was found to be equivalent to adsorption (Hg added to a preformed iron precipitate). A simple diffusion model was applied to explain the slow long term uptake of the Hg by hydrous ion oxide. Hohl and Stumm (1976) have used the term "surface complexation" to refer to metal binding by ionizable function groups on oxide surfaces such as silanol, Si-OH, on silica surfaces. These groups act like diprotic acids and are responsible for the formation of surface charge (that is H^+ and OH^- are the potential determining ions). For the first dissociation we can write (where S represents "surface"):

$$SOH_{2(s)}^{+} \overset{K_1}{=} SOH_{(s)} + H^{+}_{(aq)} \tag{2.7}$$

Intrinsic dissociation constants can be written relating the dissociation of surface groups to bulk solution pH using the Boltzmann distribution law thus:

$$K^1_{int} = \frac{(H^+)_s\ [SOH]_s}{[SOH_2]_s} = \frac{(H^+)_{aq}\ [SOH]_s}{[SOH_2]_s} \exp\left[\frac{-F\ \psi_o}{RT}\right] \tag{2.8}$$

For metal ion adsorption we can write

$$M^{m+} + n(SOH) \overset{*\beta_n}{=} (SO)_n\ M^{(m-n)+} + nH^+ \tag{2.9}$$

and the corresponding intrinsic formation constant is

$$*\beta^n_{int} = \frac{[(SO)_n M]_s\ (H^+)^n}{[SOH_s]^n\ [M^{m+}]} \cdot \exp\left[\frac{(m-n)\ F\ \psi_o}{RT}\right] \tag{2.10}$$

which can be restated in the form of an adsorption isotherm. Using

this model Schindler *et al* (1976) were able to obtain good agreement with adsorption versus pH data for Fe^{3+}, Cu^{2+}, Co^{2+} and Pb^{2+} on silica. Essentially identical models were proposed by Huang and Stumm (1973) and Hohl and Stumm (1976).

A very different approach was taken by James and Healy (1972 a, b,c) who developed a physical model which expressed adsorption free energy as the sum of three terms:

$$\Delta G^{o}_{ads} = \Delta G^{o}_{elect} + \Delta G^{o}_{solv} + \Delta G^{o}_{chem} \tag{2.11}$$

ΔG^{o}_{elect} is the contribution due to the electric double layer field and ΔG^{o}_{chem} is the specific chemical interaction (bonding) similar to that evaluated by Dugger *et al* (1964) and treated as a curve fitting parameter. The main contribution of the James and Healy model was an analytical expression for the positive term, ΔG^{o}_{solv}, the change is solvation energy in moving the ion from the bulk solution into the region of lower dielectric strength near the solid-liquid interface. The model predicts that since ΔG^{o}_{solv} depends on z^2 (where z is ion charge) this contribution will be smaller for the first hydrolysis complex (e.g., $CoOH^{+}$) than for the uncomplexed metal (e.g., Co^{2+}) and the overall ΔG_{ads} will be more favorable. Thus the model explains the relation of the "adsorption edge" to the pH of incipient hydrolysis of metal ions.

As pointed out by James *et al* (1975) and James and MacNaughton (1978) the James and Healy model, which assumes that hydrolysis precedes adsorption, results in a final isotherm very similar to surface complexation models which can be viewed as adsorption followed by hydrolysis; this in spite of radically different initial conceptualization of the models. However, the James and Healy model and similar physical models allow expression of free energy of adsorption in terms of more fundamental qualities and thus *a priori* estimation of its value. A "generalized" model of adsorption proposed by Bowden *et al* (1973) used the same isotherm as the James and Healy (1972) model but incorporated a more more complete description of the EDL structure and was successfully used to describe adsorption of ions as widely different as silicate, zinc and phosphate on goethite.

Leckie and co-workers at Stanford University (Davis, 1977; Davis *et al*, 1978) have developed a general adsorption model which can simultaneously predict surface charge and potential and the adsorption density of cations and anions including trace constituents. This model built on the work of Yates *et al* (1974) who developed a model in which the high charge of oxide surfaces was explained by allowing major electrolyte counterions to enter the shear plane and form "ion pairs" with the charged surface groups. In the case of NaCl as the swamping electrolyte, surface charge σ_o would be given (where A is surface area):

$$\sigma_o = \frac{F}{A} ([SOH_2^+] + [SOH_2^+ - Cl^-] - [SO^-] - [SO^- - Na^+]) \qquad (2.12)$$

Concentrations of each of the surface species appearing in (2.12) can be related to solution concentration using the Boltzmann distribution law and empirically-determined intrinsic stability constants (Davis *et al*, 1978). By assuming surface charge development as in (2.12) Davis *et al* (1978) were able to define intrinsic formation constants for the adsorption of trace constituents which were independent of ionic strength of the background electrolyte.

Davis (1977) also studied the effects of complexing ligands on metal adsorption (Davis and Leckie, 1978). Some ligands, notably Cl^- and organics with only one complexing site, lower metal adsorption by simply competing with the surface sites. Other ligands, those with more than one binding site, such as thiosulphate and some aromatics considered to be model "humic" monomers, may enhance adsorption over a certain range of pHs by simultaneously bonding to the surface and the metal (Elliot and Huang, 1979).

Recent studies of adsorption of pairs of metals (Benjamin, 1978) have shown that multiple groups of surface sites must exist at solid surfaces such that competition is usually minimal since different metals usually have different preferred sites. Benjamin's multiple-site model can also explain the non-linearity of metal-adsorption isotherms in terms of progressive occupation of less favorable (lower energy) sites.

Little mention has yet been made of organic solids such as humic

materials. Commonly the interaction of natural organic isolates with metals is treated as "ligand complexation" (Schnitzer and Khan, 1972) and is described by stability constants (Khan, 1969; Schnitzer, 1969; Stevenson, 1976; Pagenkopf, 1978; Brady and Pagenkopf, 1978). However, other studies, particularly of higher molecular weight humic fractions have referred to the interaction as "adsorption" (e.g., Gardiner, 1974b; Rashid, 1974; Riffaldi and Levi-Minzi, 1975). Most heavy metals of environmental interest are bound to a signficant extent by sedimentary organics (Rashid, 1971, 1974; Rashid and Leonard, 1973; Nissenbaum and Swaine, 1977) and some, notably copper and iron, form extremely stable complexes.

2.4 METALS IN SEDIMENTS

Analysis for total heavy metal content of sediments gives very limited information regarding likely environmental impact (Serne and Mercer, 1975). Information on the chemical form and association of metals with various geochemical phases in sediments is required (Agemian and Chau, 1976) so that the environmental hazard to organisms which live in, and may ingest sediments, and to pelalgic organisms in the water above the sediments can be evaluated. The separation required to determine geochemical partitioning of metals is most often performed by selective chemical extraction (Brannon *et al*, 1976; Malo, 1977) although physical methods, particularly density fractionation (Francis and Brinkley, 1976; Pilkington and Warren, 1978) have also been used. Pore waters of sediments are usually separated before commencing solid extractions, either by centrifugation or membrane filtration.

Much of the work on the development of extraction methods for selective removal of geochemical phases has been performed by soil chemists (Aguilera and Jackson, 1953; Holmgren, 1967; McKeague and Day, 1966; Chao, 1972). McLaren and Crawford (1973) studied associations of copper in soils using a selective chemical extraction scheme.

Goldberg and Arhenius (1958) used the sequence: distilled water, boiling 3% LiOH or hot ammonium acetate, and EDTA in an early study

of the metals in pelagic marine sediments. Chester and Hughes (1967) investigated marine sediments with various extractants including EDTA and hydroxylamine-hydrochloride. Piper (1971) used 0.1 N HCl for extraction of fjord sediments. Presley *et al* (1972) also studied fjord sediments. Removal of interstitial water was followed by the extraction sequence: acetic acid/hydroxylamine-hydrochloride, hot hydrogen peroxide and a mixture of HF, HNO_3 and $HClO_4$ for "residual" metals.

A refined extraction procedure was developed by Engler *et al* (1977) which avoids some of the problems of earlier extraction schemes particularly in that it preserves *in situ* redox potential and avoids grinding of sediments. The interstitial water is first extracted by centrifugation. The "exchangable" metals are then removed by ammonium acetate. "Easily reducible" metals are solubilized with hydroxylamine-hydrochloride then organics and sulphides are oxidized by hydrogen peroxide before removal of "moderately reducible" metals with the citrate-dithionate method of Holmgren (1967). The remaining (strongly bound) metals are termed "residual." The method was used by Serne and Mercer (1975) in studies of San Francisco Bay sediments and by Brannon *et al* (1976) for examining metal distribution in a wide variety of aquatic sediments. Unfortunately the procedure does not differentiate organics and sulphides.

Some severe problems are encountered with use of chemical extraction schemes on natural sediments since phases (notably iron oxides) may exist in a variety of degrees of ordering from amorphous to well-crystallized (Schwertmann, 1977), since different phases may be closely associated as in the formation of surface coatings of hydrous iron and manganese oxides on clays (Jenne, 1977) and because the kinetics of metal desorption and/or phase solubilization are variable. For the above reasons there is always a trade off between *selectivity* (for the phase intended to be attacked) and *efficiency* (proportion of metals removed from that phase) at each "selective" extraction step (Serne and Mercer, 1975). Further, after extraction of the metals from one phase they may readsorb on the other phases present (Guy *et al*, 1978; Rendell and Batley, 1980).

In spite of the previously mentioned problems and some contradictory results chemical extraction has been a useful tool for examining metal partitioning in sediments and soils and some important generalized features of metal distribution can be stated:

1) Concentrations of heavy metals in interstitial waters of reduced sediments are often much higher than predicted on the basis of thermodynamic solubility data (Brooks *et al*, 1968; Presley *et al*, 1972; Elderfield and Hepworth, 1975).
2) Carbonates are generally not quantitatively important in metal uptake by sediments (Presley *et al*, 1972).
3) Copper and nickel tend to be strongly concentrated by the organics in sediment and the organics may also be an important site for other metals (Brannon *et al*, 1976).
4) Oxides of manganese and iron are particularly important phases for some metals in sediments (Brannon *et al*, 1976).
5) An appreciable fraction (often the major fraction) of some heavy metals is very strongly bound in the "residual" phase, that is, in crystalline mineral lattices (Serne and Mercer, 1975; Brannon *et al*, 1976).

A novel approach to studying the distribution of metal in sediments was taken by Luoma and Bryan (1981). These workers examined statistical correlations of metals in selective extractions with oxidized estuarine sediment variables such as grain size, iron content and organic carbon. The sediments were obtained from a wide geographical range in Southern England (19 estuaries) thus the problem of spurious correlations encountered in single basin studies may have been avoided. Iron was found to be the major sorbent for Zn, Pb and Ag and was of subequal importance with organics for Co and Cd. Humic materials were apparently the most important component of the organics and these substances dominated the uptake of Cu and Ag and were important for all metals when iron content of the sediments was low. Manganese was the dominant sink for Co and was significant for Zn, Pb and

Cu. Significantly, the carbonate content was negatively correlated with metal concentration while no correlation with grain-size was observed except in the case of Cd. (Strong *in-basin* correlations of metals with grain size were observed however.)

Study of the partitioning of metals in sediments has been approached by laboratory incubations of natural sediments under changed physio-chemical conditions. Engler and Patrick (1975) studied the effect of oxidation of flooded soils on mobilization of metal sulphides. Khalid *et al* (1976) studied the release of metals from reduced sediments under conditions designed to simulate dredge spoil disposal. The sediments were suspended in water maintained at different P_{O_2} levels and the release of heavy metals due to increase in pε and drop in pH was monitored over a period of days. Lu and Chen (1977) performed similar experiments with comparable results. Holmes *et al* (1974) reported the effects of seasonal fluctuatation of redox conditions on metal mobilization in a contaminated estuary.

Several studies including some which employed sequential extractions have reported high concentrations of heavy metals in sulphidic sediment pore waters, in some cases orders of magnitude higher than predicted on the basis of equilibrium solubility calculations (Brooks *et al*, 1968; Nissenbaum, 1972; Presley *et al*, 1972; Duchart *et al*, 1973; Lindberg and Harriss, 1974; Elderfield and Hepworth, 1975). Explanations that have been advanced include polysulphide and bisulphide complexation and complexation by soluble organics. Little evidence is at hand regarding sulphide complexation although thermodynamic data are available for some complexes. Polysulphides are known to occur in estuarine sediments (Berner, 1969) and this mechanism of metal solubilization is certainly plausible. The role of organics, specifically humic materials, in solubilizing trace metals in the presence of sulphides has been suggested by the studies of Baker (1973), Rashid and Leonard (1973), Lindberg and Harriss (1974) and Pauli (1975). Apparently the stability of humic complexes is sometimes sufficiently high to compete significantly with sulphides for metals.

A series of papers by Guy and coworkers have discussed metal adsorption in laboratory model sediment systems (Guy *et al*, 1975; Guy

and Chakrabarti, 1975 and Guy *et al*, 1978). Adsorption and complexation studies on both isolated phases, including montmorillonite, clay, humic materials and manganese dioxide, and phases in combination gave several insights into the functioning of natural sediments as metal sources and sinks.

In this department a study was made by Delphey (1977) of trace metal partitioning in model estuarine sediments composed of humic acid (2%), montmorillonite (20%), ferrous sulphide (0.05%) and reagent sand (inert, 78%) in seawater suspension (Oakley *et al*, 1980). Partitioning of Cu, Cd, Pb and Zn was found to reach an apparent equilibrium within a few days that was independent of the mode of introduction of the metal into the system (that is, the phases with which they were initially associated). The chemical extraction scheme used by Delphey is of doubtful selectivity and efficiency, however, the results indicate that subequal proportions of the total metal were partitioned between each of the solid phases other than sand. Recently Oakley *et al* (1981) proposed a simple model for the partitioning of copper and cadmium among geochemical phases in oxidized marine sediments. The model was calibrated by fitting linear isotherms to the adsorption data for low concentrations of copper and cadmium on the model phases: montmorillonite, hydrous ferric oxide, manganese dioxide and humic acid in seawater suspension. Oakley also studied the bioavailability to estuarine polychaetes of copper and cadmium in these model substrates.

3. SCOPE AND PLAN OF THE RESEARCH

3.1 CONCEPTUAL MODEL OF AN ESTUARINE SEDIMENT SYSTEM

Before discussing specifics of the study approach it is useful to conceptualize metal interactions in an estuarine system. Figure 3.1 shows a schematic of an estuarine sediment system with special regard to the cycling of trace metals. The figure incorporates features of benthic models proposed by Bella (1975), Nelson *et al* (1977) and Davis *et al* (1978) for example. The four main compartments of the model are air, estuarine water, oxidized surface sediment and reduced sediment. Transfers of solutes across boundaries are indicated by vertical arrows and solid transfers are indicated by heavier lines, while chemical or biochemical interactions are represented by dots.

The estuarine water is in equilibrium with the atmosphere (except with regard to H_2S) and the pore water of oxidized sediment will have essentially the same composition as this overlying water. However, anaerobic sediment will have pore water of somewhat different composition (Table 2.2) due to various redox reactions discussed above.

The boundary between the oxidized and reduced sediment is usually not sharp thus the dotted line in Figure 3.1 represents only the inflection point in the $p\varepsilon$-depth curve. The "redox boundary" may flucuate seasonally and in some cases may reach the sediment surface when overlying water is relatively stagnant (Holmes *et al*, 1974). More commonly, estuarine water is rather well-mixed by tidal action and waves and frequently bottom sediments are resuspended (Anderson, 1970, 1972) sometimes to a depth below the redox boundary. This kind of process, together with bioturbation by burrowing and deposit-feeding fauna (Lee and Swartz, 1980) results in turnover of estuarine sediments (Bella, 1975) such that oxidized surface sediment is continually buried and is replaced by reduced sediment brought into the near-surface oxidizing environment. The activities of man in estuaries, particularly the dredging of navigation channels, have a similar sediment-mixing effect. Figure 3.1 indicates physical transfers and chemical reactions of a number of species of significance in metal cycling including organic and inorganic solutes and solids. Trace metals intro-

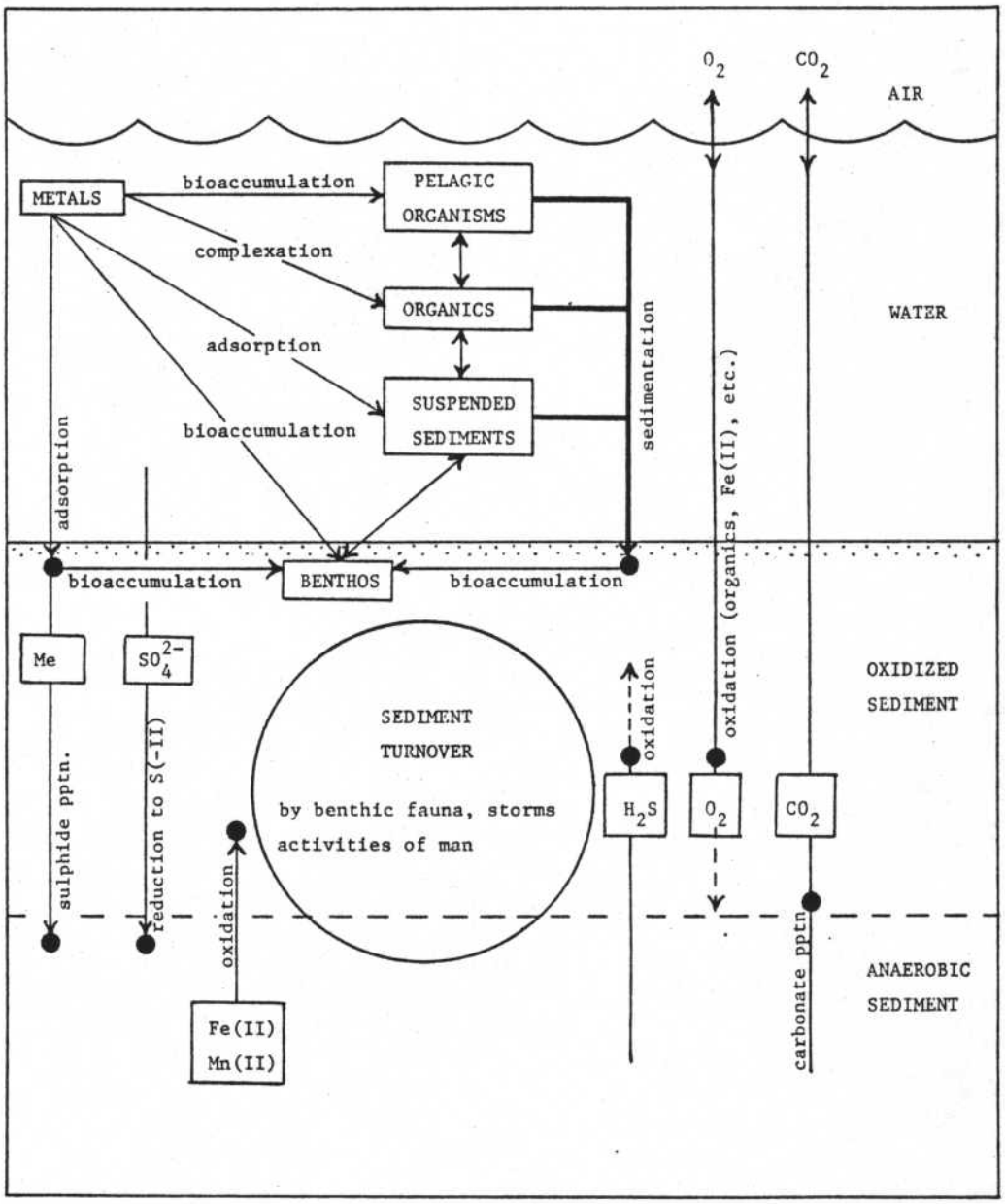


Figure 3.1. Conceptual Model of Metal Pathways in Estuarine Systems.

duced into the estuarine system (for convenience this introduction is considered to be as solutes in estuarine water) are rapidly taken-up by complexation and adsorption on organic and inorganic materials both in the water column and in the oxidized sediment. More slowly the metals may be uptaken by organisms or sedimented to the bottom deposits when bound to sedimentary particles. Metals in (oxidized) sediments may be bioaccumulated by deposit feeders (Luoma and Jenne, 1976). Ultimately the oxidized sediments are buried and some fraction of the associated metals are precipitated as sulphides.

Transfers and/or reactions that are the reverse of the above also occur for example, desorption, excretion or sediment turnover, such that a *steady state* concentration of the different metal fractions is maintained even though some constituents, notably the organic matter, (Stumm and Morgan, 1970) are thermodynamically unstable. Thus the sediment system is not at true equilibrium. However, we may apply thermodynamic principles to chemical interactions of components that are metastable but persist at steady state because of kinetic factors and/or continual input to the system (Stumm and Brauner, 1975).

3.2 STUDY PLAN

A number of variables that may influence the partitioning of metals in estuarine sediments are listed in Table 3.1. Some variables, notably pH, $p\varepsilon$ and ionic strength, have more than one type of effect. The approach taken to examine the effects of these different variables is outlined in the table.

Perhaps the most fundamental variable in an estuarine system is $p\varepsilon$. This study considered two extreme $p\varepsilon$ situations representing the two sediment compartments in Figure 3.1: a well-oxidized surface sediment with pore water of very similar composition to that of overlying water ($p\varepsilon \simeq 12$) and a reduced sediment of much lower $p\varepsilon$. Since the reduction of sulphate to sulphide is the most important redox reaction in estuarine sediments the SO_4^{2-}/S(-II) couple is likely to reflect redox potential:

Table 3.1

SYSTEM VARIABLES IN ESTUARINE SEDIMENTS

Variable	Range in Estuarine Sediments	Effects (with regard to metal partitioning)	Control (this study)
pε	12 to -4	Solid phase: hydrous Fe, Mn oxides → sulphides. Aqueous phase: SO_4^{2-} → S(-II), Cu(II) → Cu(I), etc.	Study two extreme situations: Oxidized and anaerobic sediments.
Metal conc. M_T	0 to 10^{-6}M	Affects *nonlinear* solid/solution partitioning of the metal.	Vary M_T and define linear range of partitioning.
pH	6.5 to 8.5	Solid phase: surface charge and potential. Aqueous phase: metal speciation, ligand speciation, ligand adsorption.	Vary pH and define adsorption dependence on pH (adsorption edge).
Ionic strength (salinity)	0 to 0.7M (0 to 35°/oo)	Solid phase: affects thickness of EDL, also surface charge and potential. Aqueous phase: affects activities of solutes, concentrations of ligands, Cl^-, SO_4^{2-}.	Use 35°/oo artificial seawater as a reference. Study effects of salinity on adsorption by selected phases. Study adsorption in other aqueous media.
Temperature	0 to 35°C	May shift adsorption/precipitation equilibria.	Run experiments at constant temperature (20 ± 1°C).
Sediment composition	(ref. Table 2.1)	Affects partitioning.	Determine sediment composition (nat. seds.). Determine sorbent conc. which gives approx. 50% uptake.

$$SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O \tag{3.1}$$

the equilibrium constant expression is:

$$p\varepsilon = \frac{1}{8} \log K - 1.125\ pH + \frac{1}{8} \log (SO_4^{2-}) - \frac{1}{8} \log (HS^-) \tag{3.2}$$

(Stumm and Morgan, 1970). This equation changes only slightly if the reaction is written in terms of H_2S^o rather than HS^- (H_2S^o dominates at pH less than 7). Thus when sulphate is present in reduced estuarine sediments as well as sulphide (the common situation) the $p\varepsilon$ is poised: $-2 > p\varepsilon > -5$, depending on the pH. Only when sulphate is almost totally utilized can $p\varepsilon$ drop below this range, that is, the system is buffered with respect to $p\varepsilon$. It should be noted that the above analysis is somewhat of an oversimplification because of the presence of intermediate oxidation states of sulphur (polysulphides, thiosulphate) (Berner, 1971).

The pore water composition of reduced sediments is different from overlying water (Table 2.2) with respect to some minor species and sulphur, and the main change in the solid fraction is the reduction of iron and manganese and formation of sulphides of these metals. Sulphide precipitation of heavy metals is best considered separately from adsorption and can be predicted satisfactorily from thermodynamics given free S(-II) concentration. It seems unlikely that $p\varepsilon$ change will have major effects on adsorption by solid phases such as organics, and alumino-silicates that persist over a wide $p\varepsilon$ range. Thus the assumption was made for the purposes of this study that *adsorption behavior can be modelled for both reducing and oxidizing conditions based on experimental measurements in oxidized systems.*

The rationale for the choice of model sediment solid phases and experimental work on the isolation, synthesis and characterization of these phases is presented in Chapter 4.

The approach with respect to the other variables of importance in estuarine systems (Table 3.1) was as follows. Experiments on adsorption of cadmium and copper were performed with different model solid phases in isolation under oxidizing conditions and with pH and metal concentration varied. The effects of salinity (ionic strength) and

temperature and composition of the aqueous medium were examined in some cases. The results of these investigations are presented in Chapter 5. Adsorption experiments were next performed with combinations of model solid phases and with only pH and metal concentration as variables (Chapter 6). Natural oxidized estuarine sediments were studied again with only pH and metal concentration as variables (Chapter 7). Finally the work on natural sediments was correlated with the model phase studies and a model of trace metal partitioning in estuarine sediments under various physico-chemical conditions was developed (Chapter 7).

The study as outlined above was designed to extend the work of Oakley (1980) in this department along the following lines:

1) The model sediment phases used by Oakley were not characterized (by surface area, crystallinity, stoichiometric composition, particle morphology). In the present study model phases were either isolated or synthesized under the same conditions as used by previous workers thus permitting the assumption that the product phases had the same character as reported by these earlier studies and/or characterization studies were performed.
2) Hydrous iron and manganese oxides, montmorillonite and humic acid were investigated by Oakley (1980) and were also used in the present study. To this list of phases was added a synthetic hydrous alumino-silicate gel, intended as a model for amorphous alumino-silicates ("allophanes") common in soils and sediments.
3) Oakley (1980) used only seawater as the aqueous phase (natural seawater collected from the Oregon coast, $32^{o}/oo$ salinity). The present study employed natural and artificial seawater at various dilutions (salinities) as well as other aqueous media.
4) The effect of interaction of combined model phases on metal uptake was investigated.
5) Natural sediment metal sorptive capacity was also studied.

6) Anaerobic sediments were considered as well as aerobic sediments.

It was felt that a model for trace metal partitioning in estuarine sediments developed from the extended lines of investigation outlined previously would provide a basis for prediction of the environmental significance of metals in estuaries with regard to biological availability and the activities of man such as the dredging of navigation channels.

It should be stated explicitly that this research was intended to be a comparative study of metal binding by solid phases rather than an examination of adsorption mechanisms. Thus the goal of the study demanded a very different perspective from those studies devoted to examining the adsorption process phenomenologically.

3.3 DEVELOPMENT OF A SIMPLE ADSORPTION MODEL

3.3.1 Outline of the Adsorption Model

Based on some of the adsorption models discussed previously (Section 2.2) a model of trace metal adsorption has been developed which allows simple quantitative description of metal interaction in multiple-phase sediment systems. The following development draws on studies such as those of Schindler *et al* (1976), Davis (1977) and Benjamin (1978) that were primarily designed to elucidate adsorption mechanisms and thus had a very different perspective and level of resolution from the present work.

In natural systems, including estuarine sediments, the solution phase concentrations of trace metals are very low (usually less than 10^{-6}M) while solid surfaces are in great excess; thus site limitation on available solid surfaces is not experienced (Benjamin, 1978). The result is that partitioning between solid and aqueous phases is *linear*. Where the adsorption isotherm is linear the adsorption edge (fractional adsorption plotted against pH) will occur at a unique position independent of total concentration of metal and dependent only on adsorbent (surface) concentration. This greatly simplifies the analysis

of adsorption phenomena in natural systems and model systems at "environmental" concentrations.

Consider a generalized metal sorption reaction occurring at a solid/solution interface which we represent:

$$M_s^{m+} + SH_{n,s} = SM_s^{(m-n)+} + n\ H_s^+ \tag{3.3}$$

where the subscripts, s, denote surface species, M^{m+} is the free metal ion, H^+ is included with indefinite stoichiometry denoted by n to account for the dependence of adsorption on hydrolysis reactions and on surface charge and hence on pH, and S is a surface site. This equation is similar to the ion-exchange type reaction written by Schindler *et al* (1976) in their representation of a "surface complexation" model. We may write a mass law expression for an intrinsic surface complex formation constant in terms of surface species only:

$$^*\beta_{n,int} = \frac{(SM^{(m-n)+})_s\ (H^+)_s^n}{(SH_n)_s\ (M^{m+})_s} \tag{3.4}$$

The surface species H_s^+ and M_s^{m+} are present at different concentrations than in the bulk electrolyte because of the electrostatic interaction of ions with the field of the electric double layer (EDL) near charged surfaces. The Boltzmann distribution law (see for example, Moore, 1972) can be used to relate the concentrations of a species in different energy states thus:

$$\frac{C_2}{C_1} = \exp\left(\frac{E_1 - E_2}{RT}\right) = \exp\left(\frac{\Delta E}{RT}\right) \tag{3.5}$$

where C is concentration, E is energy, subscripts 1 and 2 represent the two different energy states and R and T have their usual meanings. In this case ΔE is electrical energy and we have that:

$$[H^+]_s = [H^+]_{aq}\ \exp\left(\frac{-F\psi_o}{RT}\right) \tag{3.6}$$

and

$$[M^{m+}]_s = [M^{m+}]_{aq}\ \exp\left(\frac{-mF\psi_\beta}{RT}\right) \tag{3.7}$$

where F is the Faraday constant and ψ represents electric potential.

ψ_β is the EDL potential at the distance of approach, β, of surface-complexed species to the interface (Davis *et al*, 1978) and ψ_o is the EDL potential at the solid/solution interface which may be simply related to pH by the Nernst equation (H^+ being the potential-determining ion):

$$\psi_o = 2.3 \frac{RT}{F} (pH_{PZC} - pH) \tag{3.8}$$

where pH_{PZC} is the point of zero charge, the pH at which surface charge is zero (Parks, 1975). It has been shown (Levine and Smith, 1971; Wright and Hunter, 1973) that the derivative $-d\psi_o/d\ (pH_{PZC} - pH)$ may vary significantly from the theoretical value of 2.3 RT/F, thus (3.8) must be regarded as a first approximation, valid only close to the PZC. For solids such as clays where surface charge arises largely from isomorphic substitution for Al^{3+} or Si^{4+} in the lattice by ions of different (usually lower) valence (constant charge surfaces) ψ_o is almost independent of pH but still depends on ionic strength. The intrinsic formation constant can now be written:

$$*\beta_{n,int} = \frac{[SM^{(m-n)+}]_s\ (H^+)^n}{[SH_n]_s\ [M^{m+}]} \Pi\gamma \cdot (EDL) \tag{3.9}$$

where $\Pi\gamma$ is the product of the activity coefficients and (EDL) represents the electric double layer term which, following Benjamin (1978), is not written explicitly although it could be formulated in terms of Equations 3.6, 3.7 and 3.8. Assuming the activities of surface species, like those of solute species, depend mainly on ionic strength, the term $\Pi\gamma$ will be a constant at a given ionic strength. The EDL term is primarily a function of pH (refer Equation 3.8) and ionic strength. Electric double layer theory predicts the thickness of the electric double layer to be proportional to $I^{-1/2}$ (Stumm and Morgan, 1970), thus while ψ_o may change only slightly with I, ψ_β decreases significantly as I increases (Davis, 1977).

In a constant ionic medium (EDL) depends only on pH (Benjamin, 1978) that is, (EDL) = f (pH). (For constant charge surfaces at constant I, (EDL) is constant.) If we suppose that (EDL) is proportional to some power of (H^+) (as seems reasonable on consideration of

Equations 3.6, 3.7 and 3.8) then we can write a conditional adsorption constant (dropping subscripts and surface charge for simplicity):

$$c_K = \frac{[SM]\ (H^+)^x}{[SH_n][M^{m+}]} \tag{3.10}$$

in which the γ's are incorporated in the conditional constant at constant I and the (EDL) term has been incorporated in the expression by indicating a change in the *apparent* reaction stoichiometry. For Langmurian adsorption the total concentration of surface sites, S_T, is well defined and we can write:

$$S_T = [SH_n] + [SM] \tag{3.11}$$

and substitution of 3.11 into 3.10 yields Langmuir-type isotherms. In the case of metal adsorption the Langmuir conditions (Stumm and Morgan, 1970) are not met, particularly in the light of Benjamin's (1978) work which suggests multiple adsorption sites. Thus S_T can not be defined. However, in the case of low adsorption density (trace species) we can write:

$$S_T = k\{S_T\} \simeq [SH_n] \tag{3.12}$$

where k is a constant, the moles of surface sites per unit mass (or unit area) of surface and {} denotes mass (or areal) concentration of the adsorbent. Substituting in 3.10 we obtain the linear isotherm:

$$c_{K_{ads}} = \frac{[SM]\ (H^+)^x}{\{S_T\}\ [M^{m+}]} = \frac{\Gamma\ (H^+)^x}{[M^{m+}]} \tag{3.13}$$

where Γ is adsorption density. A complex multi-site model developed by Benjamin (1978) reduced to a mathematically identical expression under similar assumptions to those made above. Writing a mass balance on the total metal concentration:

$$\begin{aligned} M_T &= M_{TS} + [SM] \\ &= \frac{[M^{m+}]}{\alpha_o} + [SM] \end{aligned} \tag{3.14}$$

where M_{TS} is the total solution phase metal and α_o is the distribution

coefficient for the free metal ion given:

$$\alpha_o = \frac{[M^{m+}]}{M_{TS}} \tag{3.15}$$

α_o(pH) is a function only of pH for a given ionic medium. With fractional adsorption defined as:

$$f = \frac{[SM]}{M_T} = \frac{M_T - M_{TS}}{M_T} \tag{3.16}$$

we obtain finally:

$$^{c}K_{ads} = \frac{f\ (H^+)^x}{(1-f)\ \alpha_o\ \{S_T\}} = \frac{K_p (H^+)^x}{\alpha_o} \tag{3.17}$$

where the term, K_p is the slope of the adsorption isotherm at constant pH and is given:

$$K_p = \frac{f}{(1-f)\ \{S_T\}} = \frac{\Gamma}{M_{TS}} \tag{3.18}$$

Henceforth K_p will be referred to as the "linear partition coefficient."

The above model, while greatly simplified and necessarily more empirical in nature than the recent comprehensive models of adsorption such as that of Davis *et al* (1978) has the distinct advantage for the present purposes of being immediately applicable to the systems investigated in the present study. That is, the present simplified approach obviates the need for the detailed empirical work on each combination of electrolyte, sorbent and sorbate such as is required to calibrate the models developed by Stumm, Schindler and coworkers, and Leckie, Davis and coworkers.

The approach taken in the present study was to evaluate K_p by performing simple adsorption experiments in seawater media of various salinities to determine linear partitioning between the solid and solution phases. If the speciation of the metal in a given medium is known the distribution coefficient can be evaluated thus enabling the conditional adsorption coefficient, $^{c}K_{ads}$ to be determined from Equation 3.17.

3.3.2 Distribution Coefficients for Copper and Cadmium Ions in Seawater

With the object of evaluating the distribution coefficient of the free cupric and cadmium ions in seawater in mind a chemical equilibrium computer program (UMDEQ, Ingle, 1981, in prep.) was employed to compute speciation of copper and cadmium in artifical seawater at a series of different pH values between 6.0 and 8.5. The program was used with the thermodynamic data set of GEOCHEM (Appendix 1) (Mattigod and Sposito, 1979) as adapted by Dr. J. Baham (Soil Science Department, Oregon State University, pers. comm.). The artificial seawater composition was that of Kester *et al* (1967) and an open system, allowing exchange of CO_2 with the atmosphere, was assumed.

The calculated distribution coefficients for cadmium species in seawater are shown in Figures 3.2 ($35^o/oo$ salinity) and 3.3 ($5^o/oo$ salinity). The model predicts chloride complexes to predominate and shows that the distribution coefficient for free cadmium is almost independent of pH over the pH range studied. The predicted distributions are in qualitative agreement with speciation models published by Zirino and Yamamoto (1972) and Long and Angino (1977). Some quantitative differences arise from the more complete set of complexes considered in the present study, the use of slightly different thermodynamic data (Appendix A) and different methods of making activity corrections and the fact that these previous studies assumed a system closed to the atmosphere.

Figure 3.4 shows the predicted speciation of cupric copper at $35^o/oo$ salinity. Since the complexes with seawater anions (Cl^-, SO_4^{2-}) are not major species the distribution of complexes is relatively insensitive to salinity. The predicted speciation is substantially different from that of Zirino and Yamamoto (1972) and Long and Angino (1977) mainly because the log β used for the formation of $Cu(OH)_2^o$ was much lower at 10.7 than the value of 14.3 used by these earlier workers. Recently Sunda and Hanson (1979) used an electrode method to derive an intermediate value of 11.7. Another limitation of the speciation model given in Figure 3.4 is that borate complexes were neglected since the formation constants in GEOCHEM may be far too high

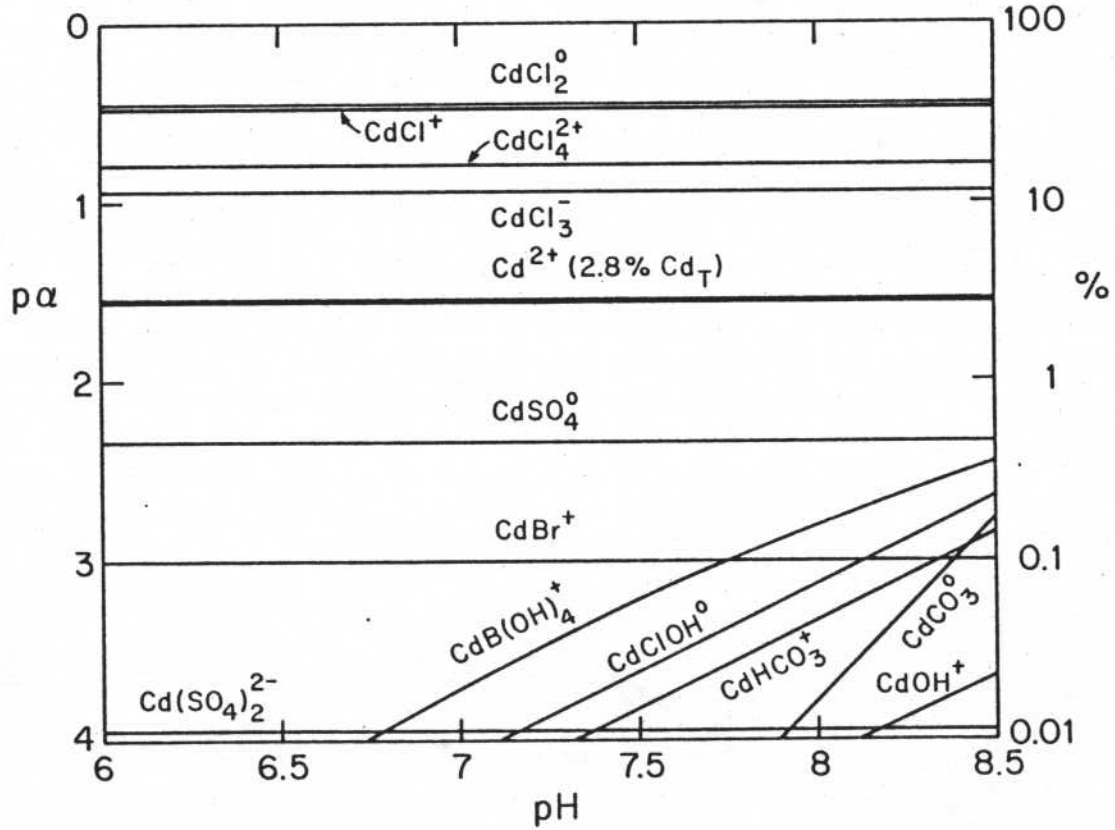


Figure 3.2. Cadmium Speciation in Artificial Seawater ($35^o/oo$, I = 0.67 M).

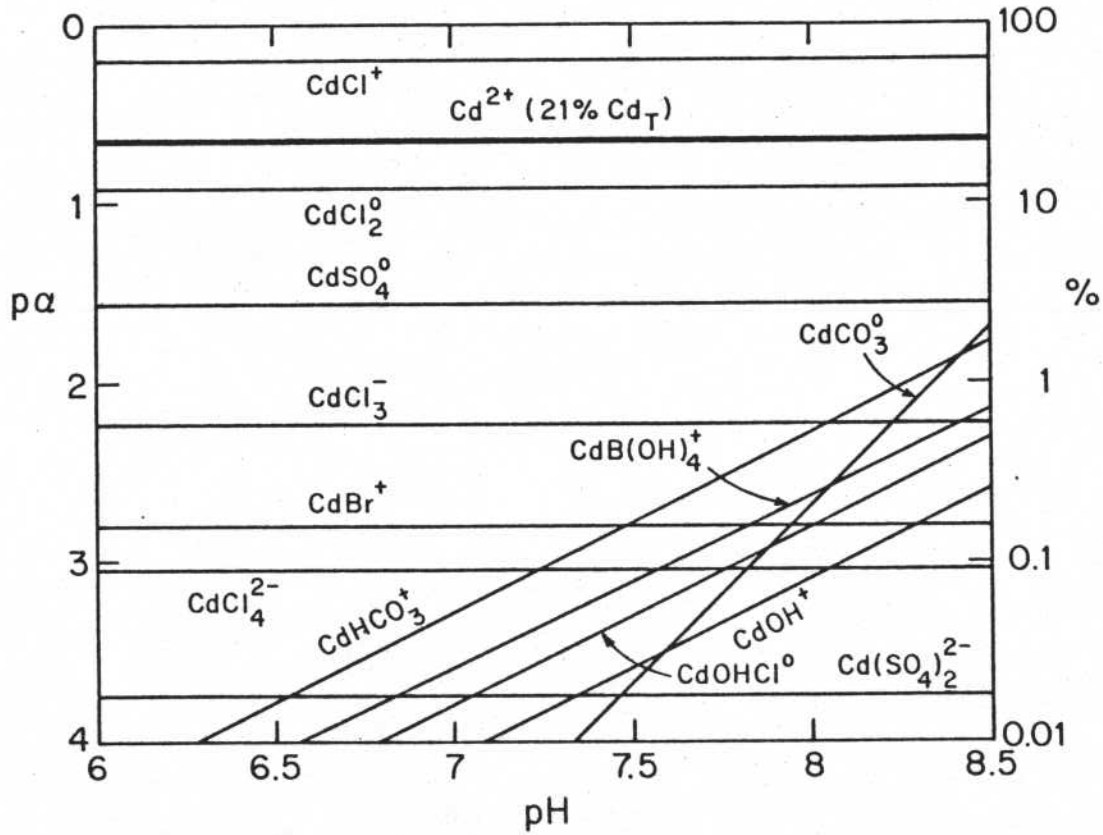


Figure 3.3. Cadmium Speciation in Artificial Seawater ($5^{o}/oo$, I = 0.096 M).

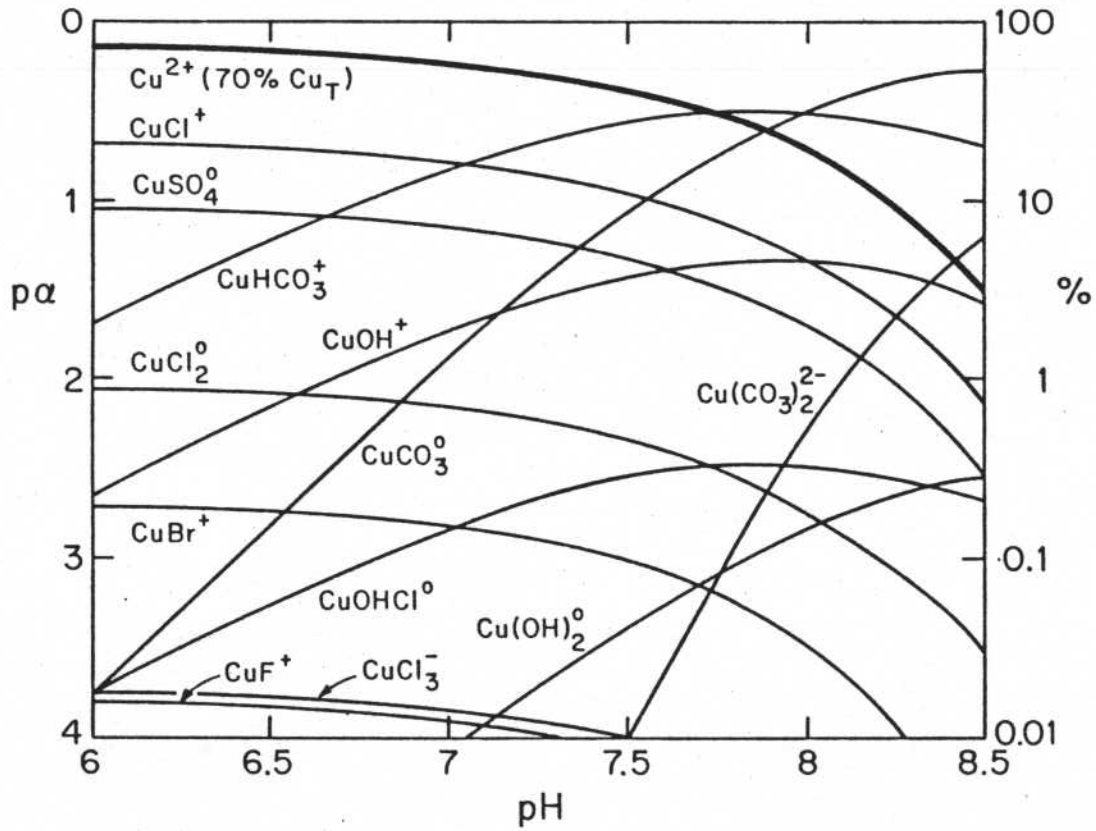


Figure 3.4 Copper Speciation in Artificial Seawater ($35^{o}/oo$, I = 0.67 M).

(Appendix A). (They predict predominance of borate complexes of copper in seawater contrary to unpublished Cu^{2+} electrode data obtained by the author.) In the absence of reliable formation constants for borate complexes and with the uncertainty regarding the true value of the constant for $Cu(OH)_2^o$ no attempt was made to use the distribution coefficient for Cu^{2+} predicted in Figure 3.4.

3.4 GENERAL LABORATORY INSTRUMENTATION AND PROCEDURES

At the "environmental" concentrations investigated in this study trace metals are greatly affected by the presence of complexing ligands and sorbing surfaces. Thus although radioactive tracers were used to follow the metals of interest the results were highly sensitive to the experimental procedures and great care was taken to ensure high purity and cleanliness and to prevent contamination of reagents or sorptive loss of metals on containers.

Analytical quality reagents were used and where necessary purification was carried out. This particularly applied to the nitric and hydrochloric acids (used to lower pH, for example to effect desorption of metals on containers) which were distilled before use. Water used for manufacturing reagents was distilled twice, once in a stainless steel Barnsted still then in a Corning Pyrex glass still, to provide a product with conductivity less than two micromhos.cm^{-1}.

Grade A glassware was employed for all critical volumetric work. All glassware was washed in 50% nitric acid and then equilibrated with the solution to be contained for at least 24 hours. The virgin plasticware employed in this study was not acid-washed, because of the embrittling and cracking effects of 50% nitric acid, but was soaked in 1N nitric acid and then equilibrated with the solution to be contained. Detergents were strictly avoided because of the presence in these cleansing agents of complexing ligands such as phosphates or NTA.

An IEC Model B20 refrigerated centrifuge equipped with either a 947 swinging bucket rotor (250 mL bottles) or an 870 angle head (50 mL or 10 mL tubes) was used for solids separations. A Fisher Model 300 sonic dismembrator was used for dispersing solids and for cleaning centrifuge tubes. An Amicon Model 12 stirred cell using 25 mm

membranes was used for "ultrafiltration" of humic material. A Heath EU 700 series modular recording spectrophotometer was used for UV-visible spectroscopy and colorimetric analyses.

Metal analyses were performed using a Perkin-Elmer 360 atomic absorption spectrophotometer equipped in flameless measurements (for *copper* and *cadmium*) with a graphite furnace connected to an HGA 2100 controller. *Iron*, *aluminum* and *manganese* were measured by flame AA although *manganese* (in the Mn(II) state) was measured on δ-MnO_2 preparations by the redox titration method of Lingane and Karplus (1946). *Silicon* was measured either by the molybdosilicate method or the heteropoly blue method (Standard Methods, 1975). *Salinity* of natural or artificial seawater was measured with a YSI Model 33 salinity/conductivity/temperature meter or by argentometric (Mohr) titration (Standard Methods, 1975).

Carbon analyses on aqueous solutions were made with a Beckman carbon analyzer (direct injection) or with an Oceanography International total carbon system (using 10 mL ampules). In both cases potassium phthalate was used to prepare standards. A LECO WR 12 carbon analyzer was used for organic carbon measurements on sediments or other solids using steel ring standards. Analysis of the *crystallinity* of sediment clay fractions and solids preparations were made on glass slide or random powder samples with a Phillips Norelco X-ray goniometer using copper $K_{\alpha 1}$ radiation (Dr. M. Harward, Soil Science Dept., OSU, pers. comm.). A Beckman Model 727B infrared spectrophotometer was used for generating IR spectra.

A Corning Model Five pH meter equipped with a Corning combination electrode was used for all pH measurements except for those in adsorption experiments for which a semi-micro electrode was required in 10 mL test tubes (Section 5.1). pH was measured according to the normal scale (NBS scale using standard buffers) defined by Bates, 1975:

$$pH = -\log_{10}(H^+) + (\text{const}) = -\log_{10}(H^+)' \qquad (3.19)$$

where (const) arises from the electric junction potential at the reference electrode. This small but unavoidable potential is different in different aqueous test media and thus changes in taking the electrode

from the buffer to seawater or other media used in this study. Since composition of open ocean seawater varies only slightly (thus approximating a constant ionic medium) oceanographers have suggested defining pH on a constant ionic medium scale (Bates, 1975):

$$p[H^+] = -\log_{10}[H^+] \tag{3.20}$$

where $[H^+]$ is *free* hydrogen ion molality. McBryde (1969, 1971) has shown that $-\log_{10}(H^+)'$ is related to $-\log_{10}[H^+]$ in NaCl or $NaNO_3$ solution by a constant thus it seems reasonable that this also goes for seawater or dilutions of seawater giving:

$$p[H^+]_x = (\text{const})_x + p(H^+)' \tag{3.21}$$

where $(\text{const})_x$ incorporates differences in junction potentials, activity coefficients and the effect of protonation of SO_4^{2-} ions. In principle the $p(H^+)'$ measurements in the present study could be related to $p[H^+]$ but this would require measurement of $(\text{const})_x$ for all the different media studied (all different salinities) and was not considered warranted.

4. SELECTION, PREPARATION AND CHARACTERIZATION OF MODEL SEDIMENT PHASES

4.1 RATIONALE

As was pointed out previously a number of geochemical phases comprising estuarine sediments are potential sinks for heavy metals and other materials of environmental concern (Jenne, 1977). Previous studies (many of which are reviewed by Jenne, 1968, 1977) on both natural and synthetic phases suggest that metal uptake may be dominated by the hydrous oxides of Mn, Fe, Al and Si, with a significant contribution by organic matter and various but generally less important contributions by clays and other silicates, carbonates and biomass components (for example, Luoma and Bryan, 1981). Sulphides may be the major sink under reducing conditions. Sediment interstitial water must also be considered but in a very special sense in that, as well as being a compartment for metals of environmental interest in its own right:

1) The reactions of interest occur in this phase or at the solid/aqueous boundary.
2) The movement of reactants occurs through this phase (with the exception of solid state diffusion).
3) Solution conditions determine surface properties of solid phases and even which solids are thermodynamically stable.

In this study, following the approach of other workers (Guy *et al*, 1975, 1978; Oakley, 1980), a relatively few model phases were chosen to simulate the functioning of an estuarine sediment with respect to trace metals.

Of the sedimentary constituents listed in Table 2.1 it was decided to attempt to represent, that is, to model, all but the carbonates. Carbonates in estuarine sediments are mostly biogenic in origin and, while often a major fraction of the sediment mass, they occur mostly as relatively large fragments of the shells of estuarine fauna with low surface areas. In reduced sediments under conditions of

relatively low pS(-II) and high P_{CO_2} authigenic ferrous carbonate (siderite) and manganous carbonate (rhodochrosite) are stable (Holdren and Bricker, 1977). Carbonate particles in marine sediments are known to be heavily coated with organics (Chave, 1970; Seuss, 1973; Johnson, 1974) presumably because the surface charge of carbonates is positive (PZC for calcite about 8 - 9.5, Somasundaran and Agar, 1967) while organics are negative at the prevailing pH of seawater. The occurrence of these organic coatings may explain the lack of precipitation of *inorganic* calcium carbonate in supersaturated surface seawater and also suggests that carbonate surfaces *per se* may be unavailable for heavy metal uptake. Further, Luoma and Bryan (1981) found that heavy metals in estuarine sediments were *negatively* correlated with carbonate contents. For these reasons no attempt was made to study uptake of heavy metals by model carbonate phases.

4.1.1 Hydrous Iron and Manganese Oxides

Since estuaries trap around 90% or more of the colloidal iron discharged by rivers (Boyle *et al*, 1977; Sholkovitz, 1976, 1978), this element may be enriched in estuarine sediments relative to river sediments and water and is likely to have major environmental significance, including strong influence on the cycling of heavy metals. Phase predominance diagrams for iron such as those presented by Jenne (1968), Gotoh and Patrick (1974), Nelson *et al* (1977) and Lindsay (1979) show wide stability fields for various ferric oxides under oxidizing to mildly reducing conditions. Goethite (α - FeOOH) is generally considered the most stable phase in soils and sediments and is the most common crystalline oxide (Schwertmann and Taylor, 1977) although crystal size may change the relative stability of the hydrous ferric oxides because of surface energy effects (Langmuir and Whittlemore, 1971).

In spite of the greater stability of crystalline hydrous oxides, poorly-ordered hydrous Fe(III) oxides (often amorphous to X-ray diffraction or XRD, analysis) occurring as coatings (Jenne, 1968, 1977) or as quasi-discrete phases are extremely common in soils and sediments (Schwertmann and Taylor, 1977). Studies of Fe^{3+} activity in soils suggests that the ΔG_f^o of soil iron is significantly less negative

than that of crystalline oxides (Lindsay, 1979) and soil (and probably sediment) iron is best regarded as a phase having a somewhat greater degree of order than a fresh Fe(III) precipitate. The poorly-ordered natural iron which often contains appreciable organic matter is termed "ferrihydrite" (Chukrov *et al*, 1972; Schwertmann and Fischer, 1973; Schwertmann, 1977). It persists in the environment as a metastable phase because solubilities of hydrous Fe(III) oxides are so low that transformations to more stable phases are extremely slow. Avotins (1975) found that transformation of synthetic amorphous hydrous ferric oxide to goethite in "clean" laboratory systems required a period of months, while in soils and sediments approaches to thermodynamic stability may take many years because of the presence of organics which coat particles and complex iron (Schwertmann, 1966).

Since estuarine sediments undergo constant overturn (Bella and Williamson, 1977) ferrous iron formed at low $p\varepsilon$ will continually be exposed to oxidizing conditions. FeS exposed to oxidation will initially be oxidized to elemental sulphur, S^o, or to sulphur oxyanions (Nelson *et al*, 1977), thus releasing Fe^{2+} ions which are then available for oxidation to hydrous ferric oxides. Laboratory oxidations of ferrous solutions may give rise to crystalline lepidocrocite (γ - FeOOH) rather than amorphous precursors of goethite such as are produced on neutralization of ferric solutions (Schwertmann and Taylor, 1977). Conditions under which lepidocrocite will form rather than amorphous products are not clearly established and often mixed products occur. However, relatively fast oxidation at low P_{CO_2} and/or pH's lower than 7 seems to favor lepidocrocite (Nelson *et al*, 1977). Nelson produced predominantly lepidocrocite in rapid laboratory oxidations of slightly alkaline FeS suspensions in the absence of CO_2 and apparently assumed that lepidocrocite will be the major product on overturn and oxidation of iron in estuarine sediments. However, estuarine sediments are likely to have high levels of CO_2. Lepidocrocite is observed in hydromorphic soils but never in *calcareous* hydromorphic soils (Schwertmann and Taylor, 1977) again, presumably, because of the inhibition of γ - FeOOH formation by aqueous inorganic carbon. High levels of complexing organics in sediments and soils may inhibit the crystallization of lepidocrocite which would otherwise occur, because

oxidation of organic-complexed iron is more likely to give ferrihydrite-type phases rather than crystalline products (Schwertmann and Fischer, 1973). Further, as Nelson *et al* (1977, p79) themselves report, diagenetic lepidocrocite has not been observed in sediments.

In the light of the above discussion it seems probable that much of the iron in estuarine sediments (being calcareous, organic-rich, at near-neutral pH and with high P_{CO_2}) is poorly-ordered ferrihydrite occurring as discrete phases and as coatings (Aston and Chester, 1973). Some of the ferrihydrite is diagenetic while the well-crystallized iron such as goethite or lepidocrocite is probably almost entirely detrital. In this study poorly-ordered hydrous Fe(III) oxide precipitates were chosen for study since these may exhibit similar sorptive properties to natural ferrihydrite. Since much of the iron in estuarine sediments is probably complexed by, or coated with organics, (Pickard and Felbeck, 1976; Krom and Sholkovitz, 1978) the effects of phase interaction between iron and humic substances on metal uptake was investigated. Much of the detrital iron occurs as coatings on mineral particles, particularly clays (Jenne, 1968, 1977) so this phase interaction was also studied.

Some of the arguments that have been advanced above for iron also apply to manganese in the estuarine environment. However, manganese is apparently impoverished relative to iron in most nearshore sediments because of its different geochemistry. A very large number (in excess of 30) hydrous oxides of manganese are known but stability diagrams based on thermodynamic data show that dioxide phases are stable under oxidizing conditions over a wide pH range (Jenne, 1968; Stumm and Morgan, 1970; Gotoh and Patrick, 1972; Lindsay, 1979; Hem, 1980). Pyrolusite, β - MnO_2) is the most stable dioxide phase (Lindsay, 1979; McKenzie, 1977) but metastable birnessite (a group of poorly-ordered hydrous oxides of variable and indefinite stoichiometry, McKenzie, 1977) is much more common in the environment. Synthetic hydrous oxides similar to natural birnessite are easily produced by oxidation of manganous solutions (Morgan and Stumm, 1964; Stumm and Morgan, 1970) under a wide variety of experimental conditions. The usual product, designated δ - MnO_2, actually has a nonintegral stoichiometry, MnO_x, where commonly: $1.8 < x < 1.95$ (Stumm and Morgan, 1970) apparently

due to formation of crystallites which incorporate Mn^{2+} or Mn^{3+} into the structure before oxidation to Mn(IV) is complete. Hydrous oxides of lower average oxidation state are also known both in laboratory systems and in soils and sediments. Stable pyrolusite can be produced by aging δ - MnO_2 in "clean" laboratory suspensions (McKenzie, 1977) but where foreign ions or organics are present recrystallization is strongly inhibited. For this reason δ - MnO_2 tends to persist in soils and sediments, very often as surface coatings on other minerals (Jenne, 1968; Lee, 1973). The above review suggests that manganese in oxidized estuarine sediments will occur largely as birnessite and for this reason, following other workers (Posselt *et al*, 1968; Lockwood and Chen, 1973; Loganthan and Burau, 1973; Gadde and Laitinen, 1976; Guy *et al*, 1975) synthetic δ - MnO_2 was used as a model phase for metal uptake studies.

4.1.2 Aluminosilicates

Of the crystalline aluminosilicates occurring in soils and sediments the phyllosilicates (clay minerals) are usually of greatest chemical reactivity. These minerals, characterized by two-dimensional (and sometimes one-dimensional) long range order have high specific surface areas and may have a high cation exchange capacity (Grim, 1968; van Olphen, 1977). For these reasons clays have been suggested as important sinks for heavy metals in the environment and the literature reveals continued interest in the sorptive uptake of metals by clays (Steger, 1973; Bittell and Miller, 1974; Lasheen, 1974; Guy *et al*, 1975; Farrah and Pickering, 1976a,b, 1977a,b, 1979; Francis and Brinkley, 1976; Garcia-Miragaya and Page, 1976; Levy and Francis, 1976; Oakley, 1980). However, Jenne (1968, 1977) has contended that the apparent sorptive capacity of clays for metals is mainly a function of oxide coatings.

The crystalline clay minerals most likely to be of importance as sinks for trace metals and other toxic materials in sediments are those of the smectite group (including montmorillonite) and, possibly, the vermiculites and the chloritic minerals formed from these clays by the addition of hydroxy-interlayers, because of relatively high

surface charge and specific surface area. The high surface charge (negative over environmental ranges of pH) arises from isomorphic substitution of ions of lesser valence for Al in the octahedral sheets (Grim, 1968; van Olphen, 1977) as well as a pH-dependent contribution from the sorption of the potential-determining ions H^+ and OH^-. Clays in estuaries are detrital in origin, although a quantitatively unimportant amount of neoformation is probably occurring (Jeans, 1971). Since montmorillonite is a favored product under relatively mild weathering conditions where sufficient Mg and Si is present (Grim, 1968; Lindsay, 1979) this clay is probably common in estuarine sediments. For example, montmorillonite is the dominant clay mineral in San Francisco Bay (Serne and Mercer, 1975). In the present study uptake of copper and cadmium by montmorillonite clays was investigated, both as adsorbents in their own right and as substrates for other sinks of heavy metals.

There is experimental evidence that the surfaces of aluminosilicate minerals in the environment are frequently coated with poorly-ordered hydrous oxides of aluminum and silicon as well as iron and manganese (Jenne, 1977). Perhaps the most direct evidence was reported by Jones and Uehara (1973) who used a novel grid preparation technique to examine these "gel-hulls" coating soil particles under the electron microscope. These X-ray amorphous gel coatings are apparently formed due to dynamic equilibria set up between the solid and the contacting aqueous phase. In particular, clay minerals undergo dissolution of aluminum and smaller amounts of silicon when suspended in water (Lindsay, 1977). The coprecipitated aluminosilicate gels coating crystalline minerals may be similar to allophane, the natural X-ray amorphous aluminosilicates characterized by Al-O-Si bonds which occur as a weathering product in volcanic ashes and some other soils (Mitchell *et al*, 1964; Fieldes and Furkert, 1966; Cloos *et al*, 1969; de Villiers, 1971; van Olphen, 1971; Wada and Harward, 1974; Wada, 1977). In some laboratory experiments in which the weathering of aluminosilicates by grinding or immersion in water was studied, amorphous coatings have been identified (Fieldes and Furkert, 1966; Wollast, 1967; Jones and Uehara, 1973). It seems likely that, in nature, grains of aluminosilicates including the clay minerals are frequently coated

with poorly-ordered "allophane-like" material, often too low in quantity to be determined by conventional methods of analysis. Some work was performed on synthetic aluminosilicate gels in the present study to gain insight into the possibility that these XRD-amorphous materials and coatings may be significant in trace metal cycling.

4.1.3 Organic Matter

Organic matter in estuarine sediments consists of a great variety of components (Trask, 1968). These include living biota (notable in estuaries are molluscs and worms and the ubiquitous bacteria) and recognizable fragments of undecomposed tissue such as pieces of bark or salt marsh vegetation. Johnson (1974) emphasized the importance in sediments of organic-mineral aggregates which may be formed in the fecal pellets excreted by deposit feeders. Also represented are products of organic decomposition and extracellular exudates, particularly lipids, amino acids, carbohydrates and polyphenolics such as lignin. Some fraction of these organic decomposition products undergo mineralization to form inorganic species but the remainder, notably the refractory polyphenolics, may persist in the environment for considerable time, particularly under anaerobic conditions (Richards, 1970) and where associated with fine-grained inorganic solids such as clays, and thus occur at appreciable steady state concentrations.

The largest single component of the organic matter in soils and sediments is the brown-colored, high molecular weight, polymeric, acidic material referred to by the operational name "humic" (Schnitzer and Khan, 1972; Jackson, 1975; Schnitzer and Kodama, 1977). Humic materials are largely responsible for the true color of natural waters (Christman, 1970; Gjessing, 1976) and may compose up to 50% of secondary-treated sewage effluent (Rebhun and Manka, 1971). Humics are not polymers of a single compound but are random polymers of classes of organic compounds which persist in the environment, notably aromatic (phenolic) moities but also incorporating other (less stable) types of compound such as amino acids. Because of their random polymeric structure, humics exhibit a continuous spectrum of properties. Structural

models have been proposed by Schnitzer and co-workers (Schnitzer and Khan, 1972; Schnitzer and Kodama, 1977) and the available evidence suggests that humic materials usually assume flexible rod configurations (Chen and Schnitzer, 1976; Sposito and Holtzclaw, 1977) that can function as polyacids and polyelectrolytes. The acidic functionalities on humic polymers, particularly carboxylic and phenolic groups, provide numerous sites for metal complexation (Pagenkopf, 1978). Humic materials were selected for study since they probably represent the bulk of organic metal-binding capacity in sediments, being the largest single organic component and having a greater metal-binding affinity than other classes of organic components.

Humic substances from very different environments including soils, freshwater sediments, marine sediments and fresh and saline waters, and including extremes of oxidizing and reducing conditions, are surprisingly similar in properties (Rashid and King, 1970b; Jackson, 1975; Gjessing, 1976). However, there is evidence that marine humus has a lower degree of aromaticity, less acicity and a somewhat greater content of N and S than terrestial humus (Rashid and King, 1970 a,b; Nissenbaum and Kaplan, 1972; Stuemer and Payne, 1976). These differences can be related to the somewhat different biochemical composition of marine and terrestial organisms. Estuarine humics, originating mainly from terrestial sources but modified by sedimentation in the brackish estuarine environment and comprised partly of marine contributions are likely to be intermediate in properties (Nissenbaum and Kaplan, 1972). For the purposes of the present study it was decided to obtain estuarine humic substances for study directly from estuarine sediment by base extraction rather than follow other studies (Guy *et al*, 1975; Oakley, 1980) in which commercially-available humic acids were employed.

4.1.4 Characterization of Solid Phases

Since solid phases of similar or identical chemical composition may have vastly different surface properties and, in particular, sorptive properties, it is extremely important to characterize solids by

properties other than chemical composition alone. Results of adsorption studies on phases for which the methods of isolation and/or preparation and surface properties such as surface area or crystallinity were not specified, are of doubtful reproducibility.

The solid phases prepared for adsorption studies in the present research were characterized by a variety of techniques. The most important methods used were X-ray diffraction for crystallinity, surface area measurement, chemical analysis of stoichiometric composition, extractability in ammonium oxalate and electron microscope examination. A variety of other methods were used to examine the humic extract as are discussed below.

4.2 AQUEOUS MEDIA

In this study most metal uptake experiments were performed in seawater ($35^{o}/oo$ salinity) which was regarded as a reference medium for comparative purposes. Artificial seawater prepared according to the formula of Kester *et al* (1967) was used for the bulk of the experimental work rather than natural seawater for two main reasons:

1) Biological growth and thus preservation is not so severe a problem in the artificial medium.
2) Different batches of natural seawater may well have small differences in composition whereas artificial seawater is a more reproducible medium.

One problem with artificial seawater is that the heavy metal content arising from contamination of constituent reagent salts may be greater than in natural seawater. If the heavy metal contents of the Baker reagent salts used were at the maximum levels this would amount to about 175 $\mu g.L^{-1}$ total heavy metals as lead. However, it is doubtful that even this maximum level of contamination could greatly affect partitioning of trace copper or cadmium, particularly in the linear partitioning range of interest.

Natural seawater was used for a limited number of experiments for comparative purposes. This seawater ($32^{o}/oo$, 4 $mg.L^{-1}$ organic carbon) was collected in polypropylene carboys from the Pacific coast near

Newport, Oregon, and filtered at 0.2 μm and autoclaved before being stored in sterile-vented carboys in the dark at 4°C.

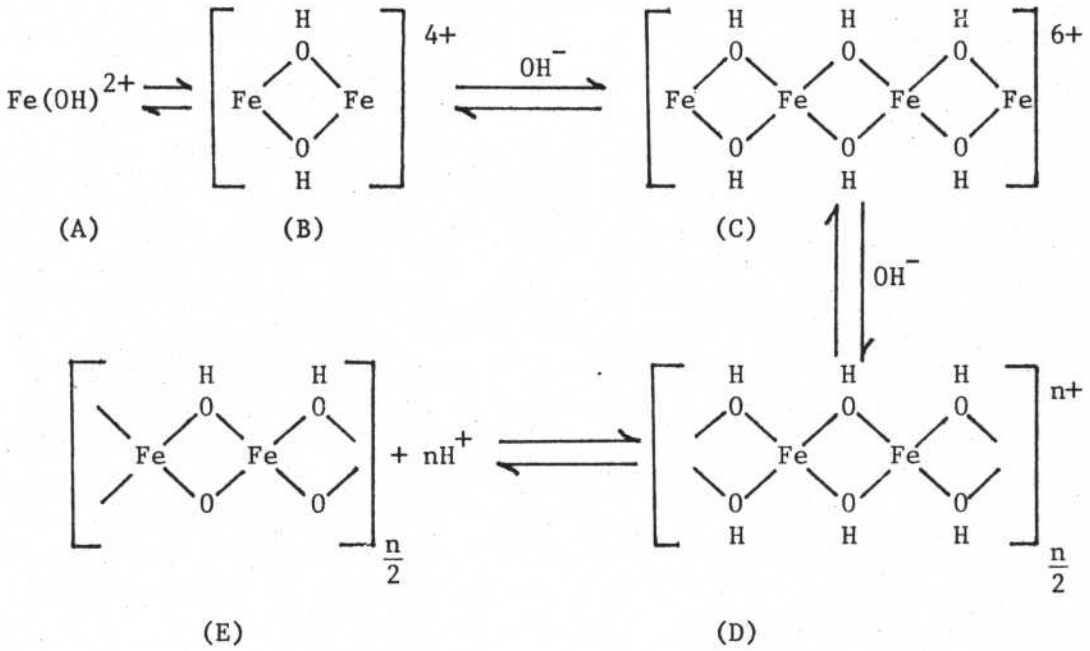
5°/oo salinity synthetic estuarine water was used as a secondary reference aqueous medium and was prepared by simply diluting artificial seawater on a mass basis with double-distilled water. Other salinities of artificial estuarine water were obtained by suitable mixing of the synthetic preparations of 0, 5 or 35 °/oo water. A few experiments were performed in sodium chloride and sodium nitrate solutions of seawater ionic strength (about 0.7 M).

4.3 IRON AND MANGANESE PHASES

4.3.1 Hydrous Iron Oxide

Ferric oxide phases used as model adsorbents are generally prepared by neutralization of Fe(III) salts. Recent studies of the hydrolysis and precipitation of ferric oxides show clearly that the products are dependent on solution conditions such as pH, temperature, ionic strength, iron concentration, identity of the anions and rate of base addition as well as aging time (Davis, 1977). Unfortunately, many workers have not specified the exact method of preparation of their hydrous ferric oxide phases.

Dousma and de Bruyn (1976) studied the rates of reaction of ferric-hydroxy species and demonstrated that formation of monomers or dimers was rapid but above a certain pH relatively slow polymerization of hydroxy species occurred. *Slow* rates of base addition (dropwise) resulted in more rapid formation of higher polymers. These polycations underwent oxolation reactions on aging accompanied by pH relaxation. The hydrolysis scheme of Dousma and de Bruyn was as follows:



Density-gradient ultracentrifugation and electron microscopy were employed by Murphy *et al* (1976 a,b,c) to characterize the ferric-hydroxy precipitates formed in solutions of different anions with a range of iron concentrations and degree of neutralization (OH^-/Fe^{3+} ratio). In the nitrate solutions studied the ferric polycations were spherical with diameters ranging from 15 - 30 A^o after three to four hours of aging. These polycations probably correlate with Dousma and de Bruyn's structure E. Aging for longer periods gave rise to the formation of short rods composed of two - five spheres. Further aging resulted in coalescence of the rods to form rafts identifiable as goethite crystallites. High ionic strength favored raft formation. Avotins (1975) found that ferric precipitates from nitrate solution had identifiable crystallinity, mainly goethite, as determined by XRD and non-extractability in ammonium oxalate, after about 15 days aging at near-neutral pH. Aging was more rapid at higher pH, apparently because goethite crystallization results in the release of protons.

On consideration of the above studies and following Davis (1977), hydrous ferric oxide precipitates for the purposes of the present study were prepared by slow neutralization of dilute Fe(III) in relatively high ionic strength (0.1 M) $NaNO_3$. The detailed procedure was

as follows:

1) A stock solution of 5×10^{-2} M Fe(III) was prepared by dissolving reagent grade iron wire in redistilled 50% nitric acid and diluting to volume. The resulting colorless solution was about 1 M in nitric acid.
2) A volumetric aliquat of the iron standard was added to a beaker and diluted about 1:9 with double-distilled water, purged with N_2 to remove CO_2.
3) Sufficient base (1 M carbonate-free NaOH) was added to raise the pH to about 3.0 whereupon the solution attained the characteristic yellow-brown color of ferric salts.
4) While the mixture was stirred continuously 0.1 M carbonate-free NaOH was added dropwise from a burette over a period of about an hour until the pH reached 8.0.
5) For the next three hours the suspension of brown-colored flocs of Fe(III) precipitate was stirred continuously and small additions of base were made to maintain the pH at 8.0 as proton release occurred during oxolation reactions.
6) After 24 hours aging the suspension was washed into the medium to be studied by successive centrifugation and siphoning of the supernatant.
7) Finally the suspension was made up to volume to give a known concentration of iron as hydrous ferric oxide.

By analogy with previous studies in which hydrous ferric oxide was prepared from nitrate solution, the precipitate resulting from the above procedure after about four hours aging probably consisted of spherical ferric-polycations of perhaps 20 A^{o} size coalesced into rafts which in turn aggregate into macroscopic flocs.

The iron suspensions were aged 24 hours before use in characterization studies. X-ray diffraction analysis revealed no crystallinity after 24 hours in concordance with the findings of Avotins (1975) and Davis (1977). The material was 100% extractable in acid ammonium oxalate reagent (Schwertmann and Taylor, 1977). The transmission

electron microscope showed the iron phase as irregular clumps of small spherical particles but revealed no signs of crystallinity. The precipitate dried at 105°C contained 54% iron by weight. By analogy with previous studies the pH(PZC) of the ferric hydroxy solid is probably around 8.0. For example, Davis (1977) measured a value of 7.9 by the salt titration method. However, the isoelectric point (IEP) in seawater may be significantly different from pH 8.0 because of specific adsorption of major ions.

The surface area was determined on a preparation of hydrous ferric oxide which had been freeze-dried after approximately 48 hours of aging and dried exhaustively in a desicator over P_2O_5. The method involved measurement of the weight of water adsorbed by samples of the dried solid in a series of desicators maintained at different relative humidities over different H_2SO_4 solutions (John Baham, Soil Science Dept., OSU, pers. comm.). A BET analysis of the data yielded a surface area of approximately 300 $m^2.g^{-1}$ which is similar to that reported by Gast *et al* (1974) for water adsorption (320 $m^2.g^{-1}$) but rather higher than the values obtained for N_2 adsorption: 257 $m^2.g^{-1}$ (Yates, 1975), 159 $m^2.g^{-1}$ (Avotins, 1975) and 182 $m^2.g^{-1}$ (Davis, 1977). Davis (1977) suggested that these BET N_2 specific surfaces are erroneously low because of porosity of the surface of freshly precipitated hydrous ferric oxide. As pointed out by Davis (1977), the size of spherical ferric polycations (about 20 A^o diameter) with a density of about 3.57 $g.cm^{-3}$ (Murphy *et al*, 1976) suggests a specific surface area of 840 $m^2.g^{-1}$, thus the water adsorption results are probably closer to the true surface area.

4.3.2 Hydrous Manganese Oxide

Poorly-ordered manganese oxides have been manufactured by a variety of methods including oxidation of Mn(II) solutions by aeration, reduction of MnO_4^- by HCl (Healy *et al*, 1966; Loganthan and Burau, 1973) and by redox reaction between MnO_4^- and Mn^{2+} under basic conditions:

$$2\ MnO_4^- + 3\ Mn^{2+} + 4\ OH^- = 5\ MnO_{2(s)} + 2\ H_2O.$$

The last method has been used by the majority of workers (Morgan and Stumm, 1964; Posselt *et al*, 1968; Murray, 1973, 1975; Lockwood and Chen, 1973; Guy *et al*, 1975, 1978; Gadde and Laitinen, 1976). The initial product is XRD amorphous but slowly attains a low degree of crystallinity resulting in a few diffuse XRD peaks. According to McKenzie (1977) the products designated δ - MnO_2 assume different microcrystalline habits in electron micrographs depending on solution conditions and method of formation. Reduction of MnO_4^- with HCl gives rise to balls of needle-shaped crystallites whereas the MnO_4^-/Mn^{2+} reaction produces thin platelets consisting of sheets of MnO_6 octahedra with 7 A^o basal spacing (this 7 A^o spacing is considered characteristic of natural birnessite but very poorly-ordered δ - MnO_2 precipitates may lack basal reflections). It is not clear whether significant differences in surface properties occur between the products of the two different reactions. In the present study δ - MnO_2 was manufactured by reaction of stoichiometric quantities of MnO_4^-, Mn^{2+} and OH^- (2:3:4) largely following the procedure of Murray (1973) who reported values for several characteristic properties of his material. The detailed procedure was as follows:

1) A solution of 2×10^{-2} M $KMnO_4$ standardized against sodium oxalate (Dawson, 1964) was added to a 250 mL beaker and stirred by magnetic stirrer.
2) A stoichiometrically equivalent quantity of standardized, carbonate-free sodium hydroxide was added from a burette.
3) An accurately measured volume of double distilled water was added such that the final volume would be 5×10^{-3} M in Mn.
4) A stoichiometric quantity of Mn^{2+} as manganous sulphate which had been standardized against the same $KMnO_4$ solution used above by the potentiometric titration method of Lingane and Karplus (1946) was added dropwise from a burette with rapid stirring over a period of an hour.

5) The suspension of dark-brown δ - MnO_2 obtained by the above procedure was aged for 24 hours before use in characterization or adsorption studies.

After the 24 hour period of standing during which time the flocs of δ - MnO_2 settled out, the supernatant solution was still very slightly pink in color (MnO_4^- color) suggesting an incomplete reaction or a non-stoichiometric reaction. Stumm and Morgan (1970) have reported that x in the MnO_x solid ranges from 1.8 to 1.95, so the latter possibility is the more likely. The stoichiometry was determined by two methods:

1) Reduction of the solid preparation with an excess of standard oxalate in acid solution and titration of excess oxalate with $KMnO_4$ standardized with the same oxalate solution.
2) Titration of the iodine released by the solid from an excess of iodine solution with standard sodium thiosulphate.

Method (1) gave $x = 1.96 \pm 0.01$ and method (2) gave $x = 1.97 \pm 0.01$, both results being slightly higher than the range reported by Stumm and Morgan (1970) and higher than $x = 1.92$ as measured by Murray (1973).

The δ - MnO_2 solid was totally extractable in acid ammonium oxalate and X-ray diffractograms lacked definite reflections indicating a low degree of ordering as reported by other workers. Considerable variability in reported values of the pH(PZC) for δ - MnO_2 occurs in the literature (Murray, 1973), however, while the pH(PZC) was not measured in the present study it is probably very low (approximately 2.0).

The surface area of a freeze-dried sample of MnO_x (72 hours aging) was $250 \pm 30\ m^2.g^{-1}$ (using the BET water sorption method of Baham pers. comm.). This compares favorably with results reported by Loganthan and Burau (1973) for BET-N_2 ($160\ m^2.g^{-1}$) and glycol retention ($350\ m^2.g^{-1}$) methods and a BET-N_2 value of $263 \pm 5\ m^2.g^{-1}$ reported by Murray (1973).

4.4 ALUMINOSILICATES

4.4.1 Montmorillonite

A 500 g sample of the Clay Mineral Society (CMS) source clay: Wyoming Montmorillonite, SWy-1 was obtained from the CMS curator (van Olphen and Fripiat, 1979). This clay has been a favorite for a great variety of studies and has been rather well characterized. Table 4.1 gives some data selected from the CMS summaries reported by van Olphen and Fripiat (1979).

The montmorillonite was prepared for use in metal uptake studies following typical procedures, for example, Posner and Quirk (1964). The clay was initially washed in 1 M NaCl with the pH repeatedly adjusted to 3.0 with HCl until it remained at this value for more than half an hour. This procedure is considered to remove "exchangeable" aluminum without unduly damaging the clay lattice structure. The clay was then washed in 1 M NaCl a further three times to convert it completely to the sodium form. Excess salt was removed by exhaustive dialysis against distilled water until no chloride was detectable in the dialysate. A 2% suspension in double distilled water was then prepared and the < 2 μm equivalent spherical diameter (< 2 μm esd) fraction separated from coarser material including quartz and some other contaminants by successive sedimentation and redispersion. The supernatants were combined and coagulated with sodium chloride thus permitting concentration by centrifugation.

A commercial reagent clay, Fisher bentonite, laboratory reagent grade, was also used for comparison with previous work (Oakley *et al*, 1980). This material was not fractionated in any way but was simply washed into the medium to be studied. Table 4.1(b) gives some data obtained from the suppliers. In spite of the very similar chemical analysis of the two clays their appearance was quite different. The Fisher clay was grey in color compared with the pale cream-yellow of the Wyoming montmorillonite and contained a substantial proportion of coarse aggregates which were not easily dispersed.

Table 4.1

CLAY DATA SUMMARY

(a) WYOMING MONTMORILLONITE, SWy-1,

(Data Summary modified after van Olphen and Fripiat, 1979)

Chemical Composition (%):	SiO_2	62.9
	Al_2O_3	19.6
	Fe_2O_3	3.35
	FeO	0.32
	MnO	0.006
	MgO	3.05
	CaO	1.68
	Na_2O	1.53
	K_2O	0.53
Loss on Heating:	-550°C : 1.59% 550 - 1000°C : 4.47%	
Cation Exchange Capacity:	76.4 meq per 100 g	
Surface Area (N_2 BET analysis):	$31.82 \pm 0.22\ m^2.g^{-1}$	
Thermal Characteristics (DTA):	endotherms:	185°C (shoulder at 235°C) (desorption of water) 755°C (dehydroxylation)
	exotherm:	980°C
Infrared Spectrum:	typical for Wyoming bentonite with moderate Fe^{3+} content, quartz and carbonate detectable	

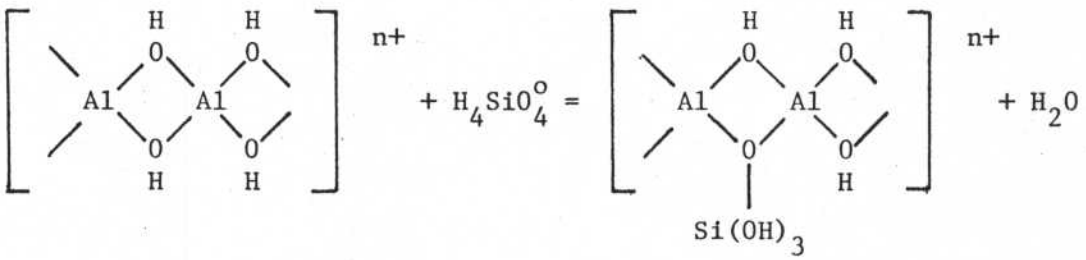
(b) FISHER REAGENT BENTONITE

(G. L. Pillori, Fisher Scientific Company, pers. comm., 1980)

Chemical Composition (%):	SiO_2	63.02
	Al_2O_3	21.08
	Fe_2O_3	3.25
	FeO	0.35
	MgO	2.67
	CaO	0.65
	Na + K	2.57 (as Na_2O)

4.4.2 Synthetic Aluminosilicate Gels

There has been renewed interest recently in the laboratory synthesis of clay minerals and of poorly-ordered precursors of clay minerals. The method of synthesis in the present study was similar to that of Hem *et al* (1973), Luciak and Huang (1974) and Wada and Kubo (1975). These workers were apparently unaware of each others contribution. Hem *et al* (1973) studied the effects on aluminum solubility of silica in concentrations ranging from 0 - 3 x 10^{-3} M (the latter value being equivalent to a concentration slightly greater than saturation with respect to amorphous silica at about 100 - 200 mg.L^{-1}. Aluminum activities were lower than predicted from $Al(OH)_3$ solubility in the presence of silica because of the formation of aluminosilicates of approximately 1:1 Si:Al molar ratio. Initially the solids formed in these systems lacked long-range order but after extended periods of aging (months or years) ordering of some of the material was detectable under the electron microscope. Tubular particles similar to halloysite and even some psuedo-hexagonal plates of 1:1 layer clays were recognized (Hem and Lind, 1974). Luciak and Huang (1974) studied the hydrolysis of aluminum as a function of Si:Al ratio. In the absence of silica, crystalline $Al(OH)_3$ was present but XRD-amorphous precipitates were produced when $H_4SiO_4^o$ was present, particularly when hydrolysis was complete. The mechanism of coprecipitation was considered to involve condensation reactions of the type:



at hydroxyl bridges. Similar reactions could also occur at the edges of hydroxy-aluminum cations. In a similar study Wada and Kubo (1975) also formed amorphous aluminosilicates and found that their materials coagulated most severely around pH 6 - 8, depending on the SiO_2/Al_2O_3

ratio. Wada and Kubo suggested that although synthetic co-precipitated alumina-silica gels are apparently similar to natural allophanes (with regard to IR spectrum, electron microscope morphology, cation exchange capacity, SiO_2/Al_2O_3 ratio, pH_{PZC}) caution should be exercised in attempting to use such materials as models of allophane.

For the purposes of the present study a synthetic aluminosilicate was prepared as follows:

1) A 5×10^{-2} M $Al(NO_3)_3$ solution in 0.1 M HNO_3 and a solution of 2×10^{-2} M Na_2SiO_3 in double-distilled water were prepared.
2) The aluminum solution was added to a large glass reagent jar and distilled water was added to dilute the aluminum to about 3×10^{-3} M.
3) Sufficient silicate solution was then added to give a 1:1 Si:Al ratio. The pH of the resulting clear mixture was about 2.3.
4) 5 M carbonate-free NaOH was added with continuous magnetic stirring to bring the pH to about 3.5. At this point the solution was still clear.
5) 1 M carbonate-free NaOH was added dropwise from a burette over a period of one hour to bring the pH to 7.0. Incipient turbidity was noticed at about pH 4.5 and the solution was considerably turbid with small white flocs at pH 7.0.
6) The suspension was stirred continuously for 24 hours then the pH, which had relaxed to about 6.3, was readjusted with NaOH to 7.0.
7) The suspension was transferred to polypropylene jugs and aged for one month with intermittent agitation before characterization studies and use in metal uptake experiments.

The product resulting from the above procedure was an amorphous (to XRD) ammonium oxalate - extractable white-colored gel. The Si:Al molar ratio of the solid was 0.83:1. Surface area was not measured but would be expected to be high. Thermal analysis of the aluminosilicate

gave the following water contents at three different temperatures:

Temperature	105°C	600°C	1000°C
% of weight accountable as $Al_2O_3 + SiO_2$	75	95	100
% H_2O	25	5	0

4.5 HUMIC SUBSTANCES

4.5.1 Extraction of Humic Material

A sample of estuarine sediment was obtained at low tide from Sally's Bend tidal flat in Yaquina Bay on the Oregon coast (Figure 4.1). The upper 20 cm of sediment was transported in an ice chest to the laboratory where it was stored at 4°C for two days before commencement of extraction. Field examination of the sample showed it to be a muddy sand of low bulk density (sediment taken at the sample site in a 60 cm core of five cm in diameter was compacted to only 34 cm in length by friction on the core sides). Except for a narrow brown-colored mud layer at the surface the sediment was dark grey in color. Some characteristics of the sediment are listed in Table 4.2(a) and Figure 4.2 shows a flow diagram of the extraction, concentration and purification of humic materials from the sediment.

Methods used to extract humic materials were a synthesis of those used by other workers (Rashid and King, 1969, Schnitzer and Khan, 1972; Davis, 1980). Calcium carbonate is known to interfere with alkaline extraction of humic materials (Schnitzer and Khan, 1972) so it was considered desirable to remove shell debris and any other $CaCO_3$ present in the sediment. A two Kg (wet) portion of sediment was transformed to a ten L glass carboy after manual removal of large shell fragments. Six L of double distilled water was added and adjusted to pH 3.5. The slurry was stirred continuously with a polyethylene paddle. A strong smell of H_2S was noted. After 24 hours the pH was adjusted to 2.0 for a further 24 hour digestion by which time bubbling had ceased entirely. The acid digestion resulted in less than 1% loss of organic carbon in the discarded supernatant.

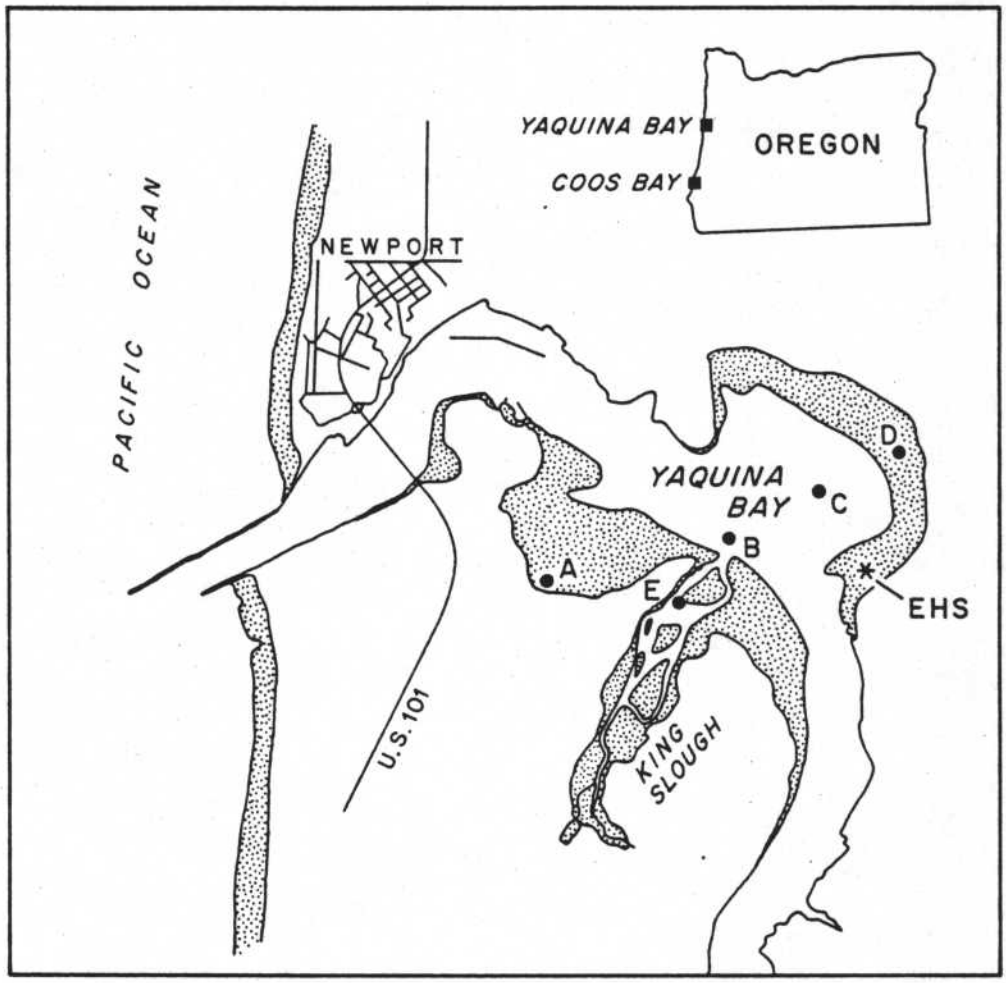


Figure 4.1. Yaquina Bay, Oregon, Showing the Locations of the Sediment Sample Used for Extraction of Estuarine Humic Substances (EHS) and Samples for Measuring Sediment Uptake of Cadmium.

Table 4.2(a)

CHARACTERISTICS OF ESTUARINE SEDIMENT USED FOR EXTRACTION OF HUMIC SUBSTANCES

* Volatile Solids (400°C, 6 hr):		2.55%
Percent Sand : Silt : Clay		61 : 37 : 2
Median Grain Size		0.098 mm
‡ Sulphide Capacity ($g.Kg^{-1}$)		179
Iron		1.16%
Other Metals (ppm)	Mn	43
	Cd	1.2
	Cu	6.6
	Zn	44.6
	Pb	9.4

NOTES:

* Performed at 400°C (six hours) instead of the more common ignition at 550 or 600°C to reduce error due to weight loss on dehydroxylation of clays (Luoma and Bryan, 1981).

‡ The capacity of a sediment to take up free sulphides (Williamson and Bella, 1975).

Table 4.2(b)

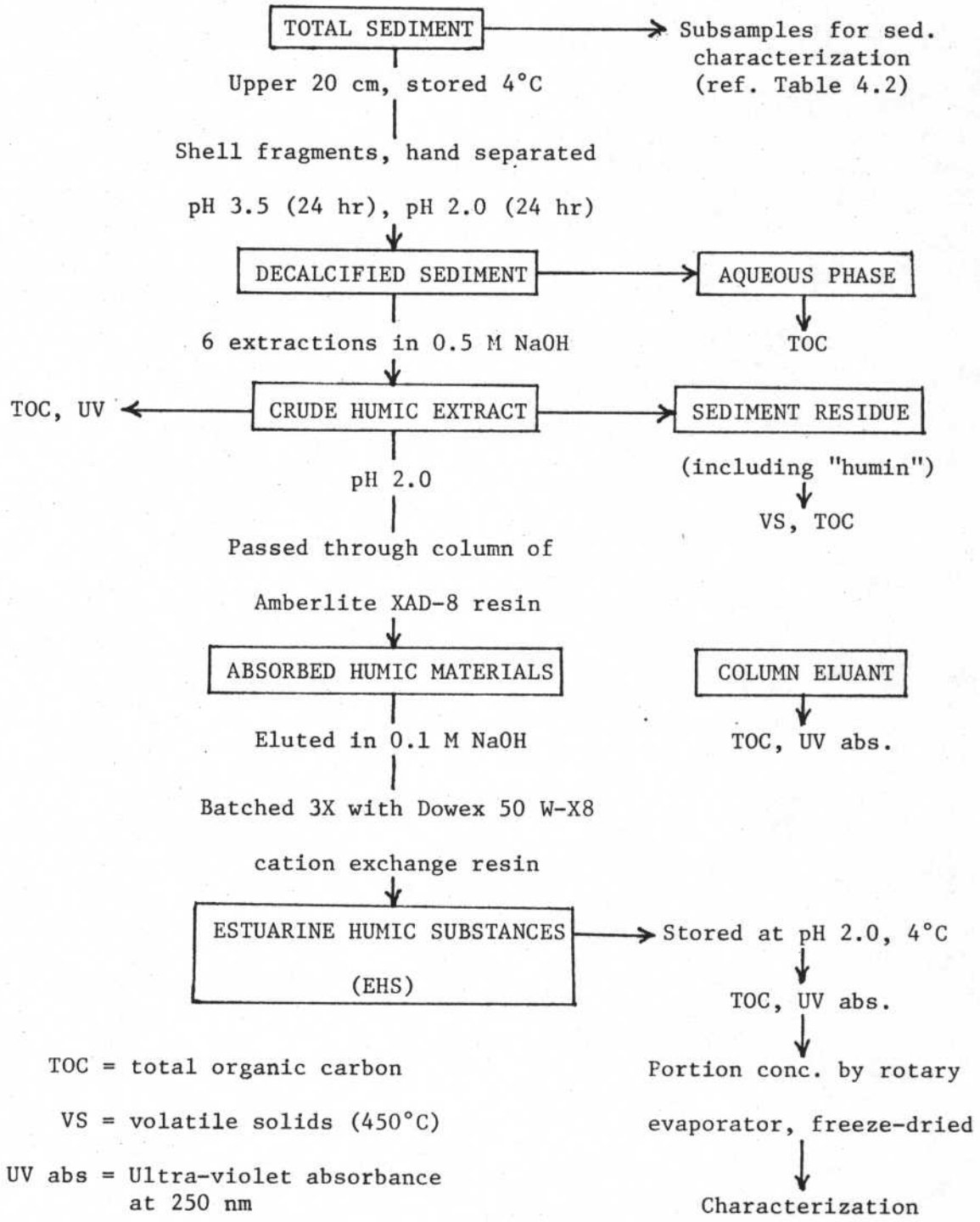
CHEMICAL ANALYSIS OF ESTUARINE HUMIC SUBSTANCES (EHS)

% "Fulvic" Fraction (pH 2.0, 24 hr):		42% (of TOC)
Total Ash:		5%
Major Components (%):	Carbon	49
	SiO_2	2.90
	Aluminum	0.36
	Iron	0.15
	(oxygen and hydrogen not determined)	
Minor Components (ppm)	Manganese*	< 2.0
	Copper	25
	Cadmium*	< 5

(* maxima represent the highest value in triplicate analyses rather than detection limit in AA method)

Figure 4.2

FLOW DIAGRAM FOR EXTRACTION AND PURIFICATION OF ESTUARINE HUMIC SUBSTANCES



TOC = total organic carbon

VS = volatile solids (450°C)

UV abs = Ultra-violet absorbance at 250 nm

The carbonate-free sediment was then transferred to a polyethylene carboy and digested with continuous stirring in 0.5 N NaOH under a nitrogen atmosphere (to prevent auto-oxidation of the humic material). Six successive 24 hour extractions were carried out. After each extraction the supernatant was centrifuged to separate suspended sediment (which was reintroduced to the extraction vessel) from the NaOH solution containing extracted humic material. The final (6th) extraction was markedly less colored than the first and had a much lower organic carbon content. The combined crude extractant contained 48% of the sediment organic carbon.

4.5.2 Concentration and Purification of the Extract

Recently macroreticular resins (Amberlite XAD-2, XAD-7, XAD-8 Rohm and Haas Co., Philadelphia) have been used to concentrate organic material from large quantities of water (Mantoura and Riley, 1975a; Stuemer and Harvey, 1977; Davis, 1980). Davis (1980) suggested that Amberlite XAD-8, an acrylic ester (methylmethacrylate) polymer, may be more efficient than XAD-2 for concentrating substances of intermediate polarity because of its ester crosslinkage. Recent papers (Thurman *et al*, 1978; Farrier *et al*, 1979) have examined the adsorption of "model" organic solutes on Amberlite XAD-8. The interactions of organics with macroreticular resins appear to be weak van der Waals or hydrophobic bonding with favorable entropy changes (Mantoura and Riley, 1975a). Since inorganic ions and hydrophilic organics pass the column the use of Amberlite XAD-8 also serves to purify the extract (Davis, 1980).

Before use raw Amberlite XAD-8 resin was cleaned by successive 24 hour Soxhlet extractions with acetone, n-hexane and methanol. Following procedures given by Rohm and Haas (1978, 1979) the 20 - 50 mesh beads were slurry-packed into glass gel chromatography columns (50 cm x 2.7 cm I.D.) and washed with ten bed volumes each of 0.1 M NaOH and 0.01 M HCl. The crude humic extract was acidified to pH 2.0 and passed from a mariotte bottle through the columns at about 30 bed volumes per hour. The UV absorbance at 250 nm was used to monitor the

eluant and prevent breakthrough. The column removed more than 95% of the absorbance at 250 nm but only 60% of the organic carbon suggesting that UV-absorbing materials were selectively retained. A maximum of ten mg carbon per gram of resin was passed before column regeneration to prevent drop in adsorption efficiency (Mantoura and Riley, 1975a). Columns were then eluted with three bed volumes of 0.1 M NaOH with the second bed volume left to stand overnight (compare Davis, 1980). The purified material was stored under nitrogen at 4°C.

The above purification procedure was sufficient to reduce the ash content of a freeze-dried sample which had been batched three times with Dowex 50 W-X8 cation exchange resin (H^+ form) to remove sodium and concentrated in a rotary evaporator at 35°C (Malcolm, 1968, 1976) to less than 5%. While this ash content is not as low as might be desired (Malcolm, 1976) it is satisfactory given that a large amount of amorphous or poorly-crystallized material in the sediment may have been extracted by the strong base.

4.5.3 Characterization of the Humic Material

The purified humic extract, henceforth referred to as Estuarine Humic Substances (EHS), was characterized in an attempt to increase the comparative value of metal uptake studies with this material. Table 4.2(b) presents some analyses for elemental composition of the EHS. The carbon content is about as expected for a combined extract, containing effectively both "humic" and "fulvic" fractions (Schnitzer and Khan, 1972). The metal content of the purified material was low (results are similar to those of Gaskill *et al*, 1977). Evidently the acidification to pH 2.0 resulted in solubilization of all but very strongly bound metals. Thus iron, aluminum and copper, which are known to be strongly complexed by humics (Schnitzer and Khan, 1972) were present in measurable but low quantities, similar to those found by Knezevic and Chen (1977) for estuarine humic extracts. Batching the EHS with Chelex-100, a metal chelating resin which workers such as Holtzclaw *et al* (1976) have used to purify humic extracts, apparently did not reduce the iron or copper content, again indicating that

these metals are bound very strongly by the humic material, possibly in sterically-hindered sites. For all intents and purposes the metals must be considered an integral part of the EHS structure rather than labile complexes.

The UV and visible absorbance spectra of the EHS, run on a Heath modular recording spectrophotometer, are presented in Figure 4.3. The EHS was diluted with 0.05 M $NaHCO_3$ (which buffers the pH at around 8.0, Chen *et al*, 1977) to a final concentration of 23 mg-C.L^{-1} for the UV spectrum and 190 mg-C.L^{-1} for the visible spectrum. The whole spectrum in the wavelength range: 230 - 750 nm is featureless, often cited as a characteristic of humic materials (Schnitzer and Khan, 1972). The absorbance (one cm cell), and thus the extinction coefficient on a mass basis, falls continuously in a smooth curve with no evidence of maxima or minima. This is evidence both that the EHS represents a continuous spectrum of electronic structures (and thus molecular structures) rather than a mixture of discrete chemical species and that (colored) contamination is relatively slight. The so-called E_4/E_6 ratio (ratio of absorbance at 465 nm to that at 665 nm, Chen *et al*, 1977) was about 4.9 suggesting moderately high average molecular weight.

Figure 4.4 shows an IR spectrum run on a KBr pellet of a freeze-dried sample of the EHS in the 4000 - 400 cm^{-1} wavenumber range on a Perkin-Elmer 727B IR spectrophotometer. Assignments of the bands in the spectrum are given where these can be made with reasonable confidence. The general pattern of the spectrum is typical of those reported for humic substances (Schnitzer and Khan, 1972; Vinkler *et al*, 1976). The bands are generally not sharp suggesting a range of chemical environments of the various absorbing groups which results in a dispersion of resonant frequencies. This again is evidence for the random polymer nature of the EHS extract. A band at 1020 cm^{-1} is probably attributable to the SiO_2 impurity which is the main contributor to the ash content of the EHS extract.

The molecular weight distribution of the EHS was investigated using ultrafiltration in an experiment similar to those of Gjessing (1970), Ogura (1974) and MacFarlane (1978). Briefly, the EHS was

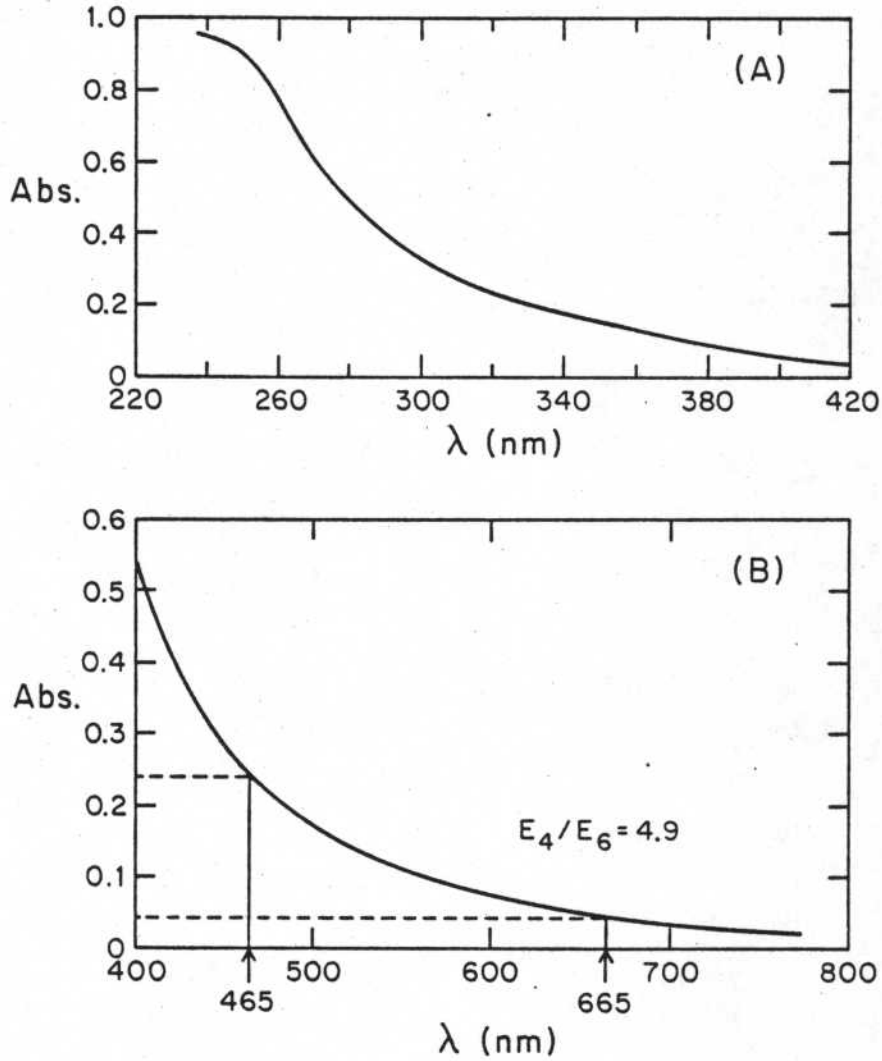
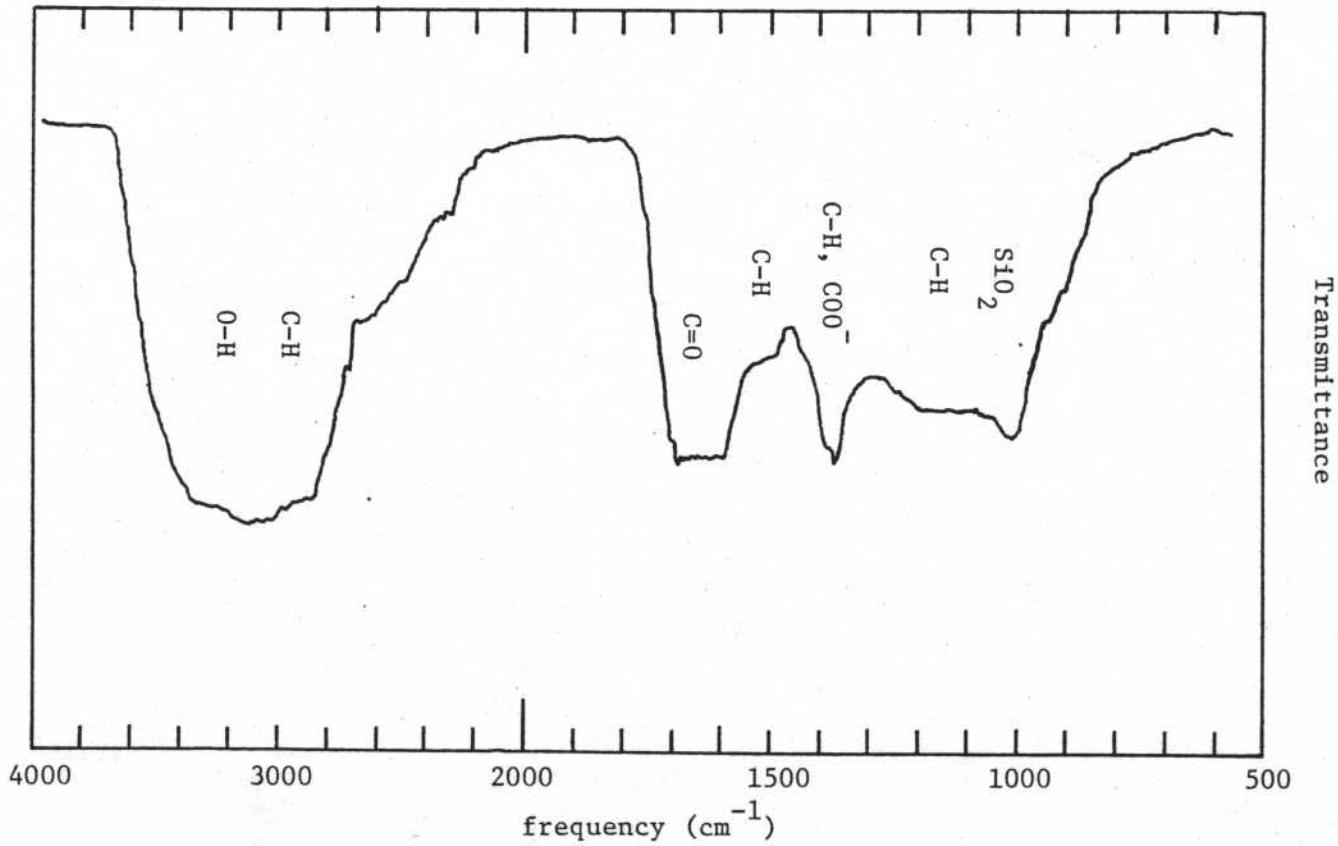


Figure 4.3. Near U.V. and Visible Absorbance Spectra of EHS. (A) Spectrum of 23 mg-C.L^{-1} EHS, (B) Spectrum of 190 mg-C.L^{-1} EHS, both in $NaHCO_3$ Solution.

Figure 4.4 Infrared Spectrum of EHS.



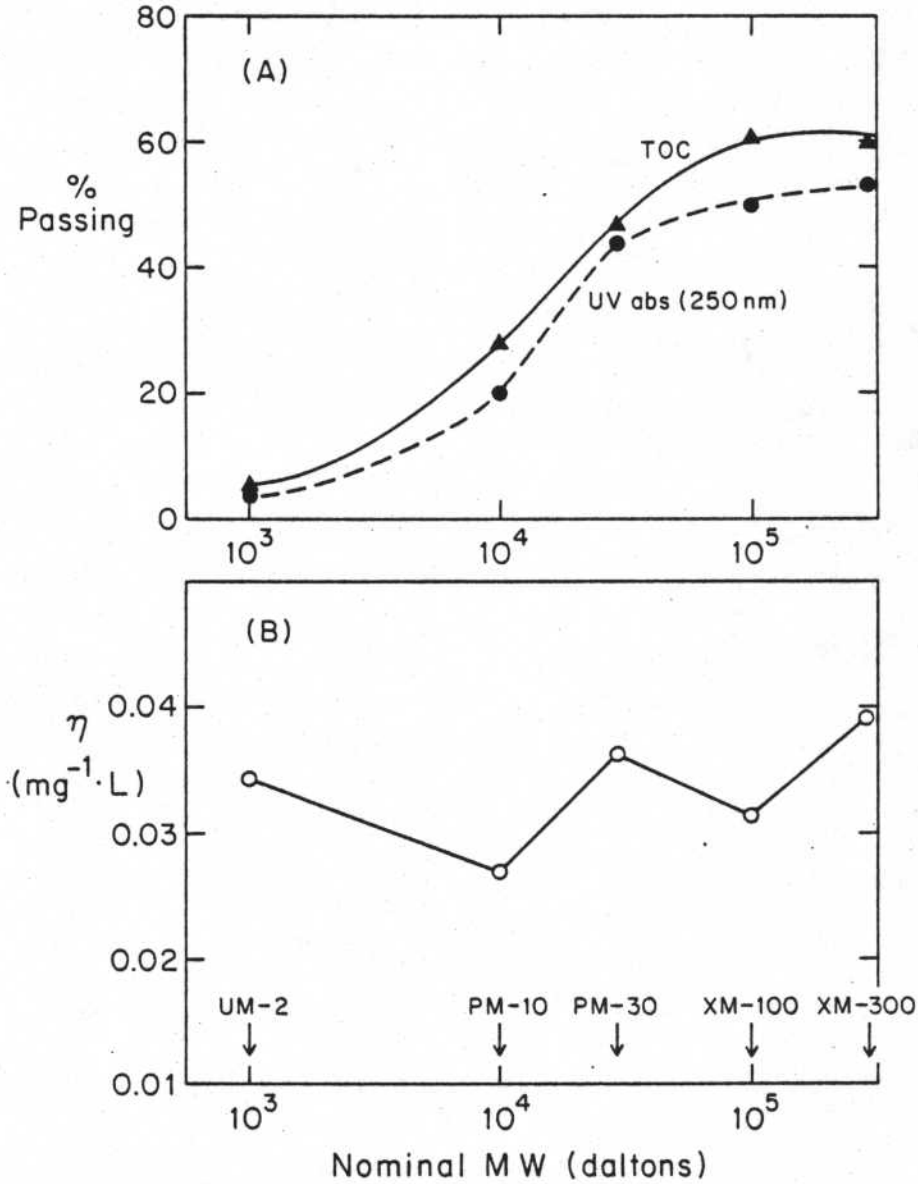


Figure 4.5. Nominal Molecular Weight Distribution of EHS by Sequential Ultrafiltration. (a) Molecular Weight Distribution of TOC and UV abs. (b) Extinction Coefficient, UV abs./TOC, as a Function of Molecular Weight.

passed through ultrafilters of five successively decreasing molecular weight cutoff values in a Model 12 Amicon stirred cell. At each ultrafiltration step the first 1.5 mL of a total of ten mL passing were discarded, the next seven mL were collected, about one mL being used for preparation of samples for UV absorbance and TOC measurement while five mL were made up to ten mL volume in 0.1 M $NaHCO_3$ buffer for the succeeding ultrafiltration step, and the remaining 1.5 mL also discarded. The "ultrafiltration" actually works by the gel exclusion principle (Amicon Corporation, 1978), thus the separation occurs over a considerable range of molecular weights and the resulting fractionation must be considered operational rather than a true molecular weight distribution.

Figure 4.5 shows the nominal molecular weight distribution of both organic carbon and UV absorbance in the EHS. Evidently much of the material is of considerable molecular weight, 50% being (nominally) above about 30,000 - 100,000 daltons. The close parallel of the organic carbon and UV absorbance distributions suggests that there is little if any significant change in extinction coefficient at 250 nm with molecular weight, thus absorbance at this wavelength can be used as a convenient and rapid monitor for EHS even where molecular size fractionation occurs (as with centrifugation, dialysis or chemical reaction).

5. STUDIES ON ISOLATED MODEL SEDIMENT PHASES

This chapter reports the results of metal uptake studies on simple two-phase systems consisting of an aqueous solution phase and a single solid phase adsorbent. The main purpose of these experiments was central to the research: to quantify the affinity of cadmium and copper for different model phases under the conditions pertaining in estuaries and thus provide suitable data for modelling the partitioning of metals in real estuarine sediments. The experiments were also designed with a number of subsidiary purposes in mind:

1) To verify that the kinetics of metal uptake are rapid such that an equilibrium model is valid.
2) To examine the effects of solution conditions, particularly salinity, pH and temperature, on metal uptake.
3) To provide a basis for examining the effects of interaction of two or more phases, as may occur in real sediments, on metal uptake.
4) To determine the range of linear partitioning of the metals, that is, the range of validity of the model development in Chapter 3.

5.1 ADSORPTION STUDIES

5.1.1 Tracer Methods

To facilitate analysis of the metal partitioning at the "environmental" concentrations of copper or cadmium employed in this study the gamma-emitting isotopes Cu-64 and Cd-109 were used as tracers. A number of advantages favoring the use of radiotracers over "conventional" methods of metal assay such as flameless atomic adsorption spectroscopy (FAAS) and anodic stripping voltametry (ASV) in adsorption studies can be identified:

1) It is possible to routinely trace very low levels of metals with high precision where even the most sensitive instrumental methods may require complex concentration and/or extraction procedures.
2) It is possible to obtain a mass balance on the total metal partitioned between the solid and liquid phase in a straightforward manner.
3) Use of radiotracers avoids the need for chemical blank corrections. All that is required is a background count correction.
4) If the metal is already present in the system as a contaminant *before* addition of the adsorbate metal, no correction is required since this does not affect the tracer activity or the partitioning of the tracer.
5) The assay can be made as precise as desired by simply increasing the counting time since the relative error is proportional to $N^{-1/2}$ where N is the count.
6) With the use of an automatic counter the samples can be processed in the absence of an operator.

Against these advantages of radiotracers must be set some disadvantages, particularly the complications in procedure arising from the necessity for safety precautions and the inevitable generation of radioactive waste.

Cadmium-109 (halflife, $T_{1/2}$, 453 days) was obtained carrier-free in dilute hydrochloric acid from ICN, Irvine, California and simply spiked into standards prepared in seawater from atomic adsorption ultimate standards. Copper-64 ($T_{1/2}$ = 12.8 hours) was made by irradiation for two Megawatt-hours ($2.2 \times 10^{16} n^{o}. cm^{-2}$) of 50 μg samples of copper in dilute nitric acid in Oregon State University's TRIGA nuclear reactor. The irradiated sample provided the total quota of copper for preparation of standards except at the very highest concentrations used.

5.1.2 Adsorption Experiments

Initially the solids prepared as described in Chapter 4 were washed exhaustively into the appropriate aqueous media. In the case of inorganic solids the washing was carried out with successive centrifugation and redispersion with a motor-driven rubber policeman or mild ultrasonication (20 Htz, 100 watts). Montmorillonite and the synthetic aluminosilicate gel were not exposed to ultrasonication since it was considered that this treatment might cause irreversible damage to these phases. A proportion of the humic material (EHS) forms a stable sol thus centrifugation, and even ultracentrifugation (Oakley, pers. comm.), is inadequate for separation of this material from water and special methods were required to introduce the material into seawater. Briefly this involved dissolving an accurately-weighed portion of purified, freeze-dried EHS in standard 0.2 M NaOH with shaking under an N_2 atmosphere then neutralizing with standard 0.2 M HCl and adding reagent salts to the resulting suspension/solution to give the composition of artificial seawater according to the formula of Kester *et al* (1967).

The washed suspension obtained in each case was made up to volume to give the desired concentration of solid determined on the basis of preliminary experiments. The suspension was then dispensed into a beaker and stirred continuously for over an hour with a magnetic stirrer. After this time five mL (in experiments with cadmium) or 25 mL (in experiments with copper) were added to each of a labelled series of 10 or 50 mL polypropylene Oak-Ridge type centrifuge tubes which were used as reaction vessels. The pH of the suspension was checked then microlitre quantities of 0.1 M or 1 M NaOH or HCl were added to the reaction tubes to obtain a range of initial pH values (usually between 6.0 and 8.5). The acid or base additions were determined by trial-and-error or from approximate titration curves for the solid suspensions and in no case resulted in more than 0.5% volume change. Two mL of cadmium working standard spiked with Cd-109 or ten mL of copper working standard labelled with Cu-64 were added to each tube. The reaction tubes were then capped, loaded into a test tube

rack and shaken in a horizontal position in a constant temperature room or thermostatted shaker bath.

The final total metal concentration in the tubes was usually in the range 2.8 - 140 $\mu g.L^{-1}$. A calculation using thermodynamic data in Stumm and Morgan (1970) showed that the minimum solubility over the pH range studied for tenorite, CuO (an oxide phase which would be much more stable than any fresh precipitate formed in the reaction vessels) is about 60 $\mu g.L^{-1}$ (at pH 8.5) thus it seems unlikely that precipitation of copper could have occurred in any of the experiments.

After equilibration the pH in the reaction tubes was measured with a Corning semimicro combination electrode connected to an Orion 701A meter. Each of the tubes were then stirred with a vortex mixer and immediately a two mL (cadmium) or ten mL (copper) subsample was taken with an A grade volumetric pipette and dispensed into a labelled disposable counting vial for assay of total tracer activity.

To quantitate the partitioning of a metal between solid and solution phases it is necessary to physically separate the two phases. In the present study centrifugation was adopted for the inorganic solids. Twenty minutes spinning on an IEC B20 centrifuge (870 angle head) at 12,000 RPM (10,000 g at the top of the liquid level and 20,000 g at the bottom of the tubes) was sufficient to remove any detectable Tyndall beam effect and iron and manganese in the supernatant were never more than 0.5% of total iron or manganese (as determined by AAS). A small subsample of the supernatant (the same volume as taken for total activity) was taken by volumetric pipette and dispensed into counting tubes for measurement of solution phase activity. The supernatant was subsampled within five minutes of centrifuging with the utmost care taken not to disturb the centrifuge plug.

The samples for measurement of solution phase activity were then treated identically to the samples for total activity before both sets of vials were counted in a Picker Autowell II gamma counter. The fractional adsorption, f, was expressed as the ratio: $(N_T - N_S)/N_T$ where N_T is the total activity and N_S is the solution phase activity, both counts being corrected for background. The estimation of f from the ratio of two quantities measured under essentially identical

conditions is preferable to the more usual practice in adsorption studies in which only the solution phase metal is analyzed and the bound metal is calculated from a mass balance on the total metal added to the system. In particular, measurement of both solution phase and total metal automatically compensates for losses of metal by sorption on container walls.

5.1.3 Discussion of the Methodology

Some further explanation of the methodology outlined above is warranted. Equilibration time was generally set at 20 hours (overnight) for cadmium, since preliminary kinetic experiments and previous work under similar conditions (Oakley, 1980) showed that the metal uptake reactions go to completion in less than this time. For copper the short half life (12.8 hours) of the tracer and the low specific activities necessitated use of a shorter incubation time and six hours was adopted. In preliminary experiments with iron no significant difference between six hour and 20 hour incubations was observed. Many other workers have reported that the kinetics of adsorption/complexation are rapid and shorter incubation periods have generally been used, often to minimize the losses to uptake on container walls. For example, Davis (1977) and Benjamin (1978) used a four hour time. However, in some systems slow metal uptake may continue for a matter of weeks. This effect is particularly significant in the case of Hg(II) sorption by hydrous ferric oxides (MacNaughton, 1973; Avotins, 1975). Avotins suggested that the slow long-term uptake, which amounted to about twice the apparent short-term mercury uptake capacity, could be accounted for by a model in which Hg migrates to interior binding sites by solid state diffusion. Similar long-term effects have been reported for adsorption of Co and Zn by δ - MnO_2 (Loganthan and Burau, 1973) and Ag, Cu and Cd on hydrous iron oxide (Davis, 1977; Benjamin, 1978).

Small volumes (seven mL in ten mL centrifuge tubes) were utilized in cadmium adsorption studies for several reasons:

1) To minimize the generation of radioactive waste.
2) To minimize consumption of prepared solid phases, particularly the EHS.
3) For reasons of space, more small-sized tubes could be handled in the confined space of a dedicated fume hood and more tubes could be loaded on the shakers.

Larger volumes (35 mL in 50 mL tubes) were employed for copper experiments. Specific activities of Cu-64 were rather low thus, particularly at the lower levels of copper studied, insufficient counts for good counting statistics could have been accumulated in reasonable counting times using smaller volumes.

Both plastic and glass containers have been used in previous studies of adsorption. There may be no inherent advantage of one material over another with regard to metal uptake by container walls, indeed Robertson (1968) found that both glass and plastic (polythene) significantly adsorbed trace metals and other trace constituents from seawater at pH 8 over a period of ten to 50 days. As to other properties the greater clarity and chemical resistance of glass must be offset against its fragility relative to plastics. In the present study plastic (polypropylene) tubes were used as reaction vessels primarily because routine handling of radioactive materials required robust containers and leakproof closures.

The solids concentrations used in the adsorption experiments were selected on the basis of preliminary experiments to give fractional adsorption in the pH range of interest (6.5 - 8.5) between five and 95%. High levels of adsorption (greater than 95%) give rise to imprecise estimates of f since the relative error in N_T is large in this case (since solution activity is low). Low levels of adsorption (less than 5%) also give poor estimates since this quantity depends on the difference between N_T and N_S which, in this case, are nearly equal quantities. N_S was generally greater than 3000 counts at a total count to background ratio of about five giving a maximum relative error in N_S (using the nomograph of Wang *et al*, 1975, p304) of 3%. Usually 15,000 counts or more were accumulated for the estimate of N_T resulting in a counting error which was negligible compared with other sources of variability such as volumetric errors.

5.2 HYDROUS OXIDES OF IRON AND MANGANESE

5.2.1 Cadmium Adsorption by Hydrous Iron Oxide

Preliminary investigations and the literature review (Chapter 2) suggested that iron may be the most important sink for cadmium and other metals in oxidized estuarine sediments. Thus more attention was devoted to adsorption studies with iron than with other solid phases.

Figure 5.1 shows a plot of fractional adsorption, f, against pH for Cd-109 labelled cadmium on synthetic ferrihydrite (freshly prepared hydrous iron oxide) in artificial seawater medium. Data from this and other experiments to be considered below are given in the appendices. The adsorption edge in Figure 5.1 has the characteristic S-shape (Leckie and James, 1974) and is quite steep, rising from 10% to 90% adsorption in only two pH units. The data for nearly two orders of magnitude range in concentration of cadmium apparently fall on the same line suggesting *linear partitioning* of the metal between solid and solution phases. Figure 5.2 shows isotherms at constant pH obtained by interpolation of the data from Figure 5.1. These isotherms are linear over most of the range studied although there is incipient non-linearity at the highest concentrations. The slopes of the linear portions of the isotherms provide estimates of K_p, the linear partitioning coefficient.

Figure 5.3 shows the same data as used in Figure 5.1 replotted as $\log K_p(pH)$ where $\log K_p$ is given (Chapter 3):

$$\log K_p = \log {}^{c}K_{ads} + \log \alpha_o + xpH \qquad (5.1)$$

The data appear to fall on a straight line as expected from (5.1), since $\log \alpha_o(pH)$ is almost independent of pH for cadmium over the range studied (Chapter 3). Since this type of plot is expected to linearize all cadmium adsorption data and in the absence of a good estimate of $\log \alpha_o(pH)$ for copper (Chapter 3) this form of presentation will be used throughout the remainder of this work.

The slope of the line in Figure 5.3 is approximately unity suggesting that *apparently* one proton is released for every cadmium atom

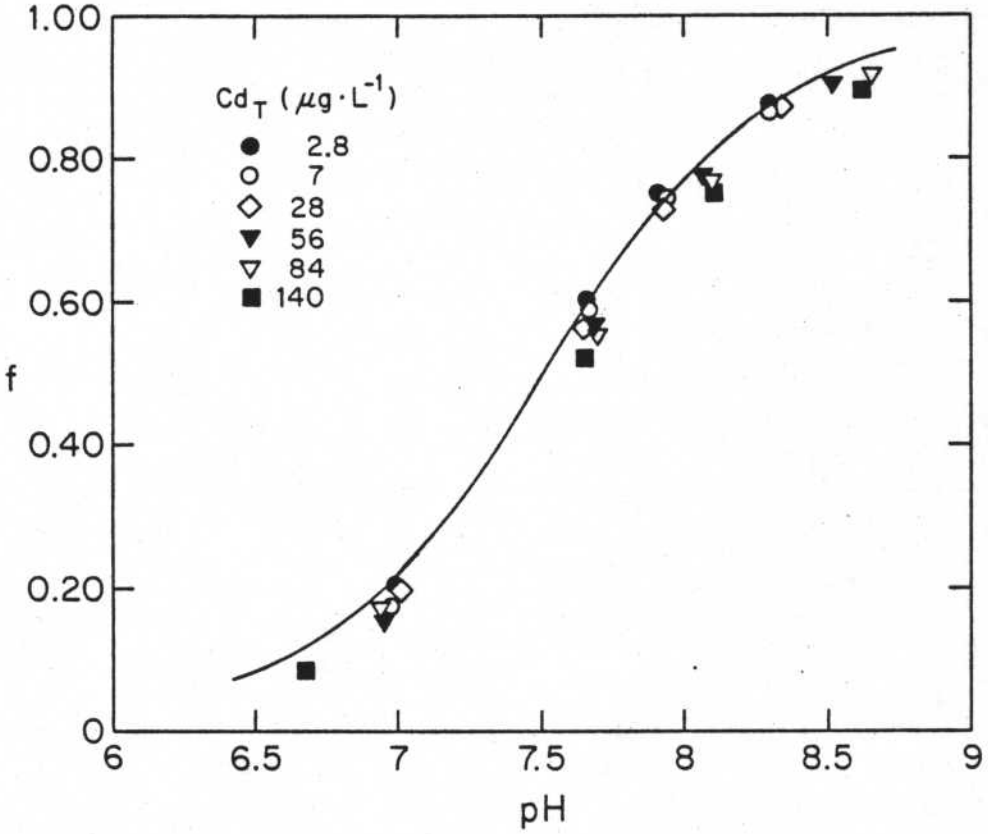


Figure 5.1. Fractional Adsorption *vs* pH for Cadmium Uptake by Hydrous Iron Oxide in Artificial Seawater. The Continuous Curve is the Fit of the Model Outlined in Chapter 3.

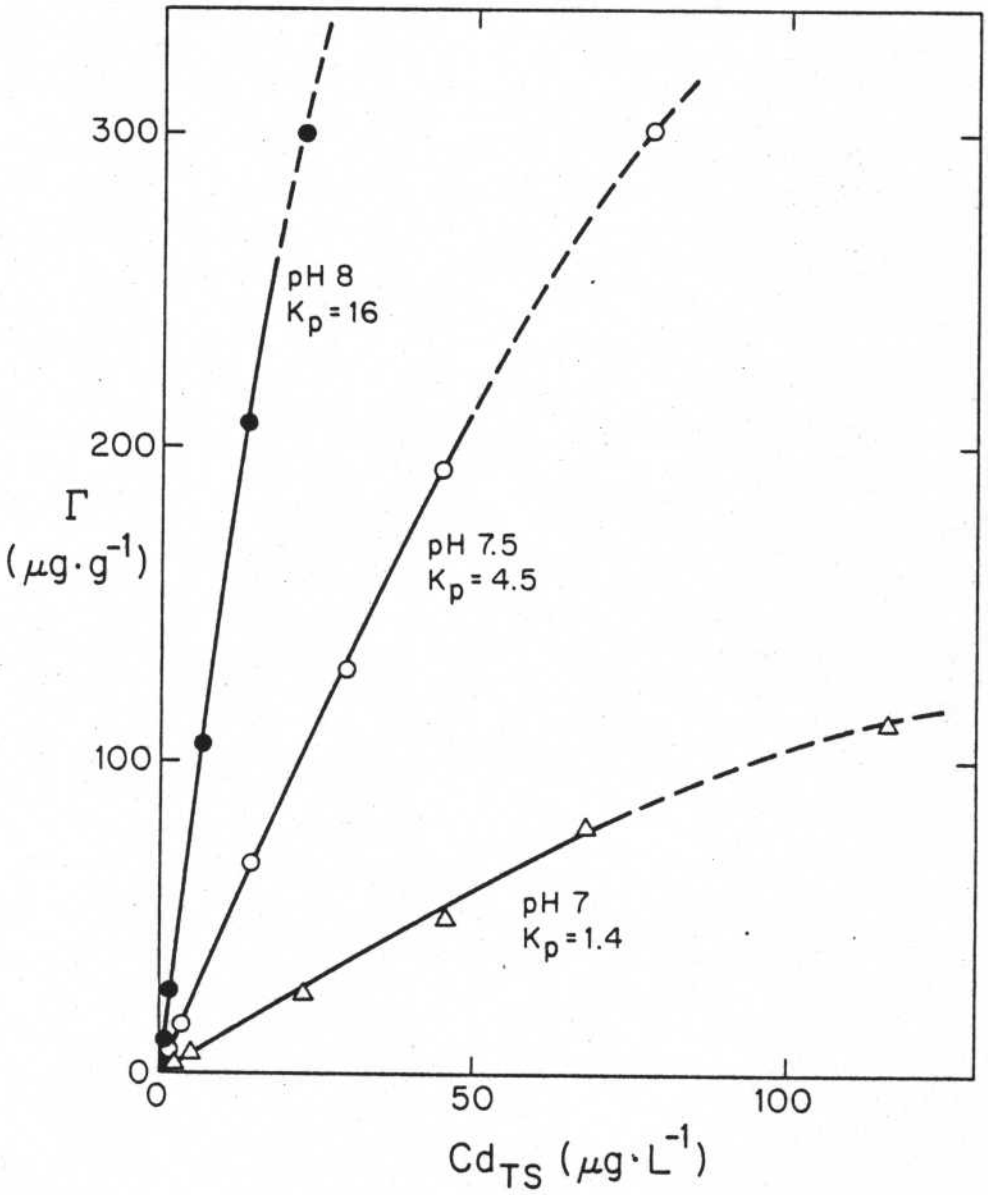


Figure 5.2. Constant pH Isotherms for Cadmium Uptake by Hydrous Iron Oxide in Artificial Seawater.

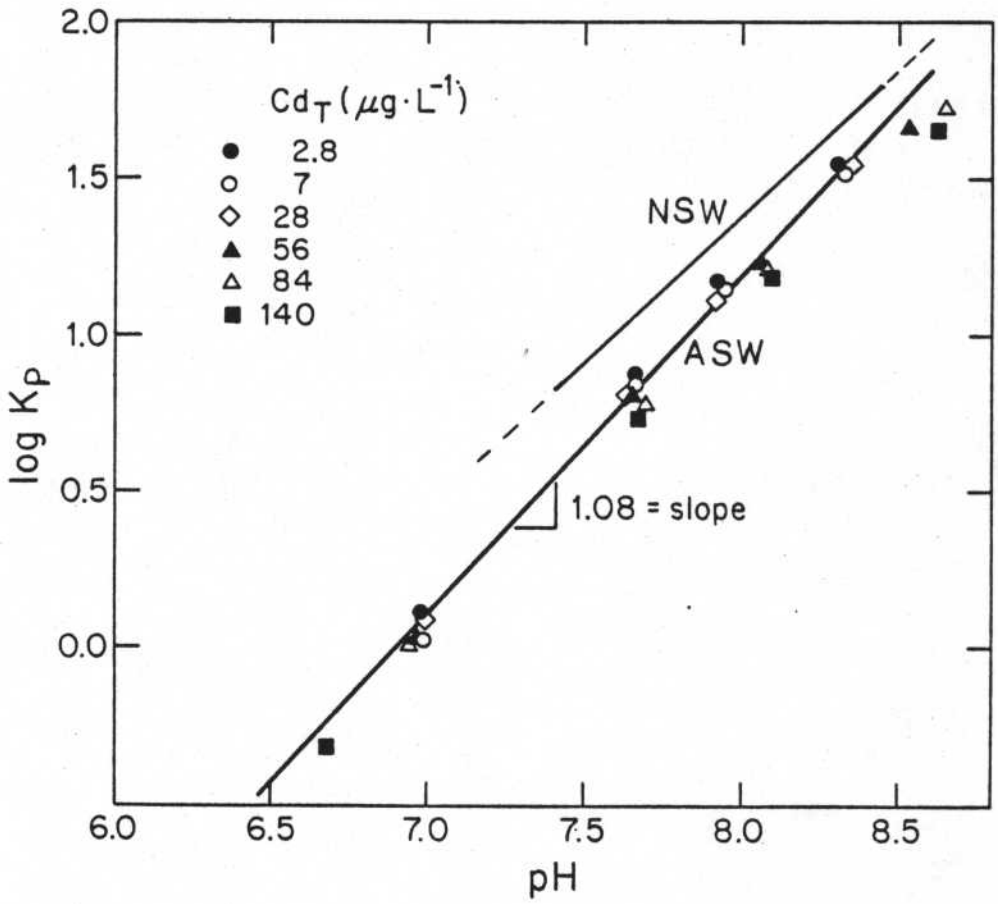


Figure 5.3. Linear Partition Coefficient *vs* pH for Cadmium Uptake by Hydrous Iron Oxide in Artificial Seawater (ASW) and Natural Seawater (NSW).

adsorbed. The *actual* stoichiometry (as measured by pH-stat titration for example) may be somewhat different due to change in surface charge (and hence the electrostatic contributions to free energy of adsorption) over the experimental pH range. Since the slope of the line is so steep a significant error in pH measurement of say, 0.1 units (a feasible level of error) gives an error in K_p of $10^{0.1}$ = 26%.

Oakley (1980) obtained a value for the linear partitioning coefficient at pH 8 of 4.4 $L.g^{-1}$ (with $\{S_T\}$ expressed as concentration of iron oxide dried at 105°C). The hydrous iron oxide is about 54% iron at this temperature thus Oakley's value becomes about 8 $L.g^{-1}$ which compares favorably with the value of 15 $L.g^{-1}$ obtained from Figure 5.3 at pH 8.

Also included in Figure 5.3 is the regression line for data (refer Appendix B) for adsorption in natural seawater medium (32°/oo salinity seawater from the Oregon Coast, filtered at 0.2 μm). Adsorption of cadmium by hydrous iron oxide is greater in the natural than in the artificial seawater.

To test the possibility that salinity may influence adsorption of cadmium an adsorption experiment was performed in artificial seawater diluted to give a range of salinities. Figure 5.4 shows the results, again plotted according to Equation 5.1. Salinity evidently has a pronounced effect on cadmium sorption such that there is more than a ten-fold decrease in K_p in going from 5 - 35 °/oo salinity. Values of the linear partitioning coefficient obtained by interpolation with the regression lines given in the appendices are plotted against salinity in Figure 5.5. The family of curves obtained for constant pH define the relationship between adsorptive affinity and salinity. The difference in adsorption in the natural and artificial seawaters shown in Figure 5.3 can be entirely accounted for on the basis of the salinity difference.

Since cadmium is strongly complexed by the chloride ion (Smith and Martell, 1976, also refer Chapter 3) while there is ample evidence that chloro-complexes of metals have very little if any tendency to adsorb to oxidic surfaces (Davis, 1977), it seems probable that the effect of salinity on cadmium adsorption is largely the effect of chloride competing with the surface for available cadmium.

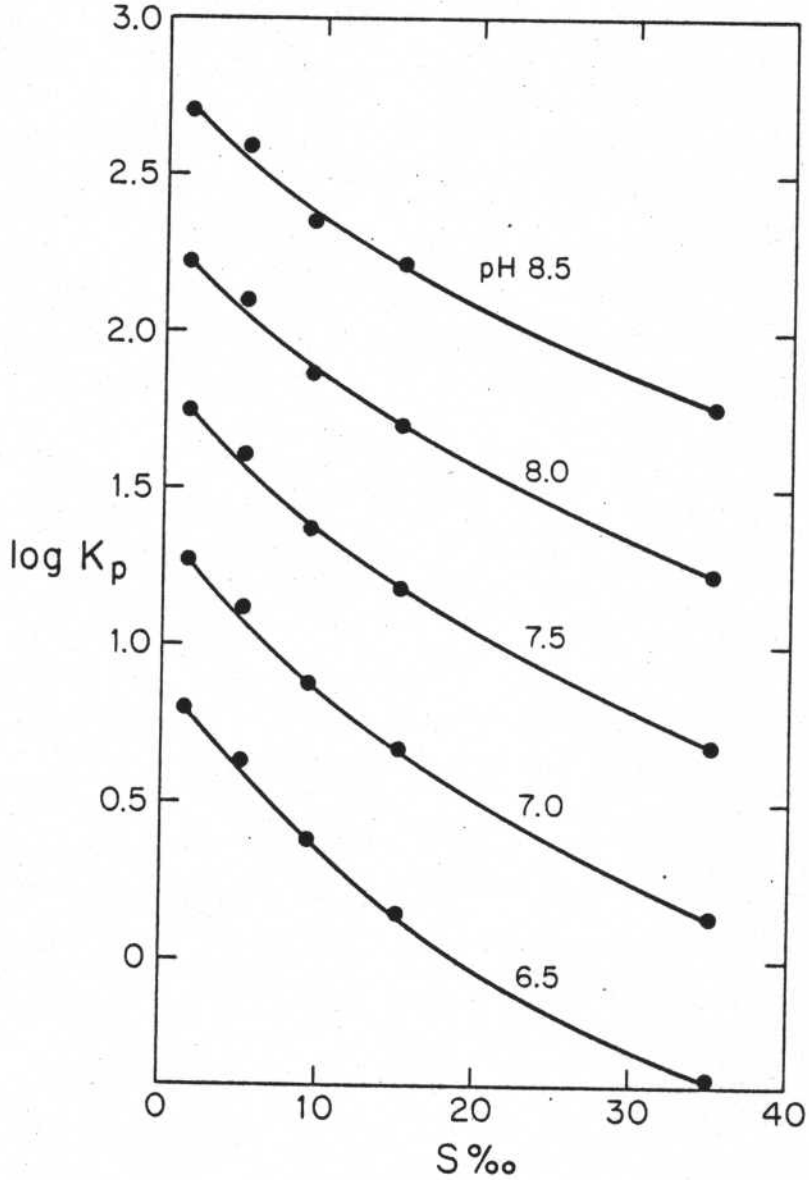


Figure 5.4. Effect of Salinity on Cadmium Uptake by Hydrous Iron Oxide in Artificial Seawater.

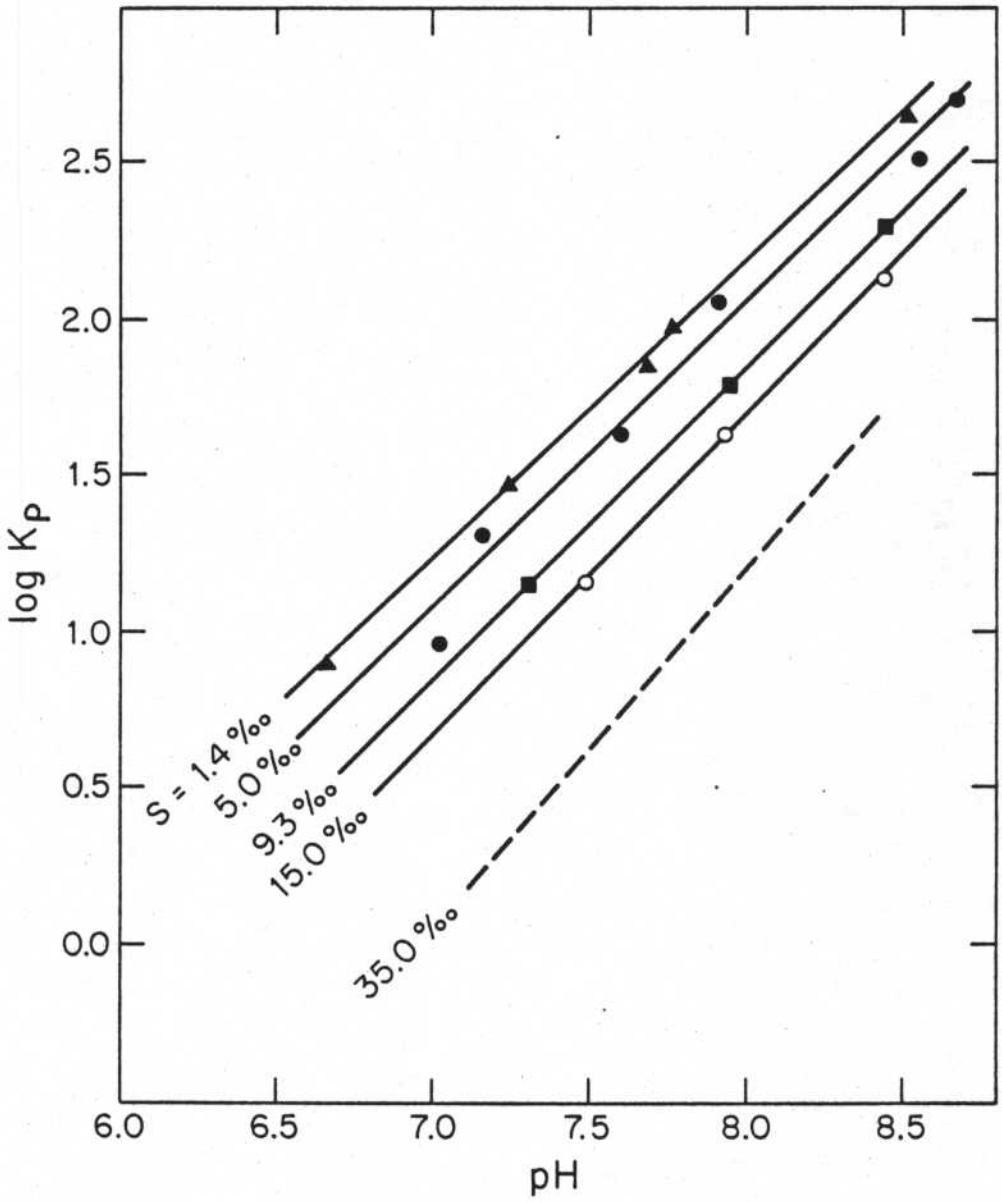


Figure 5.5. Linear Partition Coefficient, K_p *vs* Salinity for Cadmium Uptake by Hydrous Iron Oxide in Artificial Seawater.

An experiment was designed to test this hypothesis. The adsorption of cadmium by the synthetic ferrihydrite was measured in two further media: (a) 0.7M sodium nitrate ("nitrate") and (b) 0.55M sodium chloride made up to 0.7M total ionic strength with sodium nitrate ("chloride-nitrate"). These solutions both approximate the ionic strength of seawater and the second solution has the same chloride concentration as seawater. Figure 5.6 shows that adsorption in the "chloride-nitrate" was much lower than in "nitrate" but still somewhat higher than in artificial seawater. These results suggest that although the salinity effect on adsorption is indeed largely a function of chloride complexation a residual suppression of adsorption in artificial seawater remains to be explained. Possibly magnesium or calcium could be responsible in that binding of these metals changes the surface character of the iron phase. That magnesium uptake may be responsible for attenuating cadmium uptake is suggested by the work of Laurie Balistrieri (University of Washington, pers. comm.).

We can account in a quantitative way for the effect of salinity on adsorption with reference to the adsorption model outlined in Chapter 3. Consider ${}^{c}\kappa_{ads}$ defined:

$$ {}^{c}\kappa_{ads} = \frac{[SM]\ (H^{+})^{x}}{(M^{m+})\ \{S_T\}} \tag{5.2} $$

which differs from ${}^{c}K_{ads}$ (Chapter 3) only in that metal ion activity rather than concentration appears in the expression to account for ionic strength change. ${}^{c}\kappa_{ads}$ may be very nearly constant for different dilutions of an ionic medium of given relative composition, such as seawater of different salinities. Now:

$$ K_p = \frac{[SM]}{M_{TS}\ \{S_T\}} = \frac{{}^{c}\kappa_{ads}\ \gamma_{\pm m}\ \alpha_o}{(H^{+})^{x}} \tag{5.3} $$

in which the activity coefficient, $\gamma_{\pm m}$ expresses the ionic strength effect, and the distribution coefficient, α_o the metal complexation effect of salinity change. We can use (5.3) and the log α diagrams in Chapter 3 to compare the predicted ratio of K_p for cadmium on synthetic ferrihydrite in seawater at 5°/oo ($I = 0.096$, $\gamma_{\pm 2} = 0.40$,

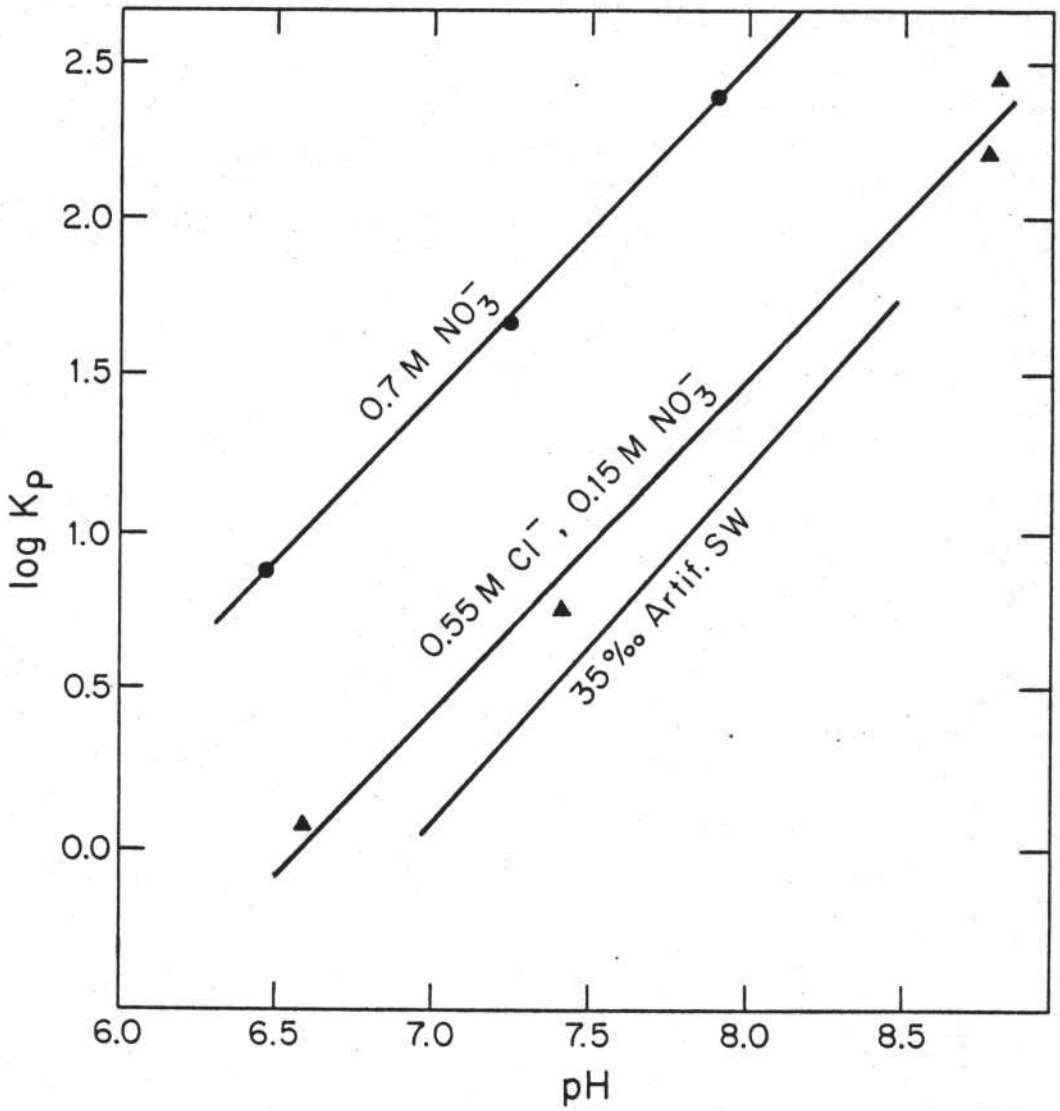


Figure 5.6. Effect of Chloride Complexation on Cadmium Uptake by Hydrous Iron Oxide.

α_o = 0.21) to that at 35°/oo (I = 0.67, $\gamma_{\pm 2}$ = 0.27, α_o = 0.028) with the observed ratio of about 8.5 (Figure 5.4).

$$\frac{(K_p)_{5^o/oo}}{(K_p)_{35^o/oo}} \simeq \frac{(\gamma_{\pm 2}\ \alpha_o)_{5^o/oo}}{(\gamma_{\pm 2}\ \alpha_o)_{35^o/oo}} = 11 \qquad (5.4)$$

The agreement of predicted and observed ratios is good considering the assumptions involved and the neglect of known effects such as changes in surface charge and surface activities with change in salinity. The approximate ratio in (5.4) should also hold for cadmium adsorption on other phases in seawater media.

The effect of temperature on cadmium uptake by the synthetic ferrihydrite phase was investigated. An experiment was run at 5°C in an otherwise identical manner to those at 20°C using a refrigerated shaker bath and the results are compared in Figure 5.7. The close correspondence suggests that the adsorption of cadmium on hydrous iron oxide is driven by the entropy change rather than enthalpy. This entropy increase may derive from the displacement of structured water at the oxide interface by the adsorbing cadmium ion.

5.2.2 Copper Adsorption on Hydrous Iron Oxide

K_p(pH) for copper adsorption on synthetic ferrihydrite in 35°/oo salinity artificial seawater is shown in Figure 5.8. There is some suggestion that adsorption is dependent on Cd_T since *suppression* of adsorption is apparent at very low Cu_T (2.8 $\mu g.L^{-1}$). This phenomena appears to be a real effect since it was observed in three separate repeats of the experiment. We might speculate that competition with the copper by the major seawater cations, Ca^{2+} and Mg^{2+} is being experienced at low concentrations. We would expect a curve for copper rather than a line as observed for cadmium since log α_o(pH) varies over the pH range studied for the former metal (Chapter 3).

Copper adsorption on the iron phase at 5°/oo (data appended but not plotted in Figure 5.8 for reasons of clarity) was apparently not significantly different from the adsorption at 35°/oo since the speciation of copper in seawater is not sensitive to salinity. However,

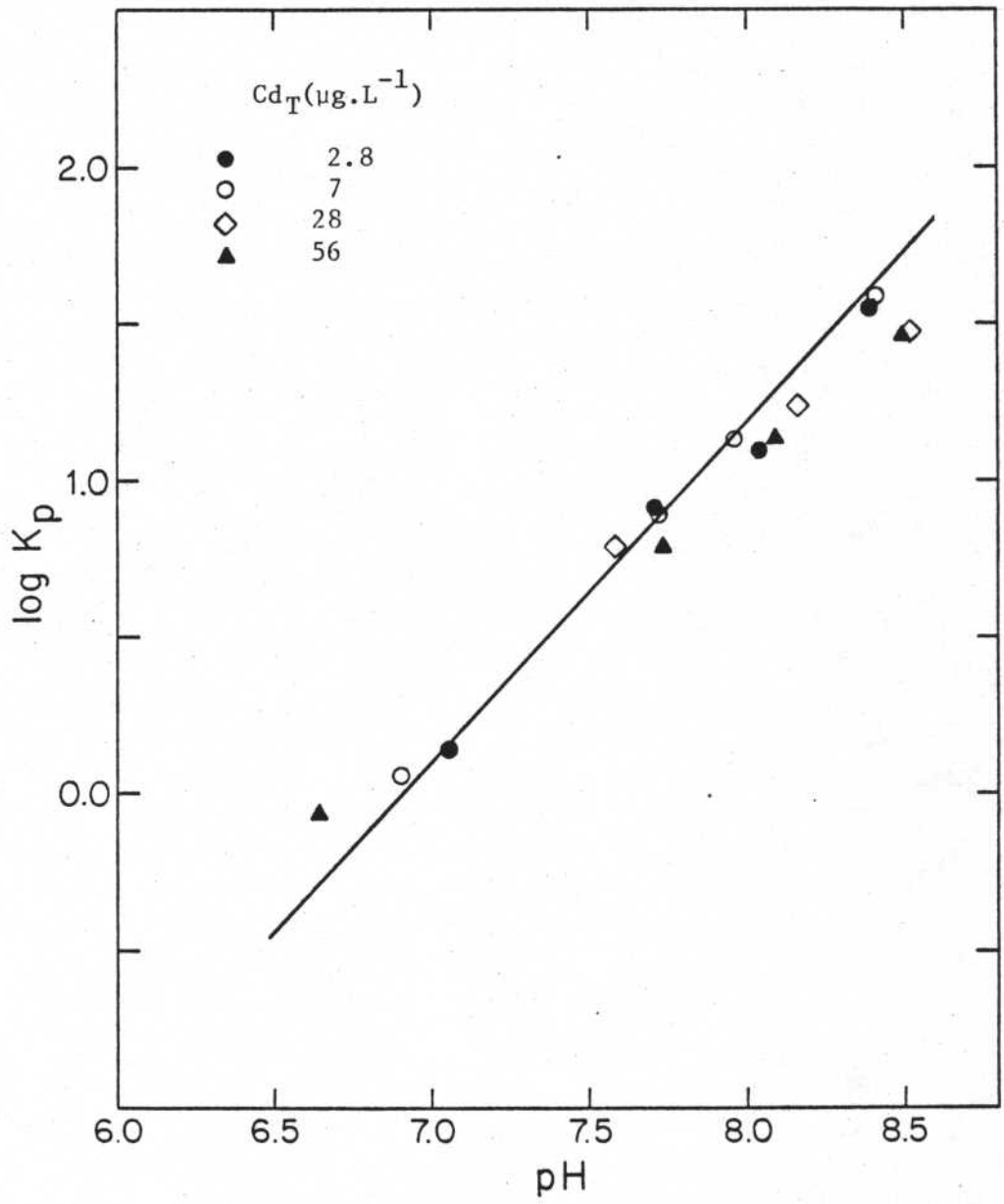


Figure 5.7. Effect of Temperature on Cadmium Uptake by Hydrous Iron Oxide in Artificial Seawater. Data Points for 5°C, Regression Line for 20°C.

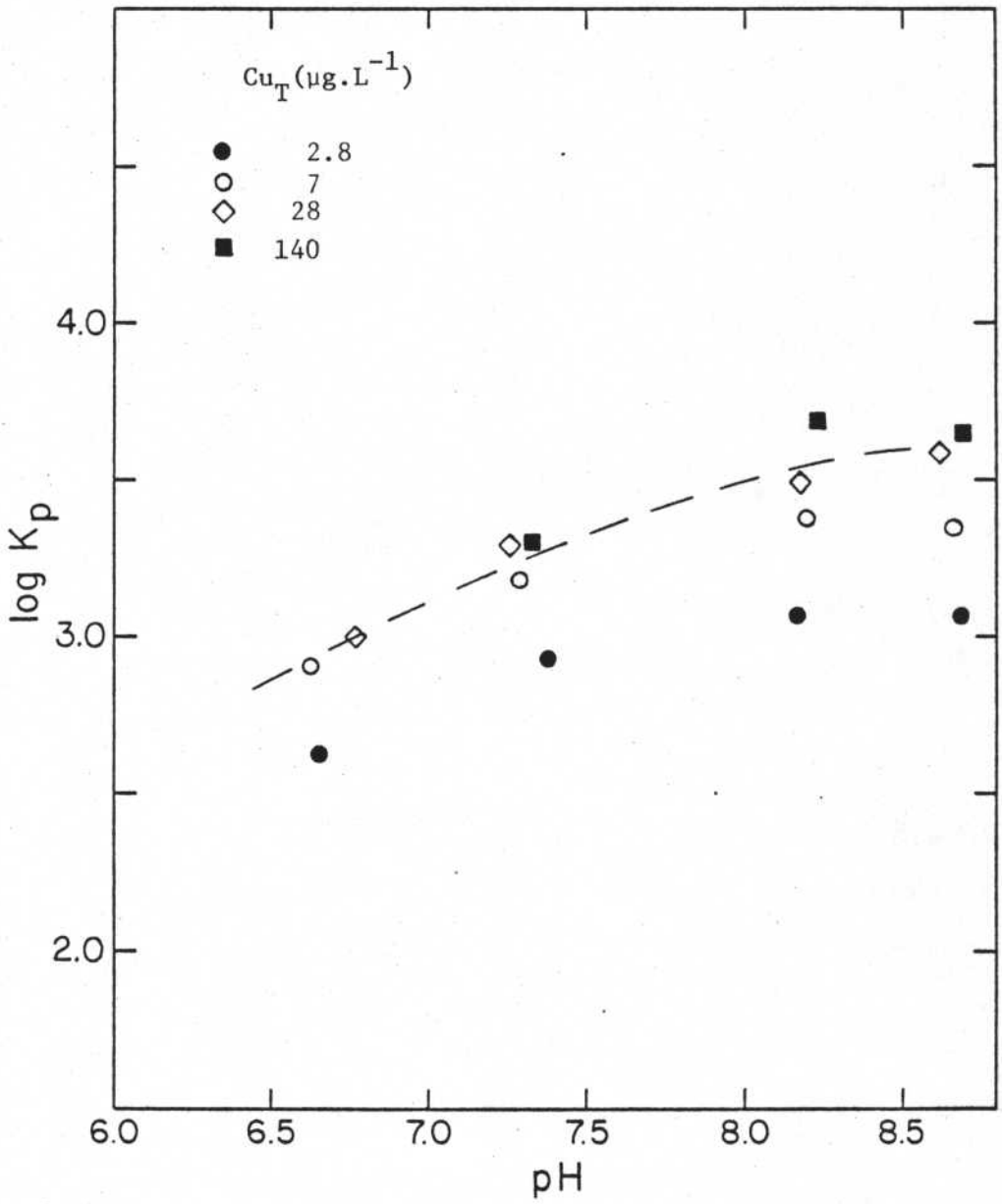


Figure 5.8. Copper Uptake by Hydrous Iron Oxide in Artificial Seawater.

the suppression of adsorption observed at 35°/oo with the data at 2.8 $\mu g.L^{-1}$ Cu_T was not present at 5°/oo thus supporting the hypothesis that this effect is related to some component of seawater such as calcium or magnesium. A study by Swallow *et al* (1980) of copper sorption by hydrous iron oxide in seawater failed to detect any competitive influence of Ca^{2+} and Mg^{2+} but the concentrations employed were much higher than used in the present study.

Oakley (1980) obtained 205 $L.g^{-1}$ for the K_p for copper sorption by hydrous iron oxide at pH 8 in natural seawater (expressed in terms of solid concentration dried at 105°C). Assuming 54% iron in this oxide material, this corresponds to 380 $L.g^{-1}$ which is much lower than the value (2500 $L.g^{-1}$) obtained from Figure 5.8.

5.2.3 Cadmium Adsorption by Hydrous Manganese Oxide

Figure 5.9 shows log K_p values plotted as a function of pH for synthetic birnessite. The 35°/oo data for Cd_T values of 2.8 and 7 $\mu g.L^{-1}$ are linearized adequately but data at 28 $\mu g.L^{-1}$ falls somewhat below the regression line while at 140 $\mu g.L^{-1}$ it is evident that high energy surface sites on the MnO_x surface have been significantly depleted. That is, the assumption in the model development (Chapter 3) that the concentration of available sites $[SH_n]$ is proportional to $\{S_T\}$ is no longer valid at these higher concentrations.

The slope of the regression line is much less than unity for cadmium adsorption on this phase, in contrast with the synthetic ferrihydrite. Metal adsorption edges which are much less steep than commonly observed for other hydrous oxides, particularly of iron and aluminum, have also been observed with hydrous manganese oxides by other workers (Posselt *et al*, 1968; Anderson and Chao, 1973; Lockwood and Chen, 1973; Loganthan and Burau, 1973; Gadde and Laitinen, 1974; Murray, 1975). This is in accord with available evidence which suggests that δ - MnO_2 acts in considerable degree as an *ion-exchanger* (with a contribution to free energy of adsorption from electrostatic attraction of the positive metal ions to the negative surface) as opposed to a purely specific-adsorbing phase such as iron oxide (van den Berg and Kramer, 1979).

The ratio: $(K_p)_{5^o/oo}/(K_p)_{35^o/oo}$ is about 13, in good agreement with the value of 11 predicted by Equation 5.4 above.

Oakley's (1980) value of 15 $L.g^{-1}$ for the linear partitioning coefficient for cadmium adsorption on MnO_x in natural seawater at pH 8, when corrected for the fact that it is expressed in terms of solid concentration dried at 105°C, is still considerably smaller than the 110 $L.g^{-1}$ obtained from Figure 5.9. A possible reason for this discrepancy is that Oakley did not obtain data at very low Cd_T values, because of the lack of sensitivity of his analytical method (flameless AA) and thus may have been working in the non-linear partitioning range of Cd_T.

5.2.4 Copper Adsorption by Hydrous Manganese Oxides

Data for adsorption of copper on hydrous manganese oxides in seawater at two reference salinities are shown in Figure 5.10. Uptake of copper by the manganese phase is almost independent of pH over the range studied. Adsorption affinity is greater at $5^o/oo$ by about 0.5 log units (a factor of three) than at $35^o/oo$ salinity in contrast to the situation for copper adsorption on iron oxide which showed no salinity dependence. Salinity (ionic strength) would be expected to influence adsorption on a surface like MnO_x which acts in part as an ion-exchanger.

Oakley (1980) measured K_p (pH 8, $32^o/oo$ salinity) at 7300 $L.g^{-1}$ in terms of hydrous manganese oxide which is about 15000 $L.g^{-1}$ in terms of manganese, considerably higher than the value of 6900 $L.g^{-1}$ from Figure 5.10. The discrepancy is attributable to the different salinities of the seawater media used in this and Oakley's studies.

5.3 ALUMINOSILICATES

5.3.1 Cadmium Adsorption by Montmorillonite

Cadmium adsorption by Wyoming montmorillonite (SWy-1) is shown in Figure 5.11. Data are for $5^o/oo$ only since at $35^o/oo$ uptake of cadmium

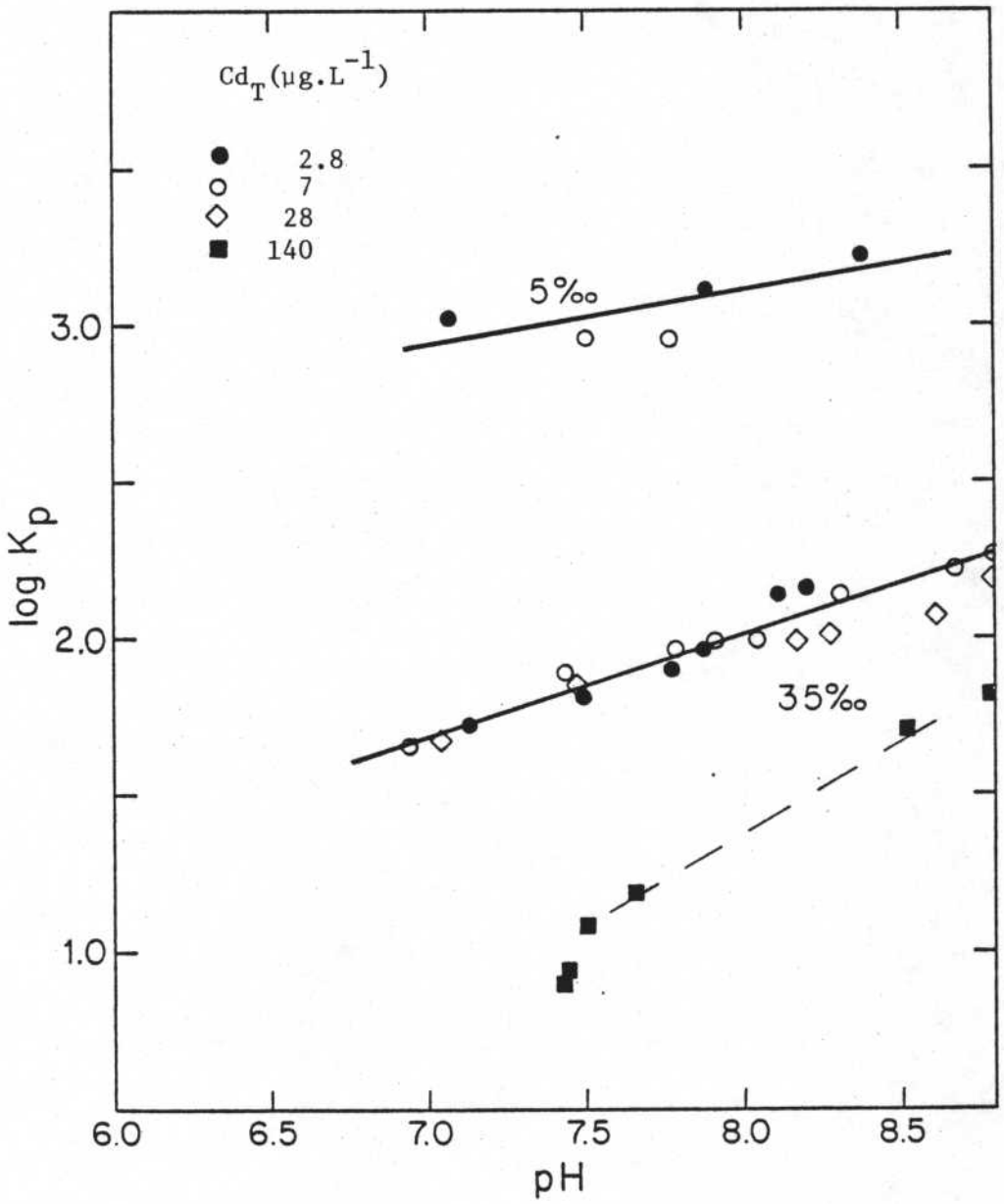


Figure 5.9. Cadmium Uptake by Hydrous Manganese Oxide in Artificial Seawater.

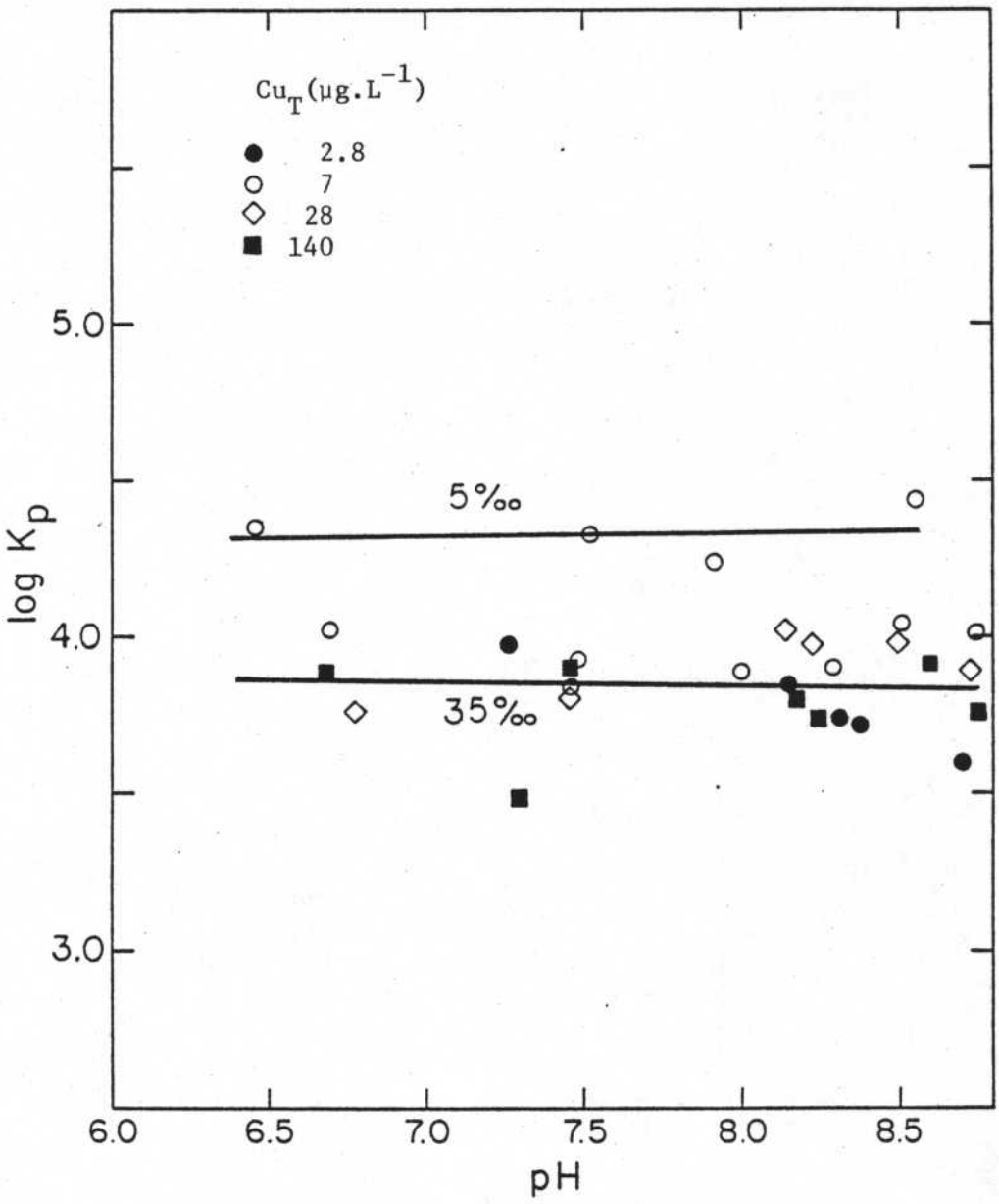


Figure 5.10. Copper Uptake by Hydrous Manganese Oxide in Artificial Seawater.

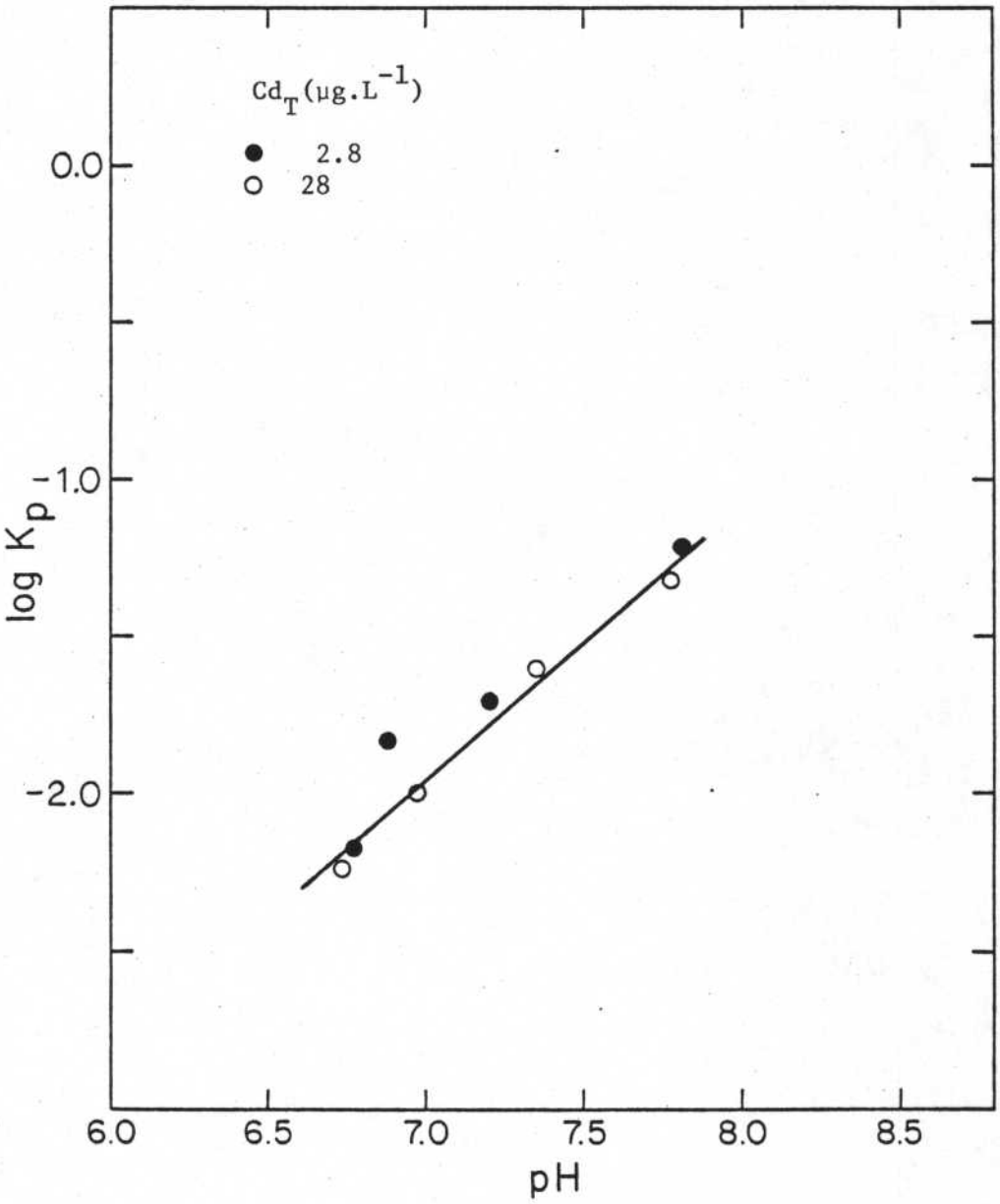


Figure 5.11. Cadmium Uptake by Montmorillonite in 5°/oo Artificial Seawater.

by this phase was barely measurable (refer Appendix C) even at a solid concentration of 35 $g.L^{-1}$. Experiments with high SWy-1 concentrations in seawater resulted in severely coagulated suspensions which were so viscous that it was doubtful whether sufficient mixing by shaking could be achieved to contact cadmium with all available adsorption sites. Thus only rough upper limits can be given for K_p at 35°/oo. Relatively much greater adsorption occurred at 5°/oo.

The specific affinity of the clay mineral for cadmium is very much lower than that of the hydrous metal oxides. What specific affinity exists may be due to the presence of constant potential sites at clay micelle edges or residual amorphous coatings of hydrous metal oxides. The normal mode of metal ion exchange on clays as observed in dilute media may be suppressed in seawater by Ca^{2+} or Mg^{2+} competition. Alternatively, compression of the electric double layer to about 3.5 A° in seawater (Stumm and Morgan, 1970) may result in virtual exclusion of the hydrated Cd^{2+} ion from the zone of diffuse layer charge.

Some experiments were performed by the author on the Fischer bentonite used by Oakley (1980) (Appendix B). While adsorption on this phase in 35°/oo seawater was considerably greater than for SWy-1 (K_p obtained from the pH 8 isotherm was 0.05 $L.g^{-1}$) it was still much smaller than the value of 1.1 $L.g^{-1}$ reported by Oakley. The apparent specific affinity of the Fischer clay for cadmium is probably related to the presence of trace oxide contaminants as coatings.

5.3.2 Copper Adsorption by Montmorillonite

Data for copper adsorption on Wyoming montmorillonite in 35°/oo artificial seawater are plotted in Figure 5.12. No data were obtained for 5°/oo seawater, however, the specific affinity of the clay for copper (as measured by K_p) is apparently so low that this kind of material is unlikely to be a significant sink in the estuarine environment at any salinity. Nevertheless the literature shows continued interest in clay minerals as sinks for trace metals including copper in saline environments (for example, O'Conner and Kester, 1975).

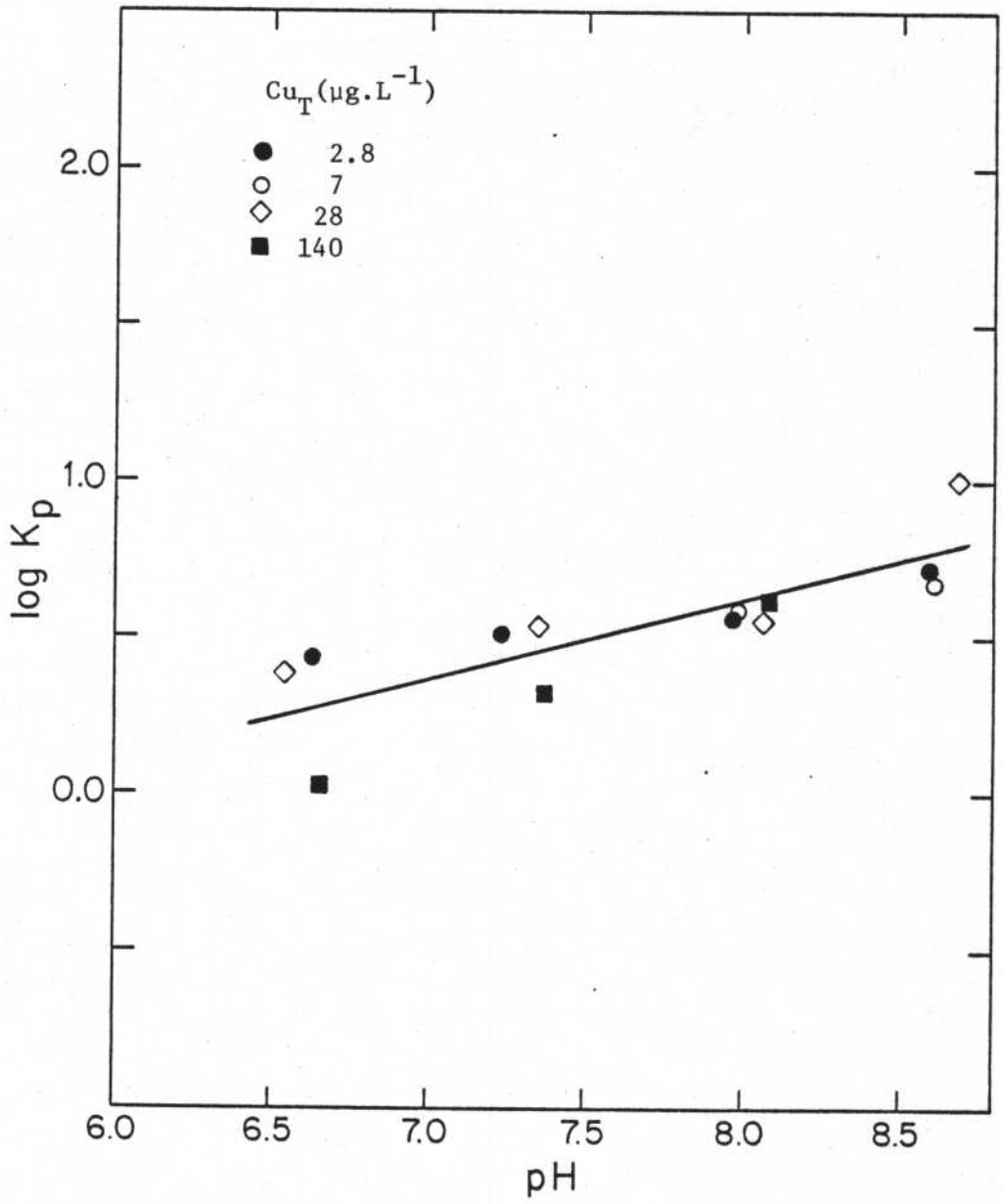


Figure 5.12. Copper Uptake by Montmorillonite in Artificial Seawater.

5.3.3 Cadmium Adsorption by the Synthetic Aluminosilicate Gel

Figure 5.13 shows log K_p plotted against pH for the aluminosilicate gel (0.83:1 Si:Al molar ratio). The log K_p values are considerably lower than for the manganese and iron phases at both reference salinities. The slope of the log K_p (pH) curves are approximately unity as for the iron phase and there is no evidence of nonlinear partitioning over the Cd_T range studied.

It might reasonably be expected that the position of the lines in Figure 5.13 would shift with change in Si:Al molar ratio in the gel under study. Specific affinity of a fresh precipitate of hydrous aluminum oxide for zinc was found by Kinniburgh *et al* (1977) to be almost as high as that of iron. As silicon is added progressively to amorphous aluminum oxide its sorptive affinity towards trace metals may decrease. Unfortunately no data are available in the literature for comparison with the K_p values obtained for the aluminosilicate in this study.

The difference in log K_p between 5 and 35°/oo was about 1.1 log units (a factor of 13) in agreement with the analysis in the above discussion of salinity effects on cadmium adsorption by the iron phase.

5.3.4 Copper Adsorption by the Synthetic Aluminosilicate Gel

Figure 5.14 shows the log K_p (pH) plot for copper uptake by the synthetic aluminosilicate gel in 35°/oo artificial seawater. There is considerable scatter in the data at higher pH values which tends to mask trends with pH. Apparently the slope is similar to that of copper uptake by synthetic ferrihydrite but the specific affinity of the aluminosilicate is much lower than that of iron.

5.4 HUMIC SUBSTANCES

5.4.1 Methodology

The measurement of metal binding by the EHS in seawater medium posed some severe operational problems not encountered with the other

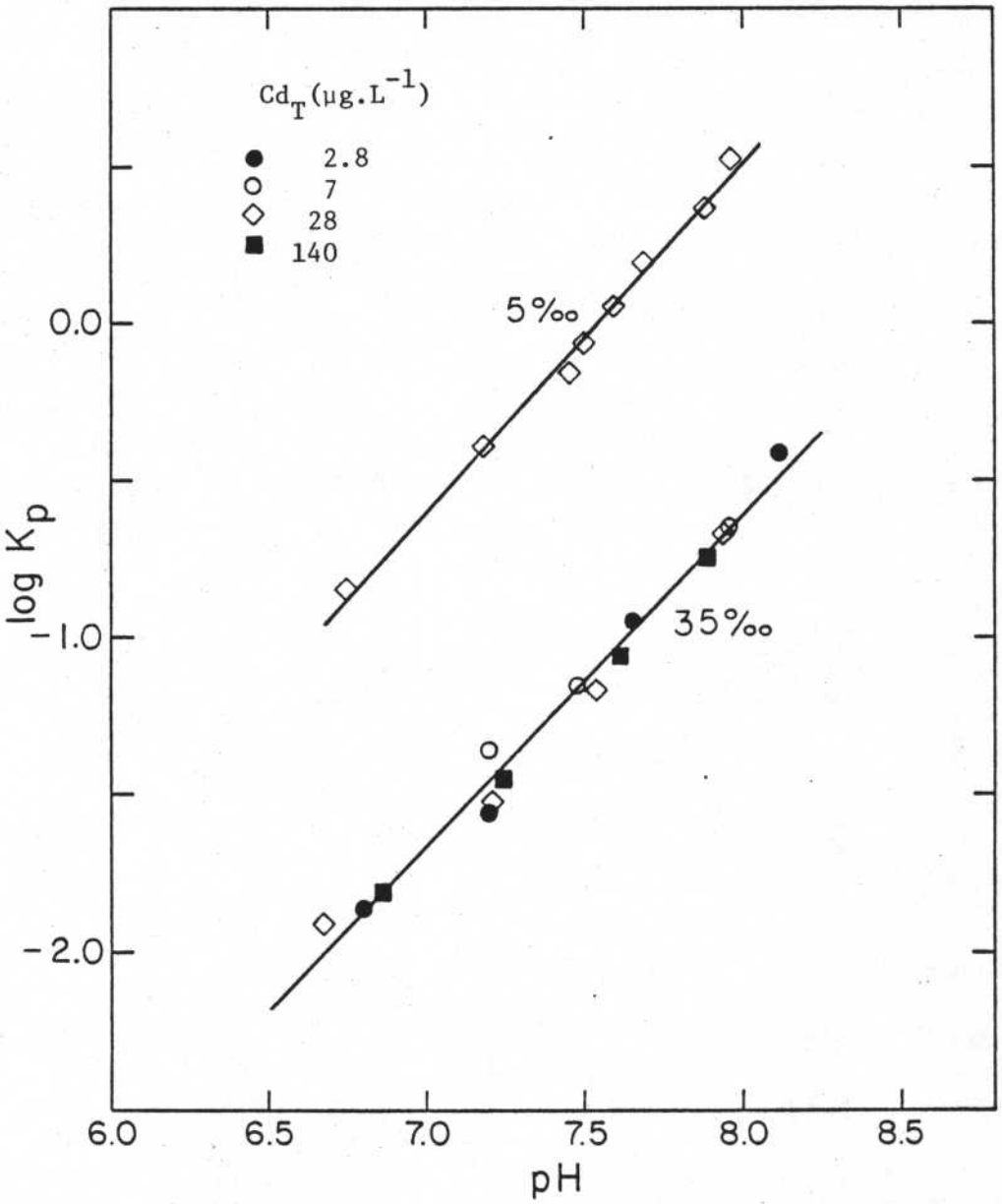


Figure 5.13. Cadmium Uptake by Synthetic Aluminosilicate in Artificial Seawater.

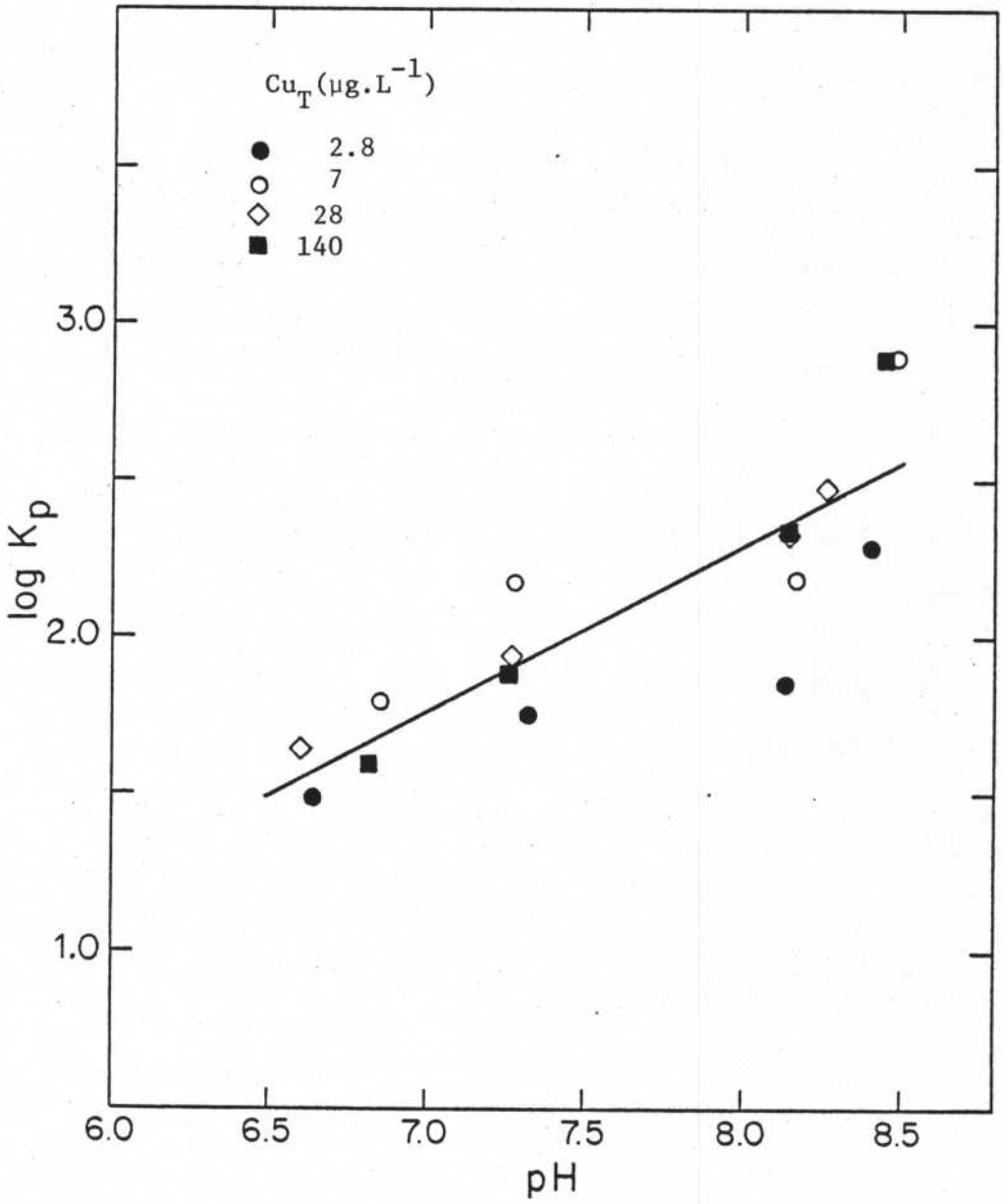


Figure 5.14. Copper Uptake by Synthetic Aluminosilicate in Artificial Seawater.

model phases. Since humic substances produce a stable sol in seawater which cannot be entirely separated by centrifugation or even ultracentrifugation (S. M. Oakley, Civil Engineering Dept., OSU, pers. comm.) it is necessary to use some other means of achieving phase separation or else avoid the problem with a completely different approach.

Originally it was intended to use a modification of the Schubert (1948) ion exchange method for evaluation of copper or cadmium uptake by the EHS. A good review of this method and its applications and limitations is found in McCarthy *et al* (1977). Unfortunately the high ionic strength and high concentrations of the divalent cations Ca^{2+} and Mg^{2+} in seawater precluded the use of an ion-exchanger in this medium. Chelating resins such as Chelex-100 were considered since these resins are highly selective for trace metals such as copper and cadmium over alkaline earth metals. However, it is probable that chelating resins would interact with the ligands (humic materials) as well as the metal since metals sorbed on these resins are known to undergo ligand exchange reactions (Khym, 1974). The ion exchange method is a very valuable technique in media of low ionic strength and low divalent cation content, but there appears to be no simple way of adapting it for use in seawater.

Oakley (1980) used ultrafiltration to separate organic-bound and unbound forms of copper and cadmium in seawater media. This author is unaware of previous reports on the use of ultrafiltration for the separation of macromolecules in laboratory metal binding studies although Krom and Sholkovitz (1978) used the technique in studies of iron and manganese association with sediment pore water organics while Lindberg and Harriss (1974) studied mercury organic associations in natural sediment samples using ultrafiltration. In copper binding studies with humic acid, Mantoura and Riley (1975b) used gel filtration, which, like ultrafiltration or pressure dialysis, works by the gel exclusion principle.

Ultrafiltration was used in the present study using the Amicon Model 12 stirred cell employed in the molecular weight distribution studies (Chapter 4) with UM2 membranes (nominal molecular weight cutoff; 1000 daltons). After taking a sample from the adsorption test

tube for measurement of total tracer activity (refer Section 5.1) the remaining material was handled as follows:

1) About one-third of the remaining EHS suspension in each reaction tube was added to the ultrafiltration cell which was pressurized (N_2, 50 KP) for 3 minutes then depressurized and allowed to equilibrate with stirring for 30 minutes before being discarded.
2) The procedure in (1) was repeated.
3) The liquid in the cell was discarded then the remaining EHS from the reaction tube was added to the cell which was pressurized again for 3 minutes before starting the stirrer.
4) The first 30% of ultrafiltrate was discarded and then the passing solution was collected in a vial to which a few μL of concentrated HCl had been added to prevent metal uptake.
5) The ultrafiltrate was subsampled by volumetric pipette and dispensed into a labelled counting vial.

The absorbance at 250 nm (1 cm cell) was monitored in selected ultrafiltrates to ensure negligible loss of EHS through the membranes.

The above procedure worked satisfactorily for cadmium (see below) but unfortunately, sorption losses of copper on the membrane and cell walls were severe and gave erratic results.

A method for measuring metal binding constants with organics that has recently become popular employs a specific ion electrode to monitor free metal ion activity during titration of the organic ligands with a metal solution (Bresnehan *et al*, 1978; Sunda and Hanson, 1979). Anodic stripping voltametry can also be used to distinguish free and bound metal (Guy and Chakrabarti, 1976; Liebermann, 1979). The data are frequently analyzed by Scatchard plots according to the equation (in typical symbolism):

$$\frac{\bar{\nu}}{[M^{m+}]} = K_i(n_i - \bar{\nu}) \qquad (5.5)$$

where $\bar{\nu}$ is the bound metal per gram of ligand (or per mole if molecular weight is known) and is analogous to Γ the adsorption density, K_i is the stability constant of the ith site-type and n_i is the number of binding sites per gram (or mole) of ligand. Typically a Scatchard plot yields one or more straight-line regions corresponding to one or more site-types.

A Scatchard analysis was employed in the present study using data for copper binding by the EHS obtained with the following procedure. The EHS sample (in seawater) was contained in a polyethylene beaker immersed in a thermostatted water bath (20°C). Magnetic stirring of the sample was maintained throughout the titration and the pH was kept constant (± 0.1 units) by microlitre additions of acid or base. The potential of an Orion 94-29 cupric ion electrode relative to an Orion double junction reference electrode was used to measure total solution phase ("unbound") copper by reference to potentials generated in a 100 $\mu g.L^{-1}$ -Cu standard made up in seawater at pH 5. After each addition of a microlitre quantity of copper by Eppendorf pipette at least 20 minutes was allowed for reaction before potential readings were taken on an Orion 701 digital voltmeter. The binding appeared to be a very fast reaction (minutes) but the electrode response was sluggish at low copper concentrations and at least 60 minutes was required for stabilization of drift below 40 $\mu g.L^{-1}$ Cu_T. Small samples were taken from the beaker at each step in the titration to enable total copper to be measured.

Metal electrodes were also used to measure EHS binding in a somewhat different procedure developed by the author which will be referred to henceforth as the "direct" electrode method as opposed to the "titration" electrode method. A series of samples of EHS together with a series of blanks (seawater only) were prepared in 100 mL plastic beakers. The same volumes of metal standard were added to both samples and blanks and pH's were adjusted to a range of values between 6.0 and 8.5. The beakers were then placed in a thermostatted water bath (20°C) while the beaker contents were stirred magnetically for a four-hour period of equilibration. After this time the potential of an Orion 94-48A cadmium electrode or Orion 94-29 copper electrode was measured relative to an Orion double junction reference electrode.

The potential, E, is related to free metal activity, (M^{m+}), by the Nernst equation:

$$E = S \log (M^{m+}) + (\text{const}) \tag{5.6}$$

where S is electrode slope. In a constant ionic medium at a given pH the free metal ion activity is in constant ratio to the total solution metal, M_{TS}, so we have that:

$$E = S \log M_{TS} + C(pH) \tag{5.7}$$

where $C(pH) = (\text{const}) + S \log (\gamma_{\pm 2}\, \alpha_o)$, $\gamma_{\pm 2}$ is the free metal ion activity coefficient and α_o is the distribution coefficient. For a sample and blank at the same pH:

$$E_b - E_s = \Delta E = S \log \{\frac{(M_{TS})_b}{(M_{TS})_s}\} \tag{5.8}$$

where b and s denote blank and sample respectively. Rearranging:

$$\frac{(M_{TS})_s}{(M_{TS})_b} = 1 - f = 10^{-(\frac{\Delta E}{S})} \tag{5.9}$$

where f is the fraction of total metal bound by the organic phase. Thus by measuring the change in potential, E, between the sample and a blank of the same pH (in practice by interpolation on a plot of E_b against pH) and with the electrode slope, S, known from a standard curve (E as a function of log M_{TS}) the bound fraction, f, is obtained.

Calibration curves for the metal ion electrodes were linear in seawater media down to below 100 $\mu g.L^{-1}$ Cd_{TS} and below 10 $\mu g.L^{-1}$ Cu_{TS}. The slope of the cadmium curves was about 29 mV per decade as predicted from the Nerst equation for a two electron reaction but, surprisingly, the slope for the copper electrode was about 40 mV per decade. For copper standards made in sodium nitrate solution the normal 29 mV per decade slope was observed with the same experimental setup while the anomalous high slope was obtained again in seawater with different apparatus. Apparently the reaction sensed by the electrode in seawater is not the same as in simpler ionic solutions. At the time of writing no explanation for this phenomenon was available to the author

while the anomalously high electrode slope had been observed in at least ten different runs with different copper standards made up in different batches of artificial seawater.

5.4.2 Cadmium Uptake by EHS

Figure 5.15 shows log K_p values obtained by both the ultrafiltration method and the direct electrode method for the Estuarine Humic substances. K_p is expressed in terms of ash-free organic matter, about 49% of which is carbon. The regression lines are given for the ultrafiltration data alone but, in spite of an overall greater level of "noise" than with cadmium uptake experiments on other phases, the agreement between methods appears to be good. The specific affinity of the EHS for cadmium is intermediate between that of the hydrous metal oxides and the aluminosilicates.

The pH dependence of K_p is rather low suggesting that the cadmium-complexing sites on the constituent humic polymers are largely deprotonated over the pH range under consideration. At lower pH values closer to the pK_a's of active complexing sites such as carboxylic groups, the pH-dependence of log K_p would be expected to be greater.

The difference: $\log (K_p)_{5^o/oo} - \log (K_p)_{35^o/oo}$ is about 1.3 log units (a factor of 20) which is greater than for the other phases considered except montmorillonite. Thus increase in ionic strength and/or calcium and magnesium concentrations results in suppression of adsorption to a greater extent than can be accounted for by the effect of change in Cd^{2+} activity. Possibly this extra degree of attenuation of adsorption is related to structural changes in the humic polymers which may progressively shift from flexible rod to random coil configurations in media of increasing ionic strength. Metal-complexing sites on the polymers would be expected to be less available for steric reasons in the latter configuration.

The K_p value for the EHS at pH 8 in $35^o/oo$ seawater ($0.9\ L.g^{-1}$) is somewhat higher than Oakley's (1980) value of $0.2\ L.g^{-1}$ for a commercial humic acid. Humic materials from different sources are known to have variable trace metal complexing ability so this kind of difference is not unexpected.

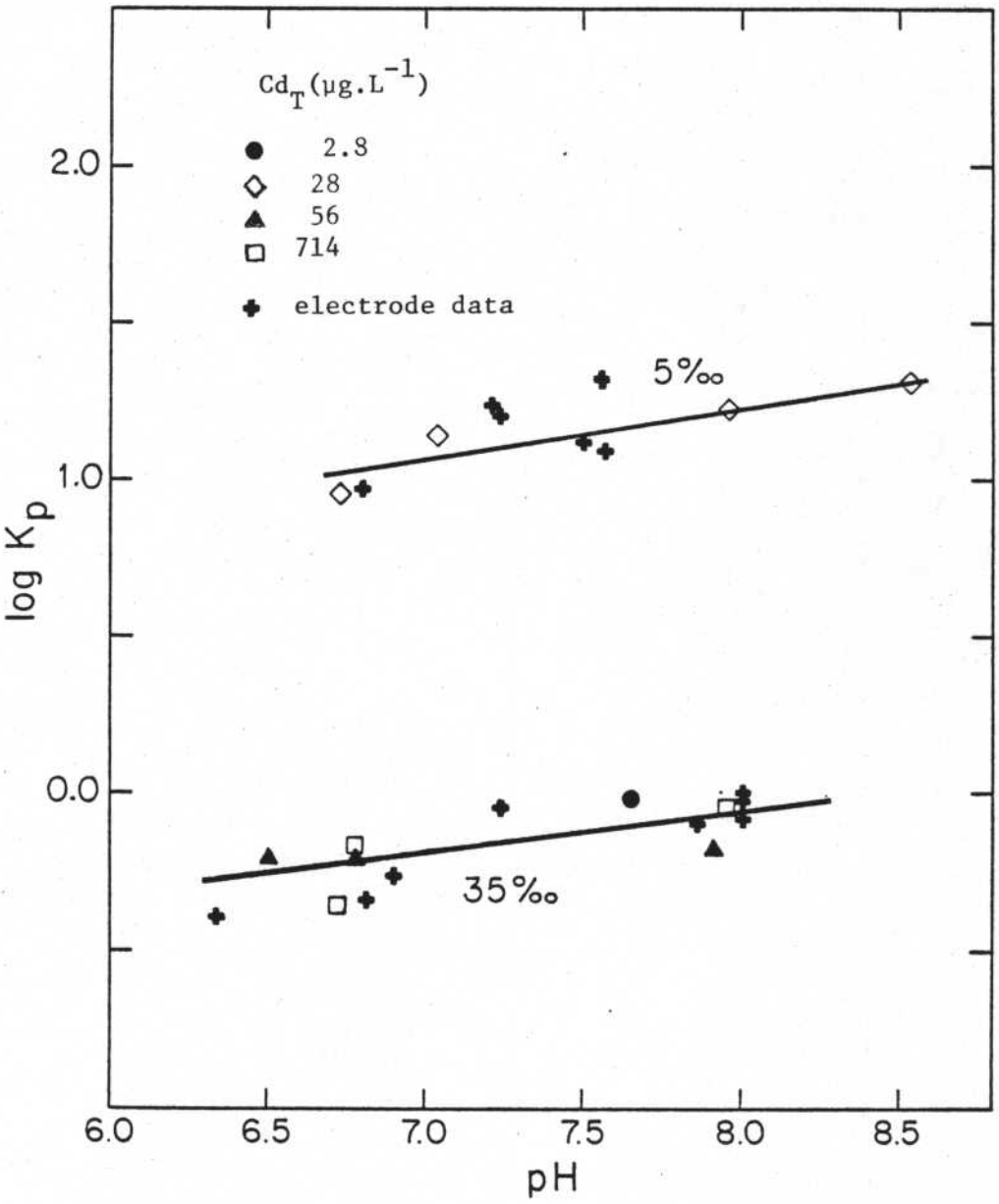


Figure 5.15. Cadmium Uptake by EHS in Artificial Seawater.

5.4.3 Copper Uptake by EHS

As was mentioned above, copper binding data obtained by the ultrafiltration method were not of sufficient quality to warrant quantitative treatment. An attempt was also made to use the "direct" electrode method (Figure 5.16). The data served to indicate the pH dependence of copper binding but it was evident that the highest energy sites were largely saturated, that is the assumption of linear partitioning did not apply under the experimental conditions.

Data for copper binding by EHS considered in the remainder of this work were obtained by the "titration" method. Figure 5.17 shows plots similar to those of Sunda and Hanson (1979) for the titration of 20.03 $mg.L^{-1}$ EHS in seawater at three different pH values with copper. The straight line in the figure ($pCu_{TS} = pCu_T$) corresponds to the calibration line and represents no binding. Thus deviation of the titration curves from this line measures the degree of binding of added copper. As could be expected on consideration of Figure 5.16 the binding of copper increases with pH.

Scatchard plots (refer Equation 5.5) of the titration data (refer Appendix C) are given in Figure 5.18. Since the electrode was calibrated in terms of total solution phase copper, Cu_{TS}, rather than free copper ion, a slight modification of the standard Scatchard equation (5.5) is involved. As has been observed by other workers (Mantoura and Riley, 1975b; Guy and Chakrabarti, 1976; Bresnehan *et al*, 1978; Sunda and Hansen, 1979) the Scatchard plots are highly non-linear indicating the presence of more than one type of binding site. The first two binding constants at each pH were estimated by the method of Bresnehan *et al* (1978) and are given in Table 5.1. Also given in this table are the values of log K_p corresponding to the two site-types which were calculated (refer Equation 5.5):

$$K_{p,i} = n_i K_i \qquad (5.10)$$

The log K_p values appear to be a linear function of pH and regression lines in Table 5.1 give the calculated relationships. The n_i values in Table 5.1 correspond to the total number of copper binding sites in

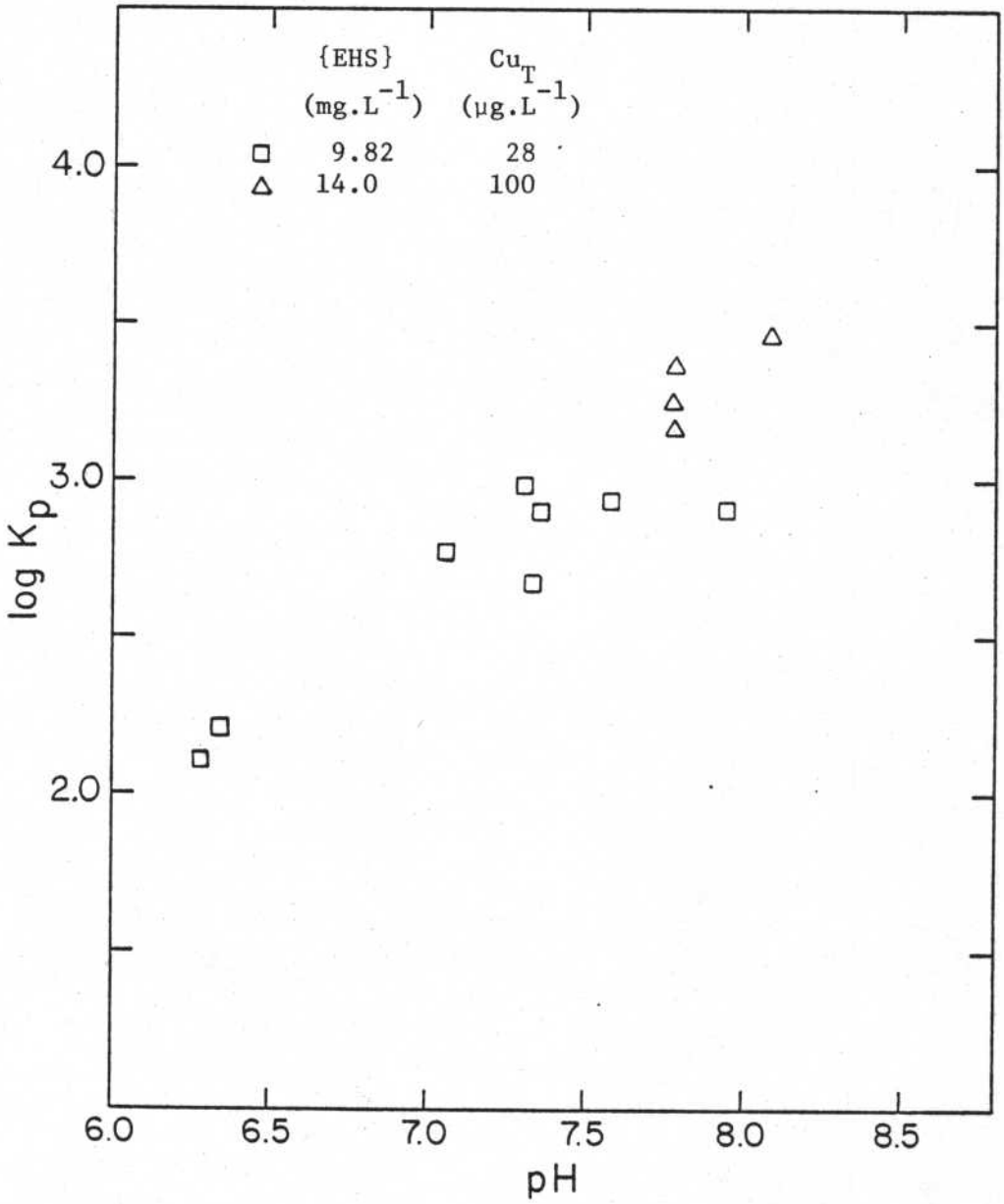


Figure 5.16. Copper Uptake by EHS in Artificial Seawater Measured by the "Direct" Electrode Method.

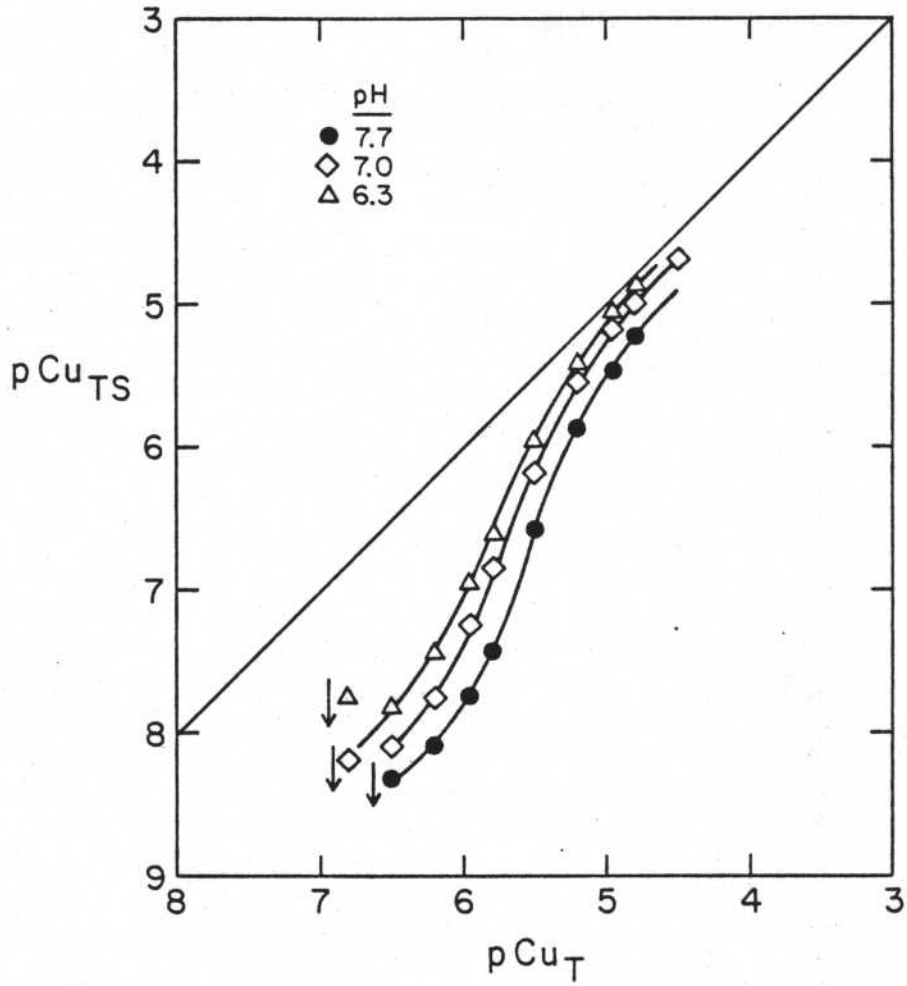


Figure 5.17. Copper Titration Curves for 20.03 mg.L^{-1} EHS in Artificial Seawater at Three Different pH Values.

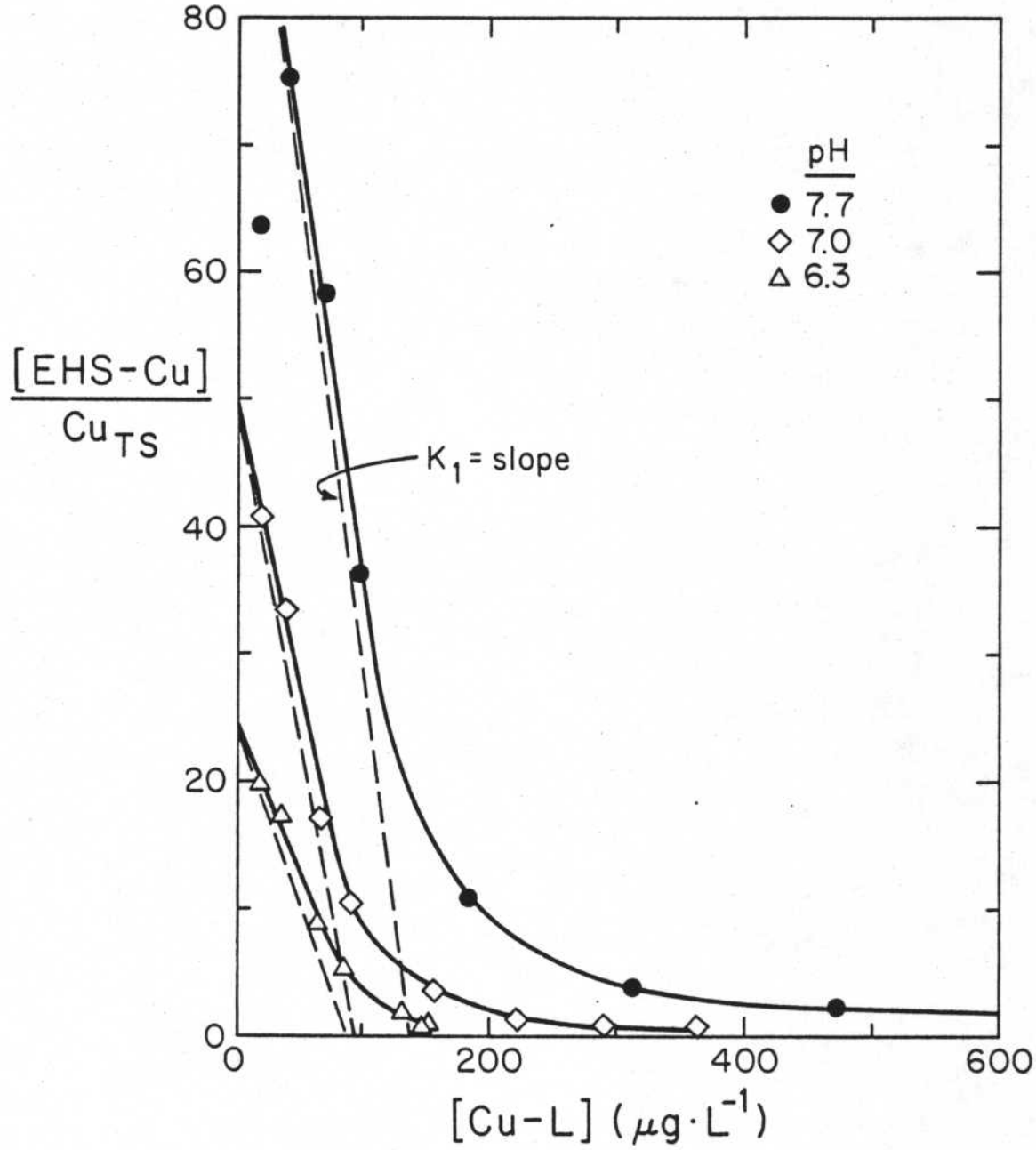


Figure 5.18. Scatchard Plots of Cu^{2+} Electrode Titration Data for Copper Binding by EHS.

Table 5.1

SUMMARY OF SCATCHARD ANALYSES FOR COPPER BINDING BY EHS IN ARTIFICIAL SEAWATER

pH	log ${}^{c}k_1^*$	log K_{p1}	n_1 ($mg.g^{-1}$)	log ${}^{c}K_2^*$	log K_{p2}	n_2 ($mg.g^{-1}$)
6.3 ± .1	7.24	3.09	4.51	5.94	1.64	3.17
7.0 ± .1	7.53	3.40	4.62	5.75	1.92	9.27
7.7 ± .1	7.68	3.71	6.80	5.56	2.15	24.5

$\log K_{p1} = 0.443\ pH + 0.30$ $\log K_{p2} = 0.364\ pH - 0.65$

* Expressed in terms of total solution phase copper, Cu_{TS} rather than free copper ion, $[Cu^{2+}]$. The log ${}^{c}K$'s would be higher by the value of $p\alpha_o$ at the given pH if they were expressed in terms of free copper (refer Chapter 3).

mg copper per g EHS. On consideration of the {EHS}:Cu_{TS} ratios, it now becomes evident that the highest energy sites would have been significantly depleted in the experiments which generated the data plotted in Figure 5.16.

Most studies of copper binding by natural organics and humic substances have been performed at relatively low pH for operational reasons but van den Berg and Kramer (1979b) have compared their own and others reported log K's for copper binding by various humic-type materials at near-neutral pH. Although it is difficult to make this kind of comparison in a simple way given the wide range of sources of the organics and different techniques of measurement in different aqueous media, the log K_1's obtained in the present study appear to be about average compared with the reported values (usually in the range: 7-9 log units). The pH trend of the log K's is also consistent with other studies given that the slope would be somewhat higher than the coefficients in the regression equations in Table 5.1 if the change in log α_o for copper with pH was accounted for (Chapter 3). The difference between log K_1 and log K_2 is similar to that observed by Sunda and Hansen (1979) for river water organics. The K_{p1} predicted at pH 8 from the regression line is about 7000 $L.g^{-1}$, much higher than Oakley's (1980) figure of 366 $L.g^{-1}$. It is possible that there is a real difference in specific affinity of the EHS and the humic acid employed by Oakley. Alternatively Oakley may not have been working in the linear partitioning region for the highest energy sites.

6. EFFECTS OF PHASE INTERACTIONS

6.1 RATIONALE

6.1.1 Background

Geochemical phases are associated to a greater or lesser degree in sediments and soils. The question arises as to the extent the constituent phases can be considered as independent sinks for trace substances of environmental concern in natural waters. If indeed the phases act as independent sinks then it should be possible to predict the partitioning of metals and other trace constituents in sediments of known composition based on studies of the affinity for phases in isolation. However, if phase interactions affect partitioning, most probably by reducing the size of the overall sink, this approach may not be valid. Thus it seemed important within the scope of the present study to examine the effects of some phase interactions occurring in estuarine sediments on metal binding.

Figure 6.1 serves as a conceptualization of possible solid phase interactions in estuarine sediments. The interactions represented could involve any or all of the end members: coulombic, covalent, van der Waals or hydrogen bonding, as with interactions between soluble molecular or ionic species. Coulombic interactions may be of greatest importance because of the comparatively long range of these forces while the formation of short range chemical bonds between solid surfaces may be sterically limited. In any case, chemical bonding may tend to give rise to a new phase. In principle some degree of interaction between all pairs of phases is possible. However, based on what is known about associations of different soil and sediment components from selective extraction studies on natural deposits and from laboratory studies of pure phases or minerals it is possible to identify the stronger interactions. Interactions of each phase with the other four (giving ${}^{5}C_{2}$ = 10 combinations) are now considered in turn.

Iron oxides of the poorly-ordered ferrihydrite type may have a PZC similar to that of fresh Fe(III) oxide precipitates (about 8) thus

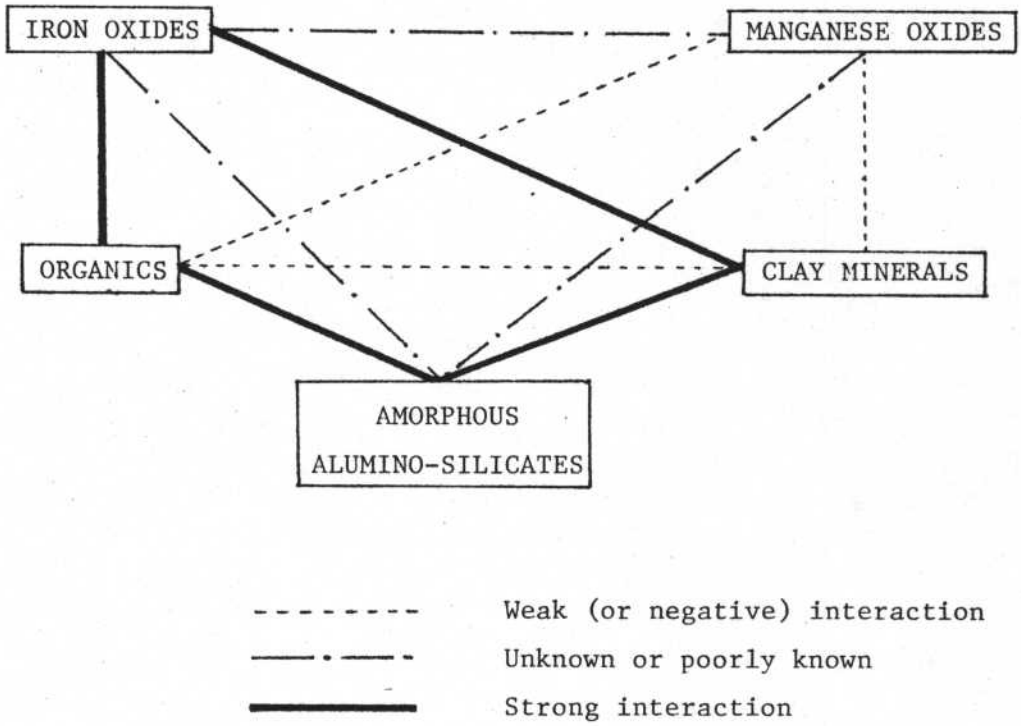


Figure 6.1 Interactions Between Various Sedimentary Phases.

these phases are neutral or positively charged over the pH range of estuarine sediment porewaters and would be expected to interact coulombically with negatively charged clays, organics and manganese oxides. Manganese tends to become separated from iron in geochemical cycling (indeed, in estuaries the manganese:iron ratio is much lower than in soils), however, Jenne (1977) cites several studies which suggest that the two metals can form coprecipitates in the natural environment. As indicated in Figure 6.1 it is not known whether *preformed* oxides interact to any extent.

Jenne (1977) discussed the reported evidence that iron concentration correlates well with the clay (< 2 μm) content of soils and sediments. Follett *et al* (1965 a,b) presented electron micrographs showing that iron in soil clay fractions was present as small grains imbedded in a matrix of amorphous material (mostly aluminosilicates) coating the crystalline clay components. Clay-iron complexes have been synthesized in the laboratory. An elegant study of iron-kaolinite systems by Follett (1965) using electron microscopy showed that spherical ferric polycations coated the silica surfaces of Kaolinite but not the alumina surfaces. Since the adsorption of iron was not inhibited by various electrolytes and there was no IR evidence for chemical bonding, while ferric particles were transferred when uncoated kaolinite was mixed with coated clays, Follett suggested that the interaction was primarily coulombic. The reactions of smectite and vermiculite clays with iron and aluminum hydrolysis products have been shown to result in the formation of hydroxy-interlayers thus giving rise to chloritic clays (Coleman *et al*, 1964: Castea *et al*, 1970 a,b; Tullock and Roth, 1975). The stability of these interlayers seems to increase with aging, apparently when partial ordering of the hydroxy-cation particles occurs. These studies suggest that much of the iron in sediments will exist as partial coatings, including interlayers, on clay mineral particles.

The interaction of iron oxides and aluminosilicates is indicated as "poorly known" in Figure 6.1, since there is less relevant evidence than for other interactions involving iron. As was mentioned above, Follett *et al* (1965 a,b) have reported that iron in some soils exists as small spheroids imbedded in an amorphous aluminosilicate matrix.

Extraction of this material with base prior to extraction by citrate-dithionate enhanced iron removal. A chemical bonding mechanism rather than an electrostatic interaction is implied. Aluminum is known to substitute in hydrous iron oxides and silicon is known to coprecipitate with iron as well as aluminum. As Jenne (1977) has stated, no information is available on the chemical properties of the ferroallophanes resulting from the inclusion of iron in amorphous aluminosilicates.

Humic materials, representing the bulk of soil and sediment organic material, are known to form very stable complexes with unhydrolyzed iron (Gamble and Schnitzer, 1973; Schnitzer, 1969), with ferric hydroxy-cations (Schnitzer and Skinner, 1964; Levashkevich, 1966; Rashid, 1974; Pickard and Felbeck, 1976) and with iron oxides (Parfitt *et al*, 1977; Kodama and Schnitzer, 1977) suggesting the possibility of strong associations of iron and organics in sediments. This is borne out by studies of natural systems (Jackson, 1975; Jenne, 1977). Schwertmann and Fischer (1973) reported that natural ferrihydrites contain appreciable quantities of organic carbon. The ratio: (iron + aluminum)/organic carbon is very nearly a constant for river waters (Perdue *et al*, 1976) and soil extracts (McKeague and Day, 1966; Wada and Higashi, 1976) suggesting the ubiquitous occurrence of organic complexes of iron and aluminum. Krom and Sholkovitz (1978) found that iron in pore waters of marine sediments was strongly associated with organics and the laboratory studies of Aston and Chester (1973) and Sholkovitz, Boyle and coworkers (1976, 1978) suggest a coflocculation mechanism acts to trap iron and organics in estuaries. Studies by Theis and Singer (1973) show that oxidation of Fe(II) is greatly inhibited by various organics although the stability of ferrous-organic complexes is not so high as that of ferric complexes. This mechanism may be operative in delaying formation of Fe(III) on overturn of estuarine sediments. Organic materials are also known to attenuate the rate of crystallization of hydrous ferric oxides (Schwertmann, 1966; Kodama and Schnitzer, 1977).

Manganese hydrous oxides seem unlikely to interact with clays and organics because of the mutual repulsion of negative surface charges.

This is supported by the finding that manganese does not correlate with clay content of soils and sediments and that most of the manganese frequently occurs in the silt-sized fraction. Thus hydrous manganese oxides probably occur as discrete particles rather than as coatings on clay minerals (Jenne, 1977) although the possibility seems to exist that Mn may be incorporated to some extent in the hydroxy-iron or aluminosilicate coatings on clays. Since the higher oxides of manganese are strong oxidizers they may destroy organics with which they come in contact.

Clay minerals are known to be coated with varying amounts of poorly-ordered oxides of aluminum and silicon as discussed in Chapter 4 wherein a strong interaction is indicated (Figure 6.1). Much of the available evidence has been reviewed by Jenne (1977).

There is a great deal of information regarding the interaction of organics, including humic substances, with clay minerals (Greenland, 1971; Theng, 1979). Adsorption of humics (and presumably other anionic organics) on clays is pH dependent being much greater at low pH's (around the apparent pK_a value, about 4.0) than at the near-neutral pH's more characteristic of natural aquatic systems. As pH rises above the pK_a adsorption falls due to the negative clay surface's repulsion of the increasingly negative humics (Schnitzer and Kodama, 1966, 1977). Expanding layer clays may absorb humics between layers at low pH but the structure collapses on increase in pH (Schnitzer and Kodama, 1966). Rashid *et al* (1972) found that adsorption of a marine humic acid on clay minerals in $35^{o}/oo$ NaCl solution was greater than in fresh water but still low, suggesting that interaction of organics with clays in seawater may be slight. These authors proposed a model wherein coulombic repulsion of negatively charged organic particles occurs until the two surfaces approach sufficiently closely to experience van der Waals attractive forces and/or undergo chemical bond formation. The greater interaction of clays and organics in the high ionic strength medium was attributed to compression of the electric double layers (and thus reduction of the repulsive coulombic forces). Overall the bonding of clays with predominantly negatively-charged organics seems to be slight at near-neutral pH's (Figure 6.1).

However, this conclusion is somewhat problematical in the light of observations that organic content of sediments and soils often correlates with clay (< 2 μm) content (Hedges, 1977). Rashid *et al* (1972) suggested that chemisorption of organics on clays may increase with time, particularly where physical adsorption is favored, thus mature sediments might be expected to contain chemically-bonded clay-organic complexes. It is well known that on drying of clay-organic mixtures chemically-bonded stable complexes result. However, while chemisorption might be important in deep marine sediments, particularly those compacted on deep burial, it may not have significance in geologically-young estuarine sediments. A more likely explanation is cation bridge formation in which unhydrolyzed metal ions neutralize organic anions and allow approach of the organic particles to the clay surface (Greenland, 1971). If this kind of bridging occurs with the cations Ca^{2+} and Mg^{2+} Rashid *et al*'s (1972) data for humic-clay interactions in NaCl solution may not be readily applicable to seawater. A related kind of phenomenon to cation bridging, possibly of even greater significance, is the formation of clay-hydroxy metal-organic complexes as discussed by Greenland (1971). In this case formation of an iron or aluminum hydroxy cation coating is followed by complexation of the hydroxy-metal layer by organics, thus giving rise to a stable ternary complex (Greenland, 1971; Levy and Francis, 1976).

Finally, there is evidence that poorly-ordered oxy-hydroxides of aluminum and silicon, as well as those of iron, are strongly associated with organics (Figure 6.1). Allophanic clays strongly retain organic matter in soils (Wada, 1977). Both unhydrolyzed aluminum and aluminum hydroxy-cations are strongly complexed by humic-type organics (Schnitzer and Skinner, 1964; Levashkevich, 1966; Schnitzer, 1969; Gamble and Schnitzer, 1973). Adsorption of humic substances on crystalline aluminum oxides and the partially-ordered allophanic aluminosilicate, imogolite has also been studied (Parfitt *et al*, 1977; Davis, 1980).

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6.1.2 Selection of Solid Phase Interactions for Study

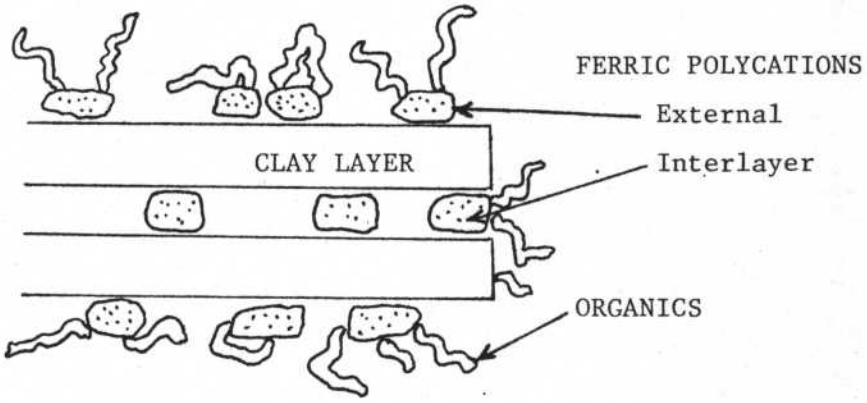
Consideration of metal binding in combined solid phase systems immediately creates a spectrum of new research problems. At trace concentrations the total uptake of a heavy metal present *prior* to solid phase interactions may be simply the sum of the uptake expected with the isolated phases, however, when the trace metal comes into contact with a preexisting solid phase complex total metal uptake is more likely to be attenuated. Isolation of solid complexes for characterization studies may be problematical where the stability of these complexes is relatively low, although it might be argued that weak solid-solid interactions may have little significance with regard to metal binding. A decision needs to be made whether to study total metal uptake in systems in which phases of interest are simply combined and allowed to react *prior* to metal dosing or to attempt to isolate the solid complex *before* metal dosing (in which case disproportionation will occur if formation of the complex is reversible). Further, it is likely that the stability of a solid complex in a high ionic strength (and, possibly, interacting) medium such as seawater may be different than in a dilute aqueous medium as in the case of the humic-clay complexes studied by Rashid *et al* (1972). Finally, a whole gamut of kinetic problems with respect to formation of solid complexes and trace metal binding are suggested: aging and partial ordering of hydrous metal oxides, catalysis of reactions, relative kinetics of trace metal binding and solid complex formation (at sites of competition) and steric hinderance of trace metal migration to binding sites in solid complexes.

To make some progress in such a morass of research problems requires choice of a relatively few situations where the opportunity for generality and the yield of relevant information are expected to be high. Fortunately the results of the metal binding studies on isolated solid phases (Chapter 5) in the light of the above review of phase interactions allows identification of those interactions best meeting these criteria. Since hydrous iron oxides are indicated as the most important sink in estuarine sediments with respect to their functioning

as heavy metal sinks, interactions with iron are immediately seen to be of dominant interest. Iron associates strongly with clays and organics as has been reasonably well documented but the degree of interaction with hydrous manganese oxides and with disordered aluminosilicates in forming ferroallophane is not well known. Thus it was decided to concentrate on simulating the involvement of iron in three types of complex:

1) Clay Mineral - Hydrous Iron Oxide (hydroxy-iron interlayered clay).
2) Hydrous Iron Oxide - Organic
3) Clay Mineral - Hydrous Iron Oxide - Organic.

These three types of complex are thought to be common in the natural environment and, specifically, in estuarine sediments. We may envision the structure of the ternary complex between an expanding layer clay mineral, an iron-hydroxy cation coating and humic-type organics as being something like this:



6.2 CLAY - IRON COMPLEXES

6.2.1 Formation and Characterization of Clay-Iron Complexes

Three methods for the preparation of hydroxy-interlayers in expanding clay minerals are reported in the literature. Carstea *et al* (1970) compared the "titration" method in which the clay suspension is stirred during simultaneous addition of base and iron (or aluminum) at equivalent rates with a method in which the clay is simply dried at

80°C with the requisite quantity of metal. The "titration" method was considered superior and was also used by Coleman *et al* (1964) and Levy and Francis (1976). Tullock and Roth (1975) synthesized hydroxy-interlayers by titrating a stirred clay suspension with acid to pH 2.5, adding the required amount of metal salt then adding base to bring the pH back to neutrality. pH 2.5 may be considered a compromise between the tendency for dissolution of the clay mineral lattice at lower pH and the hydrolysis of Fe(III) at higher pH. The method of Tullock and Roth was adopted in this study since it avoids the need for critical flow control as with the titration method.

Since iron phases and clays may occur at very different relative concentrations in estuarine sediments, hydroxy interlayers at three different Fe:clay ratios were synthesized. In each case the suspension obtained was prepared for adsorption studies at the *same* iron concentration but at differing clay concentrations (Table 6.1). The range of ratios (expressed in milli-equivalents of metal per gram of clay) investigated by the above-mentioned workers was also used in this study. At the time of preparation of the iron-clay complexes a suspension of hydrous iron oxide containing no clay was also prepared (refer Chapter 4) and aged for 24 hours. A portion of this material was used to prepare physical mixtures of hydrous iron oxide and clay; the rationale being that where the montmorillonite contacts *preformed* oxide particles it is unlikely that iron will be able to move to interlayer positions. The physical mixtures at the same iron:clay ratios as the complexes were used as controls (blanks).

The detailed method of interlayer formation was as follows:

1) Clay suspensions at the required concentrations in distilled water were titrated to pH 2.5 with continuous magnetic stirring.
2) A standard Fe(III) solution was prepared at a pH of 2.5 and added to the clay suspensions.
3) The mixture was titrated to pH 8 over a period of an hour with 0.1 M NaOH using a procedure identical to that for preparation of an isolated hydrous ferric oxide phase (Chapter 4).

Table 6.1

IRON:CLAY RATIOS IN SYNTHETIC INTERLAYERED COMPLEXES AND MIXTURES

Code	Iron:Clay Ratio	Concentrations in Final (SW) Suspension (Cd experiments)	
		Iron ($g.L^{-1}$)	Clay ($g.L^{-1}$)
A	1 meq Fe . g^{-1} clay (18.6 mg Fe . g^{-1} clay)	0.1023	5.50
B	4 meq Fe . g^{-1} clay (74.5 mg Fe . g^{-1} clay)	0.1023	1.375
C	16 meq Fe . g^{-1} clay (298 mg Fe . g^{-1} clay)	0.1023	0.344

4) The product was aged 48 hours with pH adjustments over the first four hours.

The main method of characterization of the iron-clay complexes was by X-ray diffraction. Figure 6.2 shows X-ray diffractograms of complexes compared with those of the physical mixtures (preformed hydrous iron oxides plus clay) using standard conditions of slide preparation. It is worthy of note that during the cation saturation procedure the centrifuge plugs of the "mixtures" were observed to have a mottled appearance with stratification of clay and iron oxide whereas the "complexes" appeared homogeneous, suggesting that indeed the complexes had a different nature from the mixtures. The diffractograms for the K-saturated (105°C) complex had a broad peak appearing as a shoulder with a range of basal spacings above 10 A^{o} compared with the mixture which produced a simple peak centered at 10 A^{o}. The effect of the iron phase was merely to produce a lower more diffuse peak than in diffractograms (not shown) of the clay alone. Heating the slides to 300°C tended to reduce the shoulder in the diffractograms of the complexes suggesting rather low thermal stability. Further heating to 550°C (as expected) resulted in total collapse. These results are in general agreement with those of workers such as Carstea *et al* (1970) and confirm that poorly-ordered interlayers were present. Since aging for a matter of months is known to increase interlayer stability (Carstea *et al*, 1970) and iron has been found to form less stable interlayers than aluminum (Carstea *et al*, 1970; Tullock and Roth, 1975) it is not surprising that the interlayers formed in this study were of rather low stability. Little extra information was obtained from the Mg-saturated slides in that peak positions were not very different for the mixture and complex (Figure 6.2), that is no definite chlorite-type behavior was observed on glycerol saturation. However, the fact that peaks for the complexes were broader and lower than for the mixture (which in turn had lower and broader peaks than the pure clay) is consistent with the presence of interlayers with a spectrum of basal spacings.

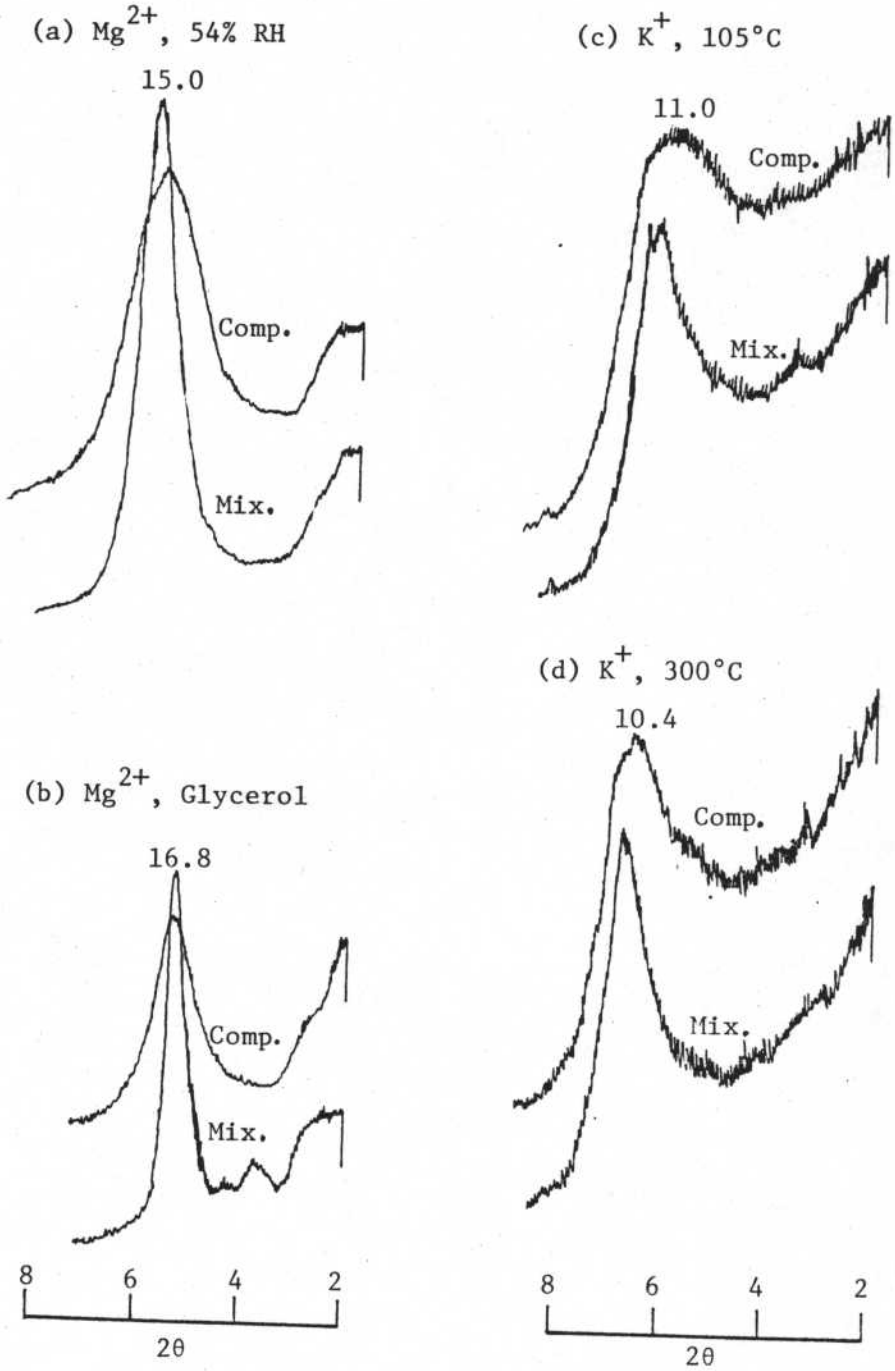


Figure 6.2. X-Ray Diffractograms of an Iron-Clay Mixture (Mix) and an Iron-Clay Complex (Comp), Both at 16 $meq.g^{-1}$ Clay.

6.2.2 Cadmium Uptake by Synthetic Iron-Clay Complexes

Cadmium adsorption experiments with hydroxy-interlayered montmorillonite were performed in the usual way (Chapter 5). The total concentration of iron was 0.1023 $g.L^{-1}$ (as iron) in all suspensions (Table 6.1) and Cd_T was either 2.8 or 7 $\mu g.L^{-1}$ (refer Appendix D). Since the affinity of montmorillonite for cadmium is so low, uptake by this phase can be neglected for the purposes of comparison of uptake by the clay-iron mixtures with that by the corresponding complexes.

Figure 6.3 shows adsorption data for the complexes and mixtures compared with uptake by the iron phase in isolation (regression line obtained from data in Appendix D). It is apparent that the clay has no significant effect on the affinity of iron oxide for cadmium, that is iron occurring as interlayers in montmorillonite has the same cadmium affinity as an isolated iron phase or iron associated only with external layers of clay (as in a physical mixture).

It might reasonably be expected that the kinetics of cadmium uptake by hydroxy-iron interlayers would be slower than for isolated iron phases. Short-term kinetics were not examined in this study so nothing can be said regarding possible attenuation of reaction rate by the presence of the clay, however, that the systems had reached apparent equilibrium at 20 hours was confirmed by results for tubes incubated for a total of 14 days. After this time total cadmium uptake had increased somewhat probably due to aging processes as suggested by the studies of Anderson (Civil Engineering Dept., University of Washington, pers. comm.) but the cadmium uptake by the iron-clay complexes was apparently still identical to that by the isolated iron phase.

The somewhat surprising results of these studies are of major importance since they suggest that natural hydroxy-iron interlayers will behave like "free" iron oxide phases (of the same degree of ordering) with respect to metal partitioning. Apparently sites on iron in interlayer positions are equally available to cadmium as sites on isolated iron phases. Further, aged hydroxy-interlayers seem to behave identically to aged iron phases in isolation with respect to cadmium.

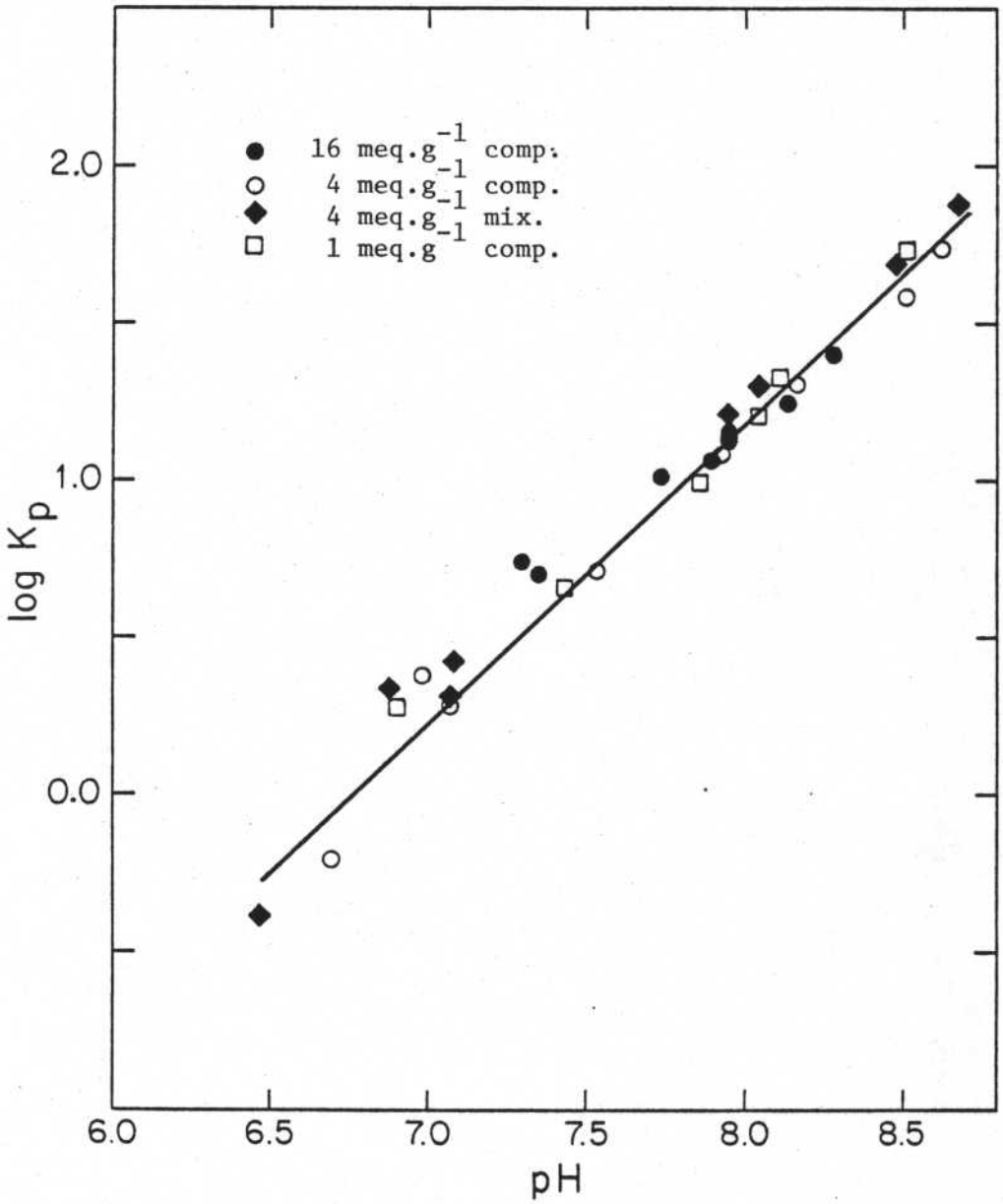


Figure 6.3. Cadmium Uptake by Iron-Clay Complexes and Mixtures in Artificial Seawater. Regression Line is for Iron Phase in Isolation.

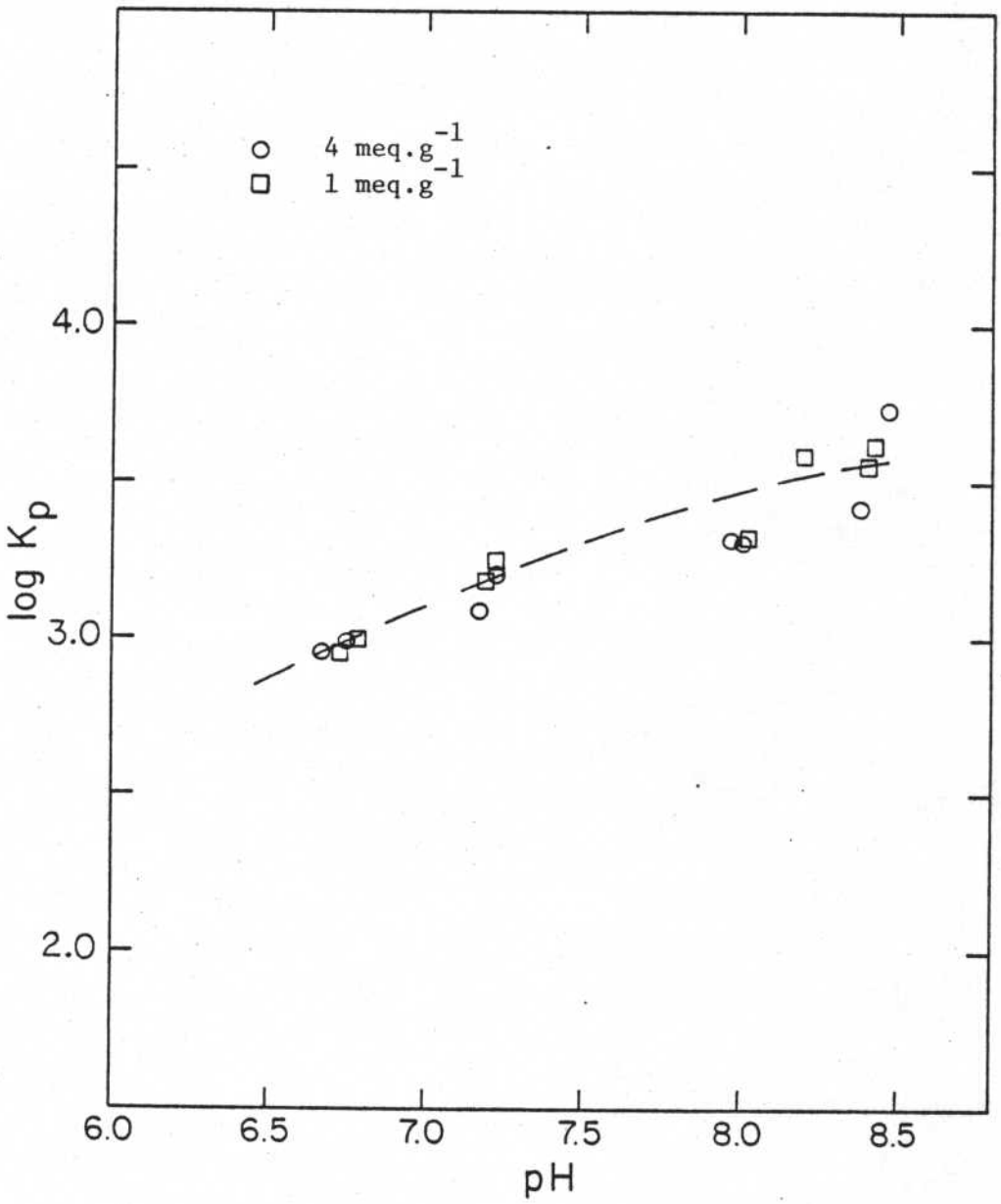


Figure 6.4. Copper Uptake by Iron-Clay Complexes in Artificial Seawater.

6.2.3 Copper Uptake by Synthetic Iron-Clay Complexes

Copper adsorption experiments were performed with suspensions of iron-clay complexes at 4 meq Fe . g^{-1} clay and 1 meq Fe . g^{-1} clay and at total copper concentrations of 7 and 28 $\mu g.L^{-1}$. Iron in all cases was at a concentration of 0.8181 $mg.L^{-1}$. Figure 6.4 shows the K_p(pH) plot for the data in Appendix D. The points for the complexes tend to fall close to the line for the iron in isolation but there is too much scatter in both sets of data to allow firm conclusions to be drawn. However, the data appear to be consistent with those for cadmium in that the clay-iron interaction does not appear to materially affect metal binding.

6.3 IRON - ORGANIC ASSOCIATION

6.3.1 Sorption of EHS by Hydrous Iron Oxide

For the purposes of manufacture of an iron-organic complex an iron phase was first synthesized using the method outlined in Chapter 4. After 24 hours aging the hydrous iron oxide was washed into seawater suspension and then estuarine humic substances (EHS) were added (also in seawater medium) and allowed to sorb on the iron phase for a further 24 hours before metal uptake experiments. Three different iron:organic carbon ratios were used (Table 6.2).

That the sorption reaction went to completion in much less than 24 hours was verified by following pH relaxation with time after addition of the EHS to an iron suspension of the same initial pH. The rise in pH due to consumption of protons was initially very rapid and reached an apparent equilibrium in less than 30 minutes. Simultaneously the supernatant decolorized from a dark brown to a pale yellow.

Unfortunately, isolation of the iron-organic phase for characterization purposes was not practicable since there is no simple non-destructive method of separation of colloidal-sized iron particles from unreacted humic particles. If centrifugation is used some (insoluble) proportion of the humic material will be admixed with the iron and sorbed humics. Filtration or ultra-filtration is similarly

Table 6.2

ORGANIC CARBON:IRON RATIOS IN IRON-EHS COMPLEXES

Code	Organic Carbon:Fe	Concentrations in Final (SW) Suspension (Cd experiments)	
		Iron ($g.L^{-1}$)	Organic Carbon ($g.L^{-1}$)
A	12:1	0.1023	0.0086
B	2:1	0.1023	0.052
C	3:1	0.1023	0.309

likely to be unsuccessful although it is possible that an electrodialysis technique making use of net charge differences between iron-organic complexes and unreacted organics might be useful.

For present purposes, to gain some insight into the nature of the iron-organic complex, an experiment was designed to examine sorptive uptake of the *soluble* fraction of the EHS (in seawater medium). The rationale was that, assuming the soluble fraction of the EHS has essentially the same functional groups as the insoluble portion, although in a different region of the total spectrum of humic properties (an assumption which appears justified for humic-type materials, Schnitzer and Khan, 1972; Jackson, 1975), the sorption of the total humic isolate should follow the same pattern as that of the soluble fraction.

The sorption experiment was performed in an analogous way to the experiments with metal uptake (Chapter 5). A mixture in seawater of hydrous iron oxide (at a constant concentration of 0.1023 $g.L^{-1}$ Fe) and EHS (at three different iron:organic carbon ratios as in Table 6.2) was added to each of 18 centrifuge tubes. The tubes were adjusted to a range of values of initial pH. A further set of tubes contained no iron and were used as blanks. After an incubation time of 20 hours at 20°C pH was measured and the tubes were all centrifuged on an IEC 20 refrigerated centrifuge for 10 minutes at 20,000 g. The solution phase humic content was assayed using absorbance at several different wavelengths in the near ultraviolet. Since the absorbances at the different wavelengths were very highly correlated the data presented are based on measurements at 250 nm only. Fractional adsorption was expressed simply:

$$f = \frac{A_b - A_s}{A_b}$$

where A_s is absorbance of the supernatant in the sample tubes and A_b that of the supernatant in the corresponding blank tubes.

Figure 6.5 shows the fractional adsorption of soluble (in seawater) EHS as a function of pH. The circled data point (1:12 organic carbon to iron ratio) probably reflects an error in assay of the low concentration of EHS. The fractional uptake of humic material

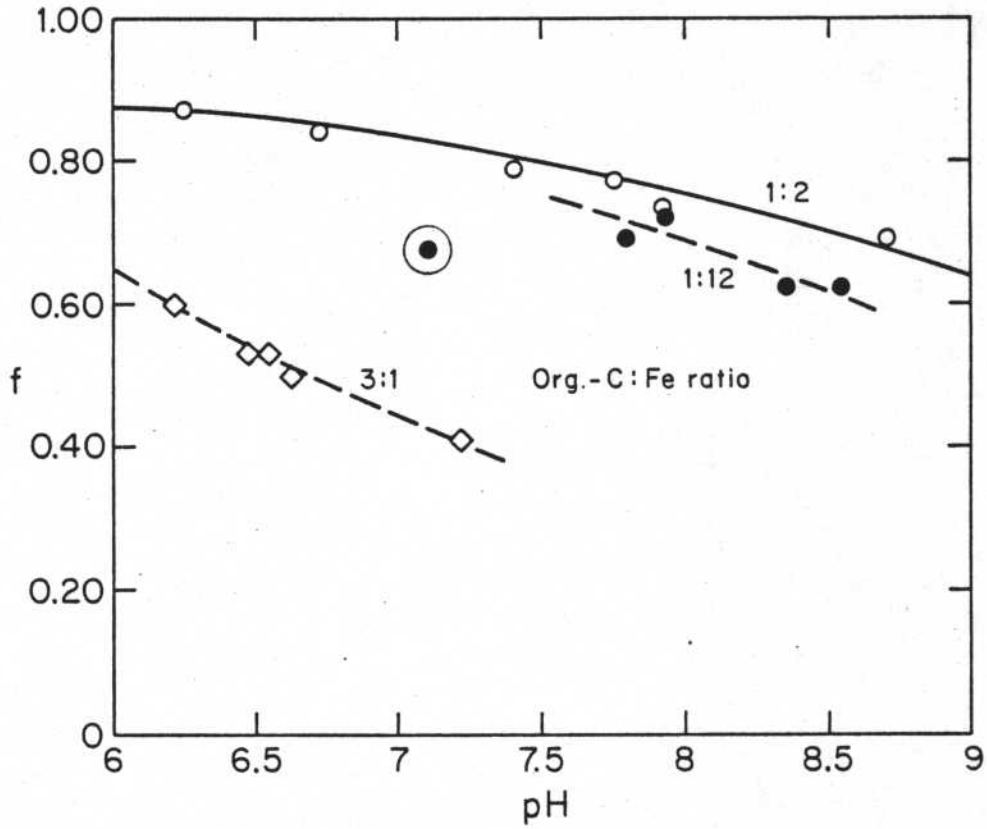


Figure 6.5. Fractional Adsorption of Soluble EHS Fraction by Hydrous Iron Oxide in Artificial Seawater at Different Organic Carbon to Iron Ratios.

decreased with increase in pH as usual for an anionic adsorbate. The adsorption edge at the two lower EHS concentrations was not nearly so steep as might have been expected and appeared to be levelling off at about 90% rather than 100%. This suggests that perhaps 10% of the *soluble* fraction of the EHS was not adsorbable by the iron phase even under highly favorable conditions of low pH and low organic carbon to iron ratio, and is in line with Davis' (1980) finding that a proportion of lake fulvic acid was not adsorbable on alumina. It is interesting that although the 3:1 sorption edge is much lower than for the 1:2 and 1:12 ratios it still represents approximately 50% uptake of EHS which means that the iron phase (about 54% iron) is sorbing considerably more than its own weight in organic matter (about 49% carbon). Since the higher molecular weight EHS fraction is likely to have an even greater affinity for solid/liquid inferfaces than the soluble fraction, total fractional uptake by the whole EHS isolate may be even higher than that of the soluble portion.

An adsorption experiment of similar design to the above but performed in 0.1 M $NaNO_3$ solution rather than seawater and using only the "fulvic" fraction of EHS gave similar results, suggesting that the composition of seawater has relatively little effect on humic uptake by iron phases.

6.3.2 Metal Uptake by Synthetic Iron-EHS Complexes

Cadmium uptake by iron-humic complexes and by a blank containing no EHS at three different organic carbon:iron ratios (Table 6.2) was studied. Total iron concentration was 0.1023 $g.L^{-1}$ as iron in all suspensions. The total measured uptake of cadmium by the complexes was compared with the predicted uptake of iron plus EHS assuming that these two components act as independent phases in mixtures.

If indeed the mixture of EHS and iron act independently towards cadmium we can write a mass balance on total cadmium:

$$Cd_T = Cd_{TS} + [\equiv Fe - Cd] + [EHS - Cd] \qquad (6.1)$$

where Cd_T and Cd_{TS} are the total cadmium and total solution phase

cadmium concentrations respectively, and ≡ Fe - Cd and EHS - Cd represent the bound cadmium. Since (refer Chapter 3):

$$K_{p,Fe} = \frac{[\equiv Fe - Cd]}{Cd_{TS}\ \{\equiv Fe\}} \quad \text{and} \quad K_{p,EHS} = \frac{[EHS - Cd]}{Cd_{TS}\ \{EHS\}} \tag{6.2}$$

we have:

$$Cd_T = Cd_{TS}\ (1 + K_{p,Fe}\ \{\equiv Fe\} + K_{p,EHS}\ \{EHS\}) \tag{6.3}$$

which can be solved for $K_{p,Fe}$:

$$K_{p,Fe} = \frac{\frac{f}{1-f} - K_{p,EHS}\ \{EHS\}}{\{\equiv Fe\}} \tag{6.4}$$

in which:

$$\frac{f}{1-f} = \frac{Cd_T - Cd_{TS}}{Cd_{TS}} \tag{6.5}$$

(6.4) was used to calculate values of $K_{p,Fe}$ using the measured values of f and pH and the known values of $K_{p,EHS}$(pH), {EHS} and {≡ Fe}.

Figure 6.6 shows the data calculated as outlined above compared with the regression line on the data (refer Appendix D) obtained for the iron phase in isolation. The data suggest that the affinity of iron for cadmium is undiminished by the presence of sorbed humic material.

This result is in accord with a model of the iron phase as a porous gel consisting of an open structure produced by aggregated spherical polycations. Such a structure would allow relatively free movement of humic particles/molecules of dimensions similar to those of the polycations. Apparently formation of the iron-organic complex does not involve occlusion of cadmium adsorption sites on either the iron or organic surfaces.

Copper adsorption experiments were not performed with iron-EHS complexes for a number of reasons. In particular, since the affinity of EHS for copper is significantly higher than that of iron, adsorption of the EHS on iron would be unlikely to greatly affect total copper uptake, even if sites on the iron particles were in fact occluded. Also, it is not possible to predict copper uptake by EHS

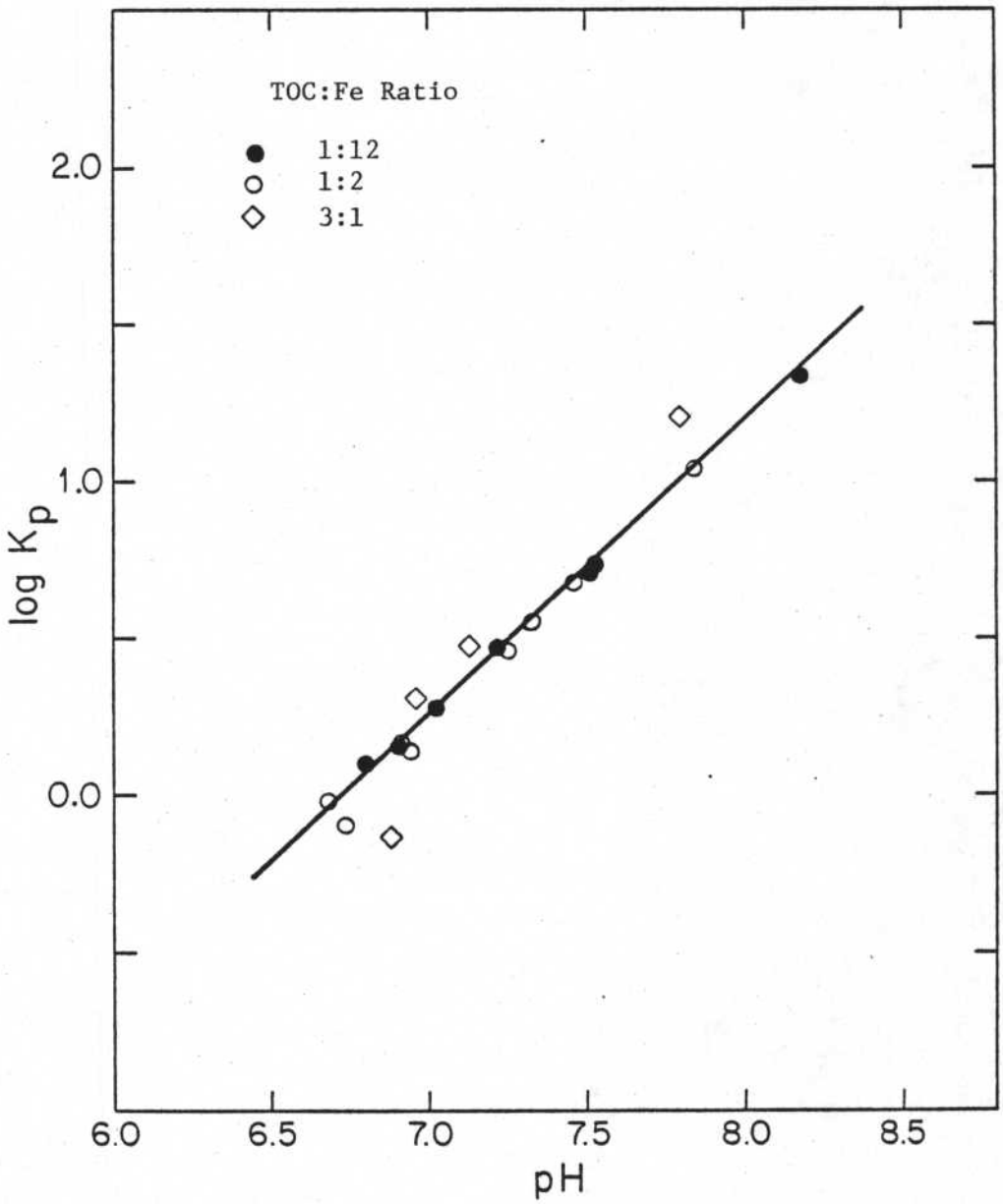


Figure 6.6. Cadmium Uptake by Iron in Iron-Organic Complexes in Artificial Seawater. Regression Line is for Iron Phase in Isolation.

accurately at pH's other than those at which the titrations reported in Chapter 5 were performed when the ratio: Cu_T:{EHS} becomes sufficiently high that significant depletion of high energy sites occurs, say when Cu_T:{EHS} is more than about 10% of n_1.

6.4 TERNARY CLAY-IRON-EHS COMPLEXES

Ternary solid component complexes between iron, montmorillonite and the EHS were manufactured by a procedure which was a logical extension of methods developed for two-component complexes. Iron-coated montmorillonite was first formed as in Section 6.2 then the interlayered clay was washed into seawater before being allowed to react with EHS. Appendix D lists the six different complexes prepared for cadmium studies. The iron-clay complexes left uncoated with organic material were used as blanks for comparison of cadmium uptake relative to that of organic-coated complexes.

Figure 6.7 shows the cadmium uptake data (no experiments were performed with copper) for the iron phase calculated assuming the iron and organic phases act independently (the uptake by the clay phase is negligible). Evidently this assumption of independence is justified since all the data plotted after correction for the EHS uptake fall closely about a line which is in the same position as expected for an isolated iron phase. Again, surprisingly, the interaction of the phases does not appear to affect equilibrium uptake of cadmium.

This result is apparently at variance with that of Levy and Francis (1976) who reported a 50% reduction in cadmium uptake when humic acid was sorbed onto an iron-coated montmorillonite and attributed this to site occlusion. However, these workers apparently did not run *simultaneous* experiments with a blank (no organic coating) and they do not state the number of data points on which their reported partitioning constants are based.

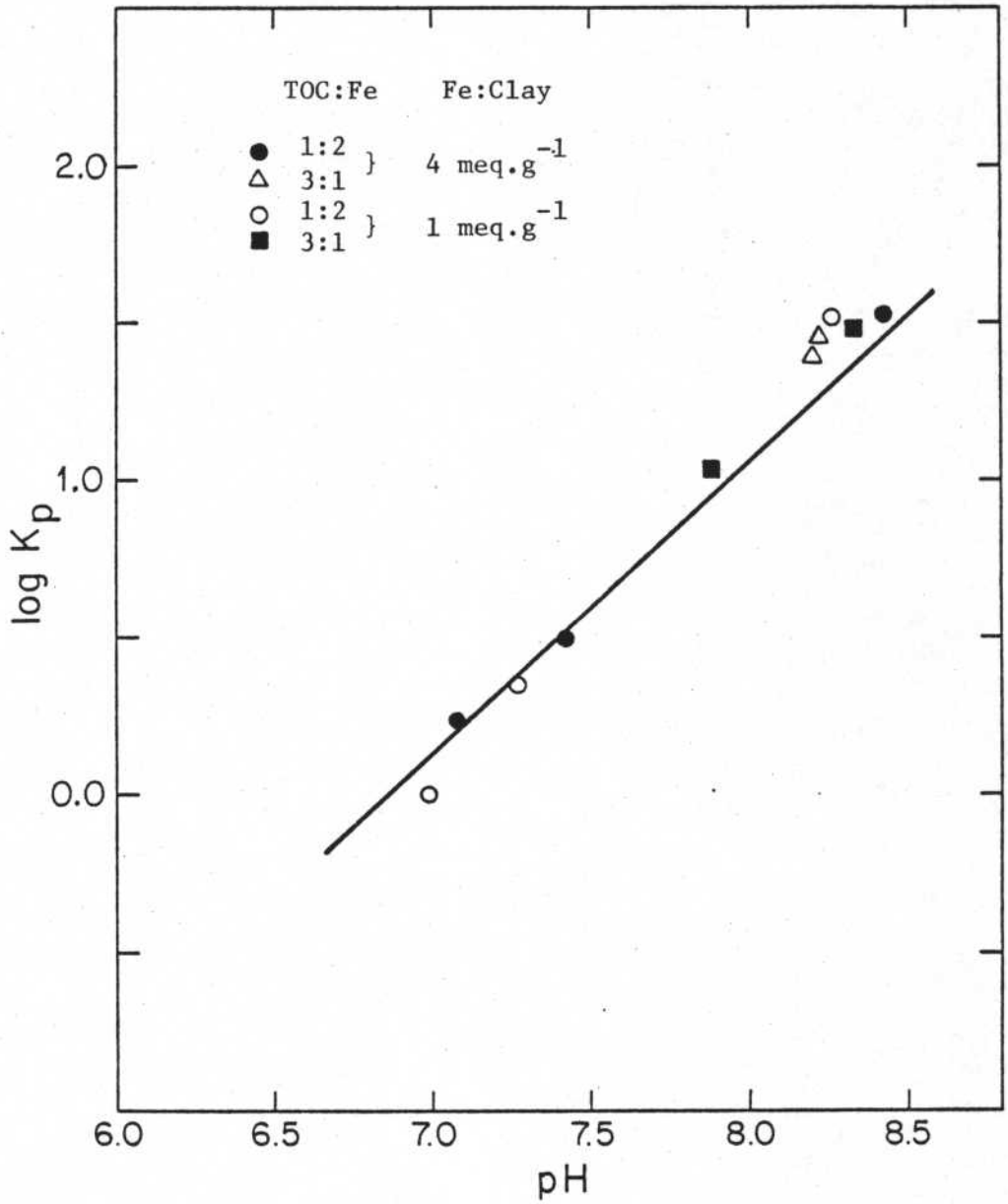


Figure 6.7. Cadmium Uptake by Ternary Clay-Iron-Organic Complexes in Artificial Seawater. Regression Line is for Uncoated Iron-Clay Complexes.

7. MODELLING TRACE METAL BEHAVIOR IN ESTUARINE SEDIMENTS

7.1 PREDICTING PARTITIONING IN ESTUARINE SEDIMENTS

7.1.1 Comparison of the Specific Affinity of Copper and Cadmium for the Various Model Sedimentary Phases

The results of the investigations into effects of selected solid phase interactions (Chapter 6) suggest that partitioning of trace metals may be independent of such interactions. Thus the partitioning in natural sediments, which can be viewed as complex assemblages of a number of (multiply-interacting) phases, may also be largely unaffected by interactions of component solids. We can be less decisive about whether or not phase interactions within sediments may affect the overall capacity of the sediments to uptake metals (that is, decrease the size of the metal sink represented by the sediments). It does seem however, that as a first approximation the size of the metal sink can be predicted on the basis of simple studies on isolated sediments such as those presented in Chapter 5.

Before attempting to predict metal distribution in sediments we will briefly compare the specific affinity of copper and cadmium for the solid phases studied in Chapters 4 and 5. The regression lines for log K_p(pH) for cadmium uptake by the model phases are plotted in Figures 7.1 (35°/oo salinity) and 7.2 (5°/oo salinity). The figures allow comparisons between the phases as to their specific affinities for cadmium (measured by K_p) and the pH dependence of this affinity (measured by the slope of the lines). Only an approximate upper bound can be given for montmorillonite clay at 35°/oo salinity since the specific affinity of this phase for cadmium is very low (Chapter 5). The specific affinities of the five phases vary by over four orders of magnitude.

Although the absolute magnitude of the specific affinity of the various phases for cadmium changes by an order of magnitude or more over the salinity range: 5-35°/oo, the relative magnitudes change only slightly and the order of this affinity remains: hydrous manganese oxides > hydrous iron oxides > estuarine humic substances >

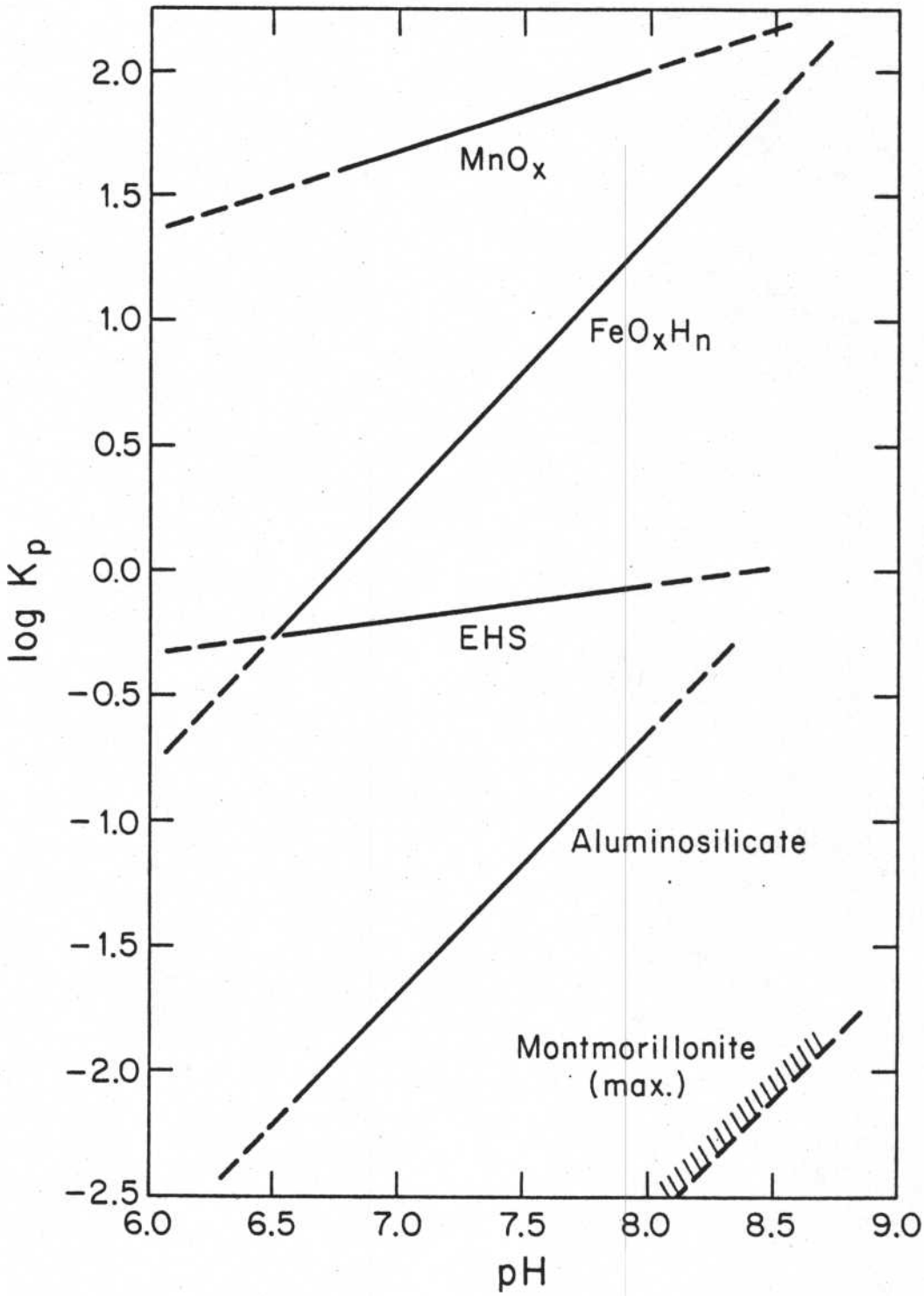


Figure 7.1. Comparison of the Specific Affinity of Model Solid Phases for Cadmium in 35°/oo Artificial Seawater.

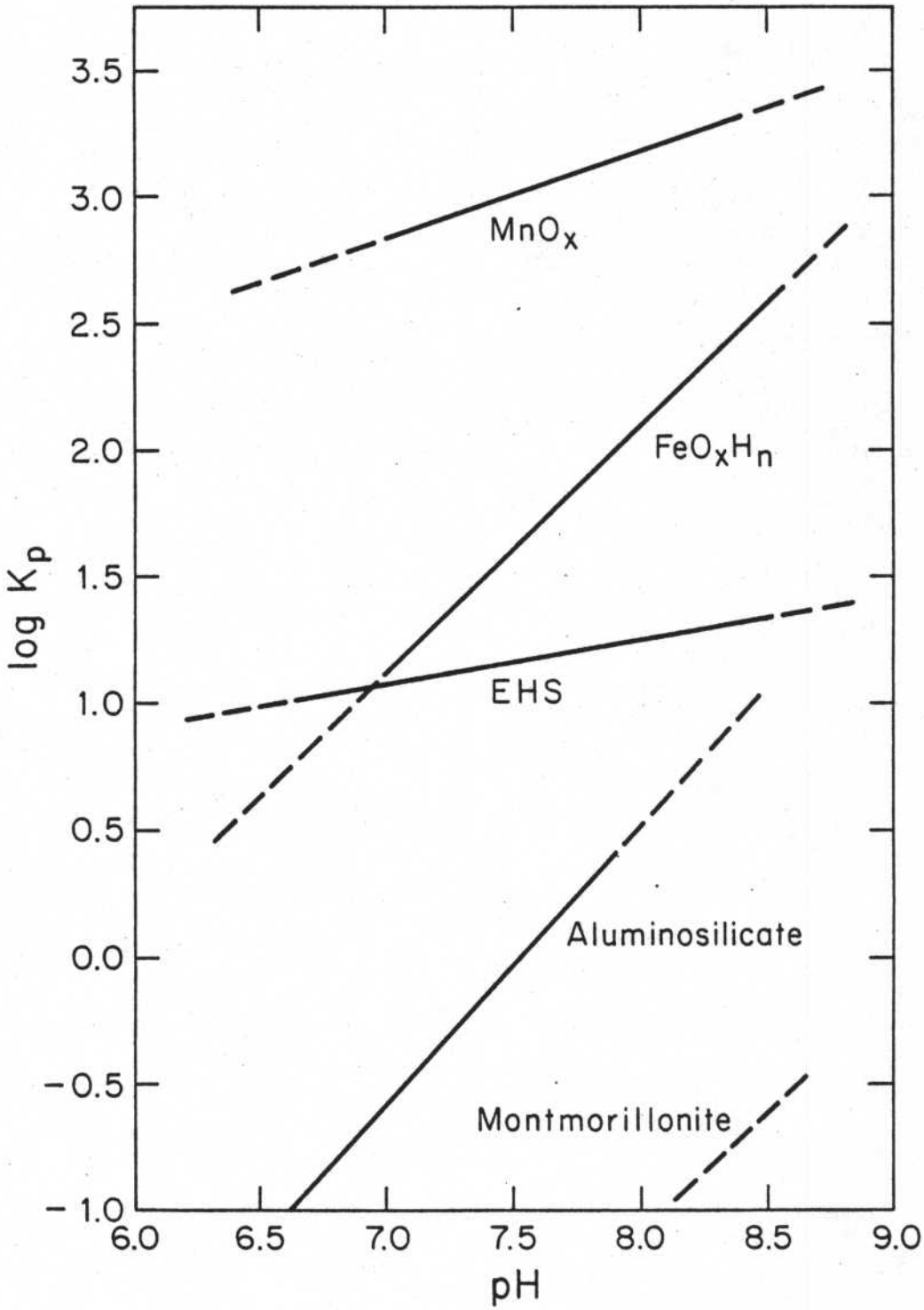


Figure 7.2. Comparison of the Specific Affinity of Model Solid Phases for Cadmium in 5°/oo Artificial Seawater.

aluminosilicates > montmorillonite clay over the range of salinities encountered in estuaries.

Figure 7.3 shows a similar diagram for specific affinity of the model phases for copper at a salinity of 35°/oo. Little change would occur with change in salinity except in the case of the hydrous manganese oxide. The lines for the EHS correspond to the first and second site type. It is apparent that the order of the model phases with regard to their specific affinity for copper is: hydrous manganese oxides > estuarine humic substances > hydrous iron oxides > aluminosilicates > montmorillonite clay. The specific affinities of the phases are much higher for copper than for cadmium. Otherwise the main difference from the cadmium diagrams is that the organics have increased in relative importance, at least where high energy sites are not depleted (Chapter 5). This is in line with a considerable body of literature (Schmidt 1978) which suggests that copper is strongly complexed by naturally-occurring organics.

7.1.2 A Model for Trace Metal Partitioning in Estuarine Sediments

Oakley (1980) has outlined a simple model for treating the partitioning of a metal in a sediment comprised of a number of different phases which is analogous to metal speciation in a solution containing a number of competing ligands. Table 7.1 shows the analogy in a systematic way using somewhat different symbolism from Oakley. The mathematical description is not identical as stated by Oakley unless higher order complexes for example: $CdCl_2^o$, $CdCl_3^-$ are considered as involving *separate* ligands (that is: Cl_2^{2-}, Cl_3^{3-}).

The model on the left side of Table 7.1 may be of utility with consideration of relatively dilute slurries of sediments that occur, for example, on dumping of dredge spoils. However, usually concentrations of natural sediment components are expressed in dimensionless concentration units, for example, percent by weight or $g.Kg^{-1}$, thus requiring a slight modification of the approach in Table 7.1.

For sediment comprised of N phases at any degree of dispersion (whether settled or suspended) we can write:

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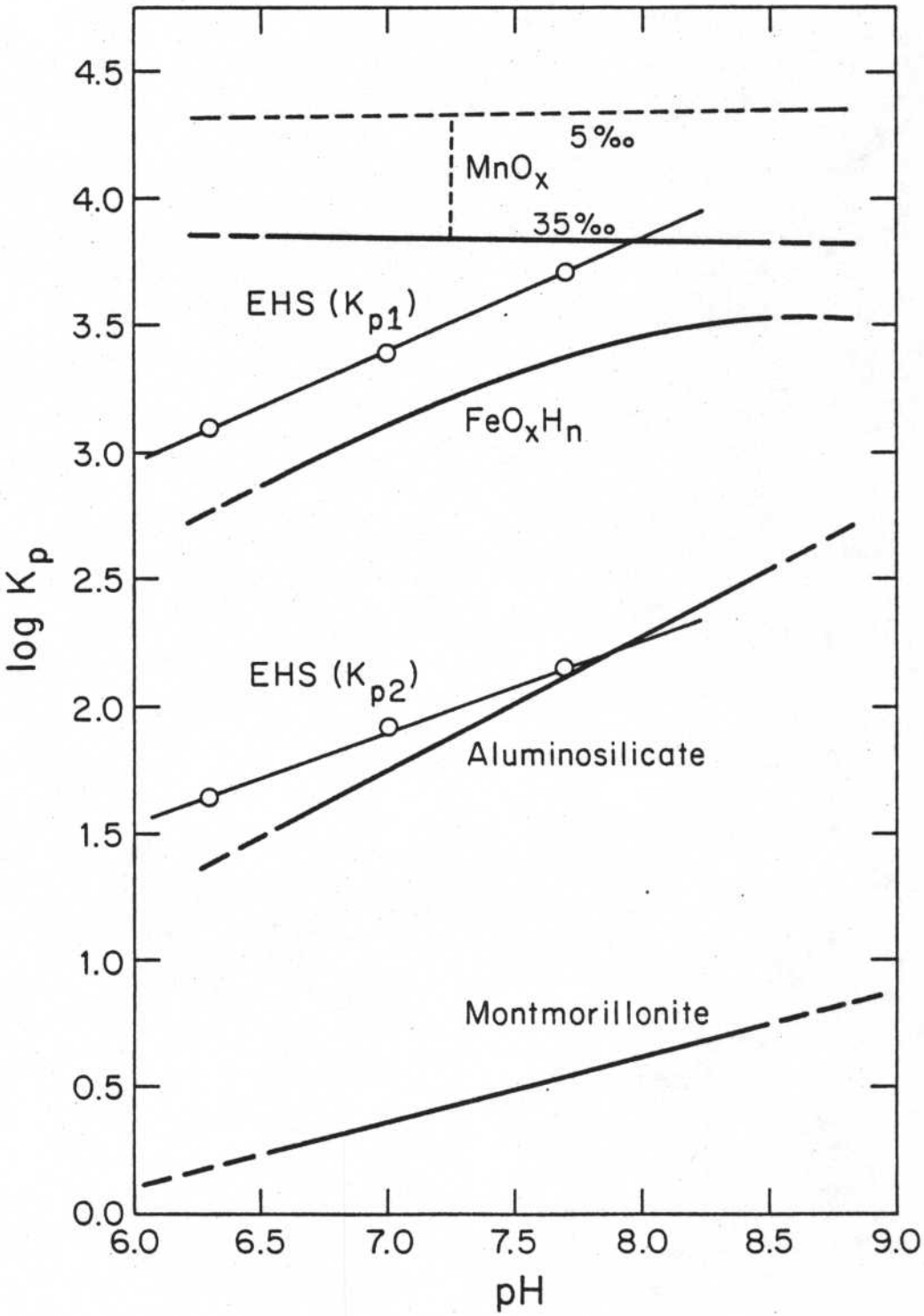

Figure 7.3. Comparison of the Specific Affinity of Model Solid Phases for Copper in 35°/oo Artificial Seawater.

Table 7.1

METAL PARTITIONING IN SEDIMENTS AND SPECIATION IN SOLUTION AS ANALOGS

	Partitioning in Sediments	Speciation in Solution
1	* Total solution phase metal concentration, M_{TS}	Free metal concentration, $[M^{m+}]$
2	Concentration of phase n, $\{S_T\}_n$	Concentration of ligand n, $[L_n]$
3	* Linear partitioning coefficient, $K_{p,n}$	Conditional complex formation constant, ${}^cK_n$
4	Concentration of metal associated with nth phase, $K_{p,n}\ M_{TS}\ \{S_T\}_n$	Concentration of complex species, ${}^cK_n\ [M^{m+}]\ [L_n]$
5	Total metal concentration, $M_T = M_{TS}\ (1 + \sum_{n=1}^{N} K_{p,n}\ \{S_T\}_n)$	Total metal concentration, $M_T = [M^{m+}]\ (1 + \sum_{n=1}^{N} {}^cK_n\ [L_n])$
6	Distribution coefficient, $D_n = \dfrac{K_{p,n}\ \{S_T\}_n}{(1 + \sum_{n=1}^{N} K_{p,n}\ \{S_T\}_n)}$	Distribution coefficient, $\alpha_n = \dfrac{{}^cK_n\ [L_n]}{(1 + \sum_{n=1}^{N} {}^cK_n\ [L_n])}$

* If the linear partitioning coefficient was expressed in terms of free rather than total solution phase metal the analogy here would be exact (refer Chapter 3).

$$F_n = \frac{\{S_T\}_n}{TS} = \frac{\{S_T\}_n}{\sum_{n=1}^{N} \{S_T\}_n} \tag{7.1}$$

where F_n is the dimensionless concentration of the nth phase (a fraction) and TS is the total solids content of the sediment slurry. In the case of a bed sediment it may be more useful to express (effective) TS in terms of commonly measured bulk sediment parameters such as bulk density, γ_b and porosity, θ. With a little algebra we obtain:

$$TS = 10^3 \left(\frac{\gamma_b}{\theta} - \rho_w\right) \tag{7.2}$$

where γ_b and ρ_w, the density of interstitial water, are given in typical units of $g.cm^{-3}$ and TS is given in typical units of $g.L^{-1}$.

The overall K_p for the total sediment is given by definition:

$$K_{tot} = \frac{[\text{Sed-M}]}{M_{TS} \cdot \sum_{n=1}^{N} \{S_T\}_n} \tag{7.3}$$

where [Sed-M] represents the concentration of sediment-bound metal which is the sum of the concentrations bound to N individual phases comprising the sediment. From Table 7.1:

$$[\text{Sed-M}] = \sum_{n=1}^{N} K_{p,n} M_{TS} \{S_T\}_n \tag{7.4}$$

thus:

$$K_{tot} = \frac{\sum_{n=1}^{N} K_{p,n} M_{TS} \{S_T\}_n}{M_{TS} \cdot \sum_{n=1}^{N} \{S_T\}_n} \tag{7.5}$$

and using (7.1) we obtain finally:

$$K_{tot} = \sum_{n=1}^{N} K_{p,n} F_n \tag{7.6}$$

This equation allows the overall (total) sediment partitioning coefficient, a quantity which is measurable on natural sediments as well as model sediments, to be predicted from data for isolated phases.

It is also useful to define a sediment partitioning coefficient, P_n, similar, but not identical, to the distribution coefficient in Table 7.1, and which measures the fraction of sediment-bound metal associated with the nth phase:

$$P_n = \frac{K_{p,n} \cdot F_n}{\sum_{n=1}^{N} K_{p,n} F_n} \tag{7.7}$$

This last equation allows a comparison of the proportional contribution of the different phases to the total sediment capacity for uptake of trace metals. Inherent in this analysis is the assumption that competition from other trace metals for adsorption sites can be neglected. Since trace metal adsorption densities in sediments are very low, and in the light of Benjamin's (1978) work which demonstrated that trace metal competition for oxide binding sites is generally minimal, this is probably a reasonable assumption.

7.1.3 Prediction of Trace Metal Uptake by Idealized Model Sediments

Before comparing model predictions with direct measurements of metal uptake by natural sediments we will consider metal partitioning in idealized model sediments that simulate natural sediments over typical ranges of composition. These model sediments are considered to be comprised only of the five phases studied in Chapters 4 - 6 (namely, hydrous iron and manganese oxides, montmorillonite, and aluminosilicate gel and estuarine humic substances) together with a hypothetical inert sand.

Table 7.2(a) which was adapted from the same sources used to construct Table 2.1, shows the typical range and average concentration of the "prototypes" of the model sedimentary phases. The remaining dry weight of the sediment is assumed to be mostly felspathic and/or quartz sand of negligible inherent metal-binding capacity, although coatings on these sand grains may have appreciable metal-affinity. The clay content of estuarine sediments can vary considerably, de-

Table 7.2

CADMIUM PARTITIONING IN ESTUARINE SEDIMENTS OF AVERGE COMPOSITION

(a) RANGES OF CONCENTRATION OF SELECTED SEDIMENTARY PHASES IN AEROBIC ESTUARINE SEDIMENTS

	Component	Concentration (% dry weight)	
		Typical Range	Average
1)	Hydrous Iron Oxides (as iron)	1 - 5	2
2)	Hydrous Manganese Oxides (as manganese)	0 - 0.2	0.02
3)	Clay Minerals (< 2 μm fraction)	0 - 30...70?	5?
4)	"Extractable" $SiO_2 + Al_2O_3$	?	?
5)	Organic Matter (about 50% "humic")	0 - 10	4

(b) PREDICTED CADMIUM PARTITIONING IN A MODEL SEDIMENT OF "AVERAGE" COMPOSITION AT pH 8 AND 5°/oo SALINITY

	Model Phase	F_n (%)	$K_{p,n}$ ($L.g^{-1}$)	$K_{p,n}F_n$	P_n (%)
1)	FeO_xH_n (as iron)	2	130	2.6	80
2)	MnO_x (as manganese)	0.02	1500	0.3	9
3)	Montmorillonite	< 100	0.1	< 0.1	< 3
4)	Aluminosilicate (as $SiO_2 + Al_2O_3$)	?	3.3	low?	-
5)	Humic Substances	2	17	0.34	10

$$K_{tot} = \Sigma K_{p,n}P_n \simeq 3.24\ L.g^{-1} (100\%)$$

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pending on the nature of the watershed soils and in-basin hydraulic, hydrological and sedimentological factors (Postma, 1967; Allen, 1970), thus it is difficult to give more than an approximate figure in Table 7.2. In San Francisco Bay the clay (< 2 μm, mostly montmorillonite) content is sometimes as high as 70% but this is probably an extreme example. It is even more difficult to give a value for the concentration of amorphous aluminosilicates in sediments. Some data are available for "extractable" Al_2O_3 and SiO_2 in terrestial soils but the author is unwilling to commit himself regarding the applicability of these figures to estuarine sedimentary environments which contrast greatly with soils in regard to physico-chemical conditions. Fortunately, data are abundant for the components likely to be more significant in metal binding, the iron and manganese oxides and organic matter. It is of interest to note that the ratio of manganese to iron is much lower in typical estuarine sediments than in typical soils. This difference arises because of mechanisms that act in estuaries to entrap iron discharged by rivers much more efficiently than manganese (Sholkovitz, 1978).

Table 7.2(b) shows the concentrations, F_n, of the model phases in a sediment simulating a natural estuarine deposit of average composition. It is assumed that about 50% of the total sediment organic content is "humic" in character (a typical value for base-extractable organics) and that the remainder of the organic content has a negligible capacity for metal binding. We could of course, assume that all the "average" sediment organic fraction had the same affinity for metals as humic substances and thus double the predicted contribution of organics to total binding capacity. Also given in Table 7.2(b) are the linear partitioning coefficients for cadmium at 5°/oo salinity and pH 8 by way of example. The sum of the products: $K_{p,n} \cdot F_n$ gives K_{tot} ($L.g^{-1}$) the total sediment partitioning coefficient according to Equation 7.6. The percent of sediment-bound cadmium associated with each phase is given in the last column (P_n values).

The analysis predicts that hydrous iron oxides should dominate the capacity of oxidized estuarine sediments for cadmium under the stated conditions. Manganese oxides and organic matter are predicted

to be associated with about 10% each of the cadmium content. The clay contribution is seen to be negligible since, even if essentially 100% of the sediment was montmorillonite it would bind only 3% of the cadmium. The aluminosilicate was neglected in Table 7.2(b) because of the lack of any good means of weighting this phase in regard to it's metal binding capacity. However, for this phase to contribute a sink of equal size to that of the organic matter and manganese it would have to be present at a concentration of 10% by weight. It seems unlikely that extractable $Al_2O_3 + SiO_2$ would approach 10% with the exception of those sediments containing large quantities of recent volcanic ashes.

Figure 7.4 shows data obtained by the method in Table 7.2 plotted as a pie graph in which area represents metal-binding capacity. The partitioning at $5^o/oo$ salinity and pH 8 is compared with that at $35^o/oo$, pH 8 and at $5^o/oo$, pH 7. The capacity of the sediment for cadmium decreases by more than an order of magnitude with the change in salinity from $5\text{-}35^o/oo$ (at constant pH = 8) but the relative importance of the contributing phases changes only slightly. The effect of pH change from 8-7 (constant salinity = $5^o/oo$) is seen to decrease total sediment capacity for cadmium and also decrease the relative importance of the iron phase.

Figure 7.5 shows the partitioning of copper in an estuarine sediment at pH 8 and pH 7 ($35^o/oo$ salinity). The partitioning and total copper uptake may not change greatly with change in salinity. Since the "average" sediment capacity for copper uptake is much greater than capacity for cadmium uptake the pie graphs are drawn on a scale very different from that used in Figure 7.4. The assumption is made that partitioning is linear between solid and solution phases but this may not be the case for copper uptake by the EHS at high Cu_T:{EHS} ratios (when copper concentrations are very high or sediments are present as dilute suspension) if high energy sites are significantly depleted (Chapter 5).

The figures predict that the organic fraction of the sediment will be the dominant sink for copper given that high energy sites are not depleted. Iron is of slightly lesser significance while the con-

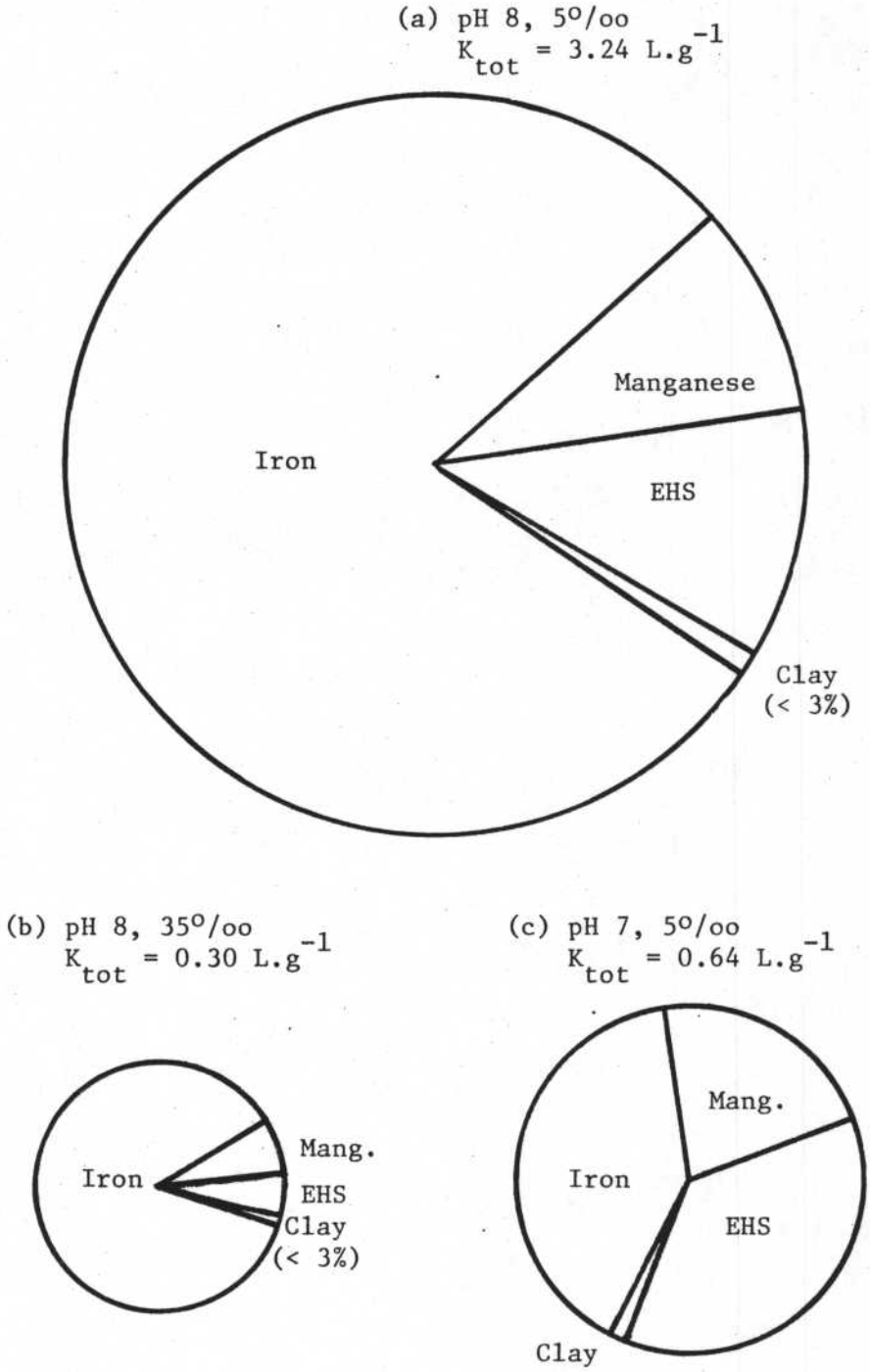


Figure 7.4. Cadmium Partitioning in a Model Estuarine Sediment of Average Composition.

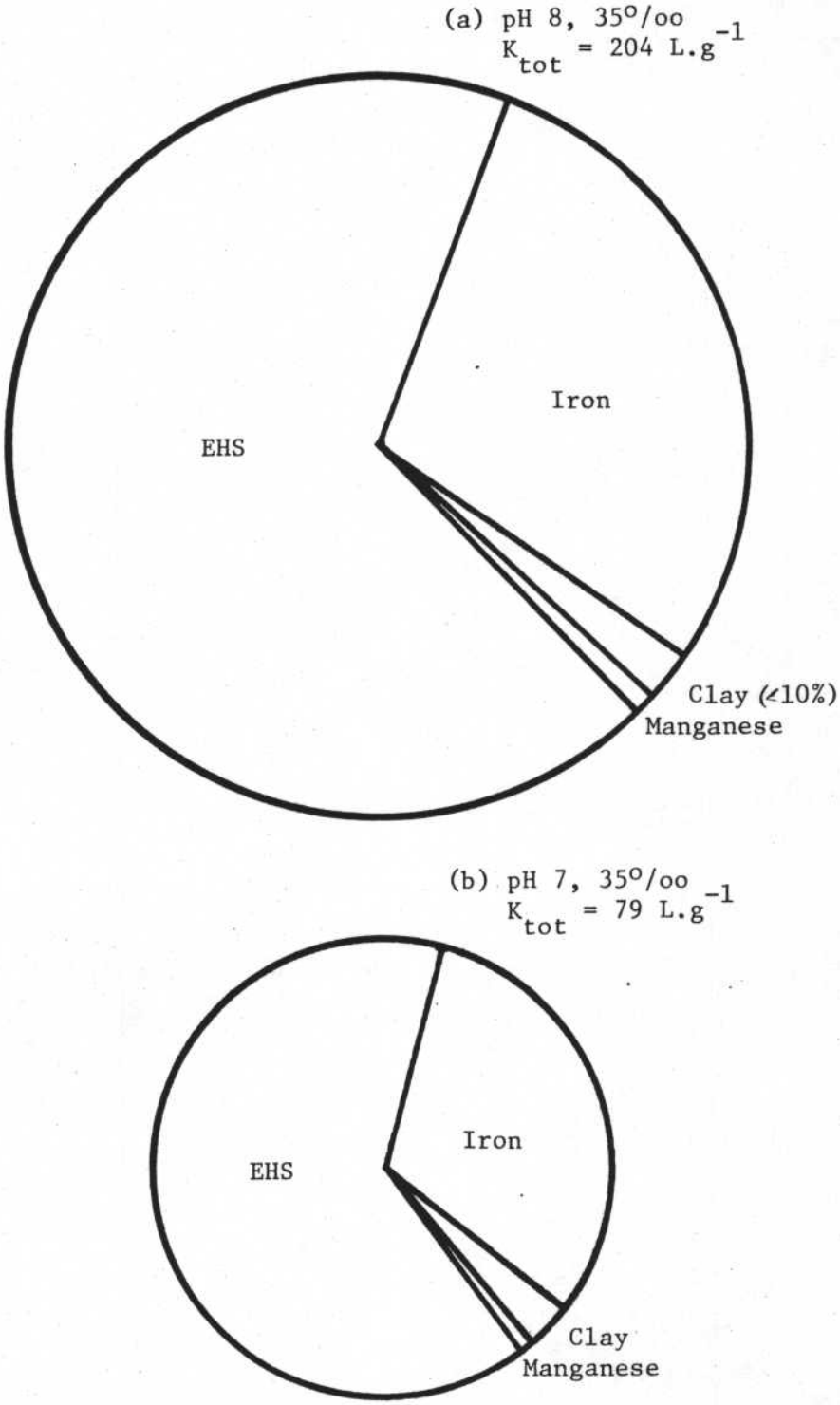


Figure 7.5. Copper Partitioning in a Model Estuarine Sediment of Average Composition.

tribution of manganese is relatively much lower than in the case of cadmium. The model predicts that copper binding capacity of the model sediment will fall somewhat with decrease in pH but the total capacity changes only by a factor of three between pH 7 and pH 8 compared with a factor of ten for cadmium. The change in pH does bring about a slight shift in the relative contribution of iron and organics in Figure 7.5, iron becoming slightly more significant at lower pH's. As in the case of cadmium the contribution of montmorillonite to the total copper sink is negligible. The contribution of the aluminosilicate was neglected in Figure 7.5 for lack of a suitable weighting factor. However, this contribution, similarly to the case for cadmium, would only amount to 10% of the total sediment copper-binding capacity if the aluminosilicate was present at as high a concentration as 10% by weight.

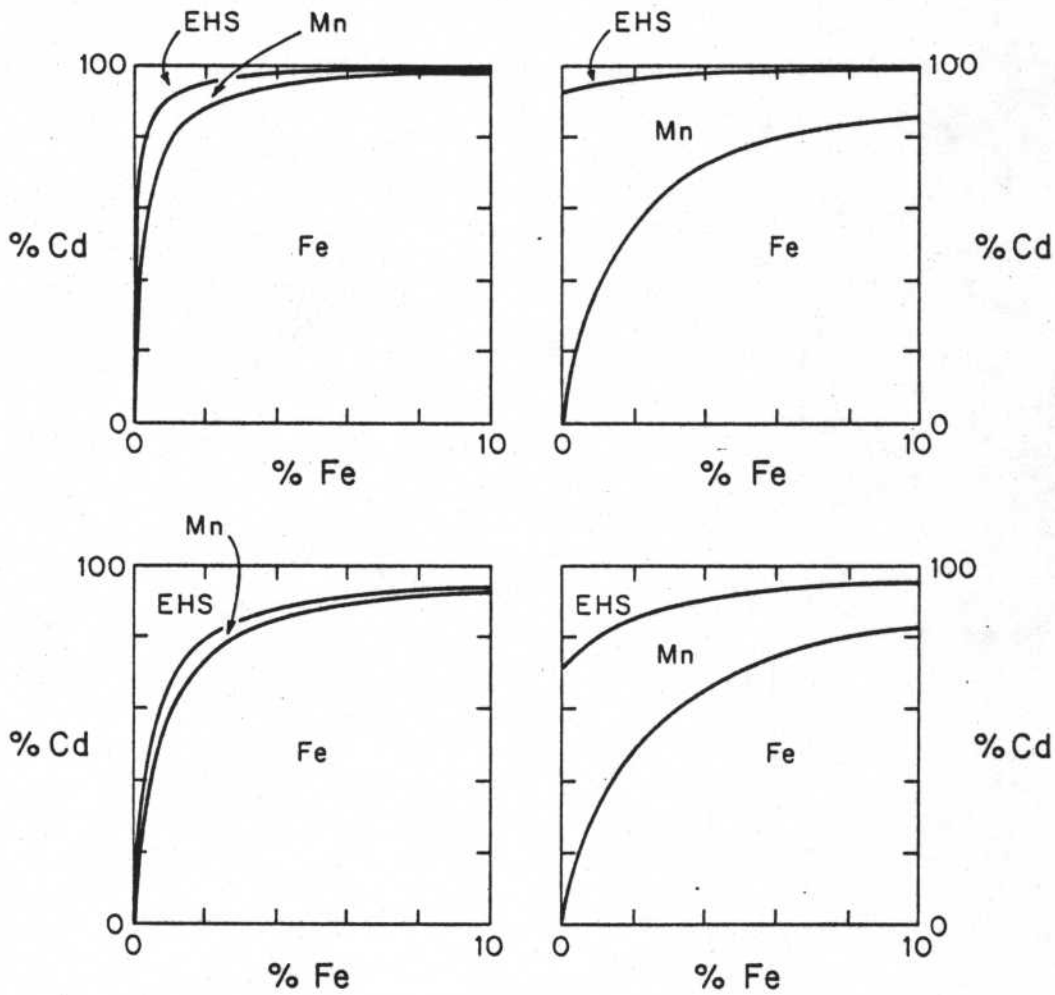
The composition of real estuarine sediments can range widely (Table 7.2). Thus it is important to gain some insight into the sensitivity of metal partitioning to change in sediment composition. To do this the copper and cadmium partitioning was calculated for the ranges of sediment composition given in Table 7.2. Since the available evidence suggests clays are insignificant as metal sinks *per se* and since the appropriate weighting for aluminosilicates is unknown these phases were not considered.

Figure 7.6 shows the variation of cadmium partitioning with change in sediment composition ($35^{o}/oo$ salinity, pH 8). Iron was chosen as the independent variable since it dominates cadmium uptake in an "average" model sediment and three different combinations of concentration of manganese and EHS were chosen. The figures show quantitatively what is expected intuitively; that the organic and manganese phases only become more important sinks for cadmium than iron when present at very high concentrations (at the upper end of the commonly observed range in estuarine sediments) and then only when iron content is average or low.

Partitioning of copper is even simpler than that of cadmium since only two phases need be considered: EHS and iron. Thus graphical representation would probably be superfluous in this case. Only at

(a) 0.02% Mang.
2% EHS

(b) 0.2% Mang.
2% EHS



(c) 0.02% Mang.
10% EHS

(d) 0.2% Mang.
10% EHS

Figure 7.6. Cadmium Partitioning in Model Estuarine Sediments as a Function of Sediment Composition.

low iron and organic contents and very high manganese (an unlikely combination since these components tend to be slightly positively correlated in real sediments) is manganese expected to be a significant sink for copper. The relative importance of iron and organics depends entirely on their relative concentration in the sediment. These phases will be of equal importance at 35°/oo salinity and pH 8 when:

$$\frac{F_{Fe}}{F_{EHS}} = \frac{K_{p,EHS}}{K_{p,Fe}} = 2.3$$

7.2 COMPARISON OF PREDICTED METAL UPTAKE WITH STUDIES ON NATURAL SEDIMENTS

7.2.1 Approaches for Testing the Metal Partitioning Model

A number of different approaches could conceivably be taken to test the applicability of the metal partitioning model outlined in the previous section to natural sediments. Perhaps the most feasible methods are as follows:

1) Compare results of selective extraction studies with model predictions for individual phases.
2) Compare total sediment metal analyses with total metal contents predicted from data given for iron, manganese and organic carbon and pore water metal analyses.
3) Measure metal uptake by natural estuarine sediments under controlled conditions and compare measured and predicted K_{tot} values. As a variation on this approach measure the metal uptake after each step in a sequence of selective extractions.

A number of so-called "selective" extraction studies of metals in marine and estuarine sediments have been reported (see Chapter 2 for a discussion). Unfortunately, besides the lack of true selectivity and efficiency of the common extractants (Guy *et al*, 1978; Rendell

and Batley, 1980) there is presently no method for separation of organic and sulphide-bound metals. Thus those studies that have been performed on anaerobic sediments in which solid sulphides occur (that is, deposits a few cm below the bed surface in most estuarine sediments) cannot be compared in a *quantitative* way to predictions based on the model presented above. Method (2) above would also be very difficult to use in a quantitative way because some of the total iron and manganese present would occur as solid sulphides rather than as oxides. Analyses of iron and manganese oxides as distinct from sulphides of these metals would be required for this approach. Also, as we shall see in the following section which considers metal behaviour in anaerobic sediments, the trace metal speciation in sulphidic pore waters may be vastly different from that in oxic estuarine waters and thus α_o, the free metal ion distribution coefficient which appears in the expression for K_p is very different from that in oxic estuarine waters. It would also seem to be difficult to use method (2) for aerobic surficial sediments since these sediments may not be in instantaneous equilibrium with the overlying water because of the dynamic nature of estuarine hydraulics. In any case not all of the *total* sediment trace metal content is in equilibrium with the aqueous phase since some fraction of the metal content (termed the "residual") is incorporated in mineral lattices (Engler *et al*, 1977).

Given the above problems with comparisons of selective extraction and total metal studies with model predictions it seems preferable for the moment to make such comparisons in a qualitative way only. This consideration of the problems involved has, however, suggested some refined approaches to field studies of metal contents of sediments which should be used in future research to enable quantitative comparisons to be made and these will be discussed below. The third method for testing the model has been employed using the results of studies in this department on natural sediment uptake of cadmium (Bleriot, 1980; Nivault, 1981) as will also be discussed below.

7.2.2 Discussion of the Partitioning Model in the Light of Selective Extraction Studies

A number of selective extraction studies on predominantly anaerobic sediments from core or grab samples suggest that cadmium is mostly associated with the oxides and organic + sulphide phases (Chester and Hughes, 1967; Gupta and Chen, 1975; Serne and Mercer, 1975; Brannon *et al*, 1976). This is in qualitative agreement with the model in the previous section which predicts that iron oxides will dominate cadmium partitioning in almost all oxic marine and estuarine sediments. The "easily reducible" oxides (usually extracted with hydroxylamine-hydrochloride, Engler *et al*, 1977) and associated with manganese oxides and poorly crystalline iron oxides usually contain more cadmium than the "moderately reducible" oxides (mostly crystalline detrital iron oxides). In anaerobic sediments almost all cadmium is found in the sulphide + organic fraction (extracted by peroxide) and is probably present as solid sulphides since the presence of free sulphides depresses free metal concentrations to very low levels (Section 7.3) thus effectively suppressing adsorption or binding by organics.

Copper is mostly associated with the peroxide-extractable fraction in both anaerobic and aerobic sediments although a proportion may also be associated with the "reducible" fractions (oxides) in aerobic sediments (Serne and Mercer, 1975). In aerobic sediments most of the copper is bound by peroxide-extractable organics in agreement with the predictions of the partitioning model. In anaerobic sediments the copper is probably mostly present as solid sulphides (also extractable by peroxide) as will be discussed below. In both aerobic and anaerobic sediments a significant proportion of total sediment copper may be present in the "residual" fraction extractable only by concentrated acids. This copper is not in equilibrium with the sediment pore water but is probably bound in crystalline silicate lattices.

The selective extraction study of Luoma and Bryan (1981) has special relevance to the present study since these workers studied oxidized surficial sediments separately from subsurface sediments.

The sediment samples were obtained from nineteen different estuaries in southern England and were extracted by standard geochemical reagents. Trace metal analyses were correlated with sediment parameters such as grain size and iron content and statistical "filtering" was used to isolate the effects of particular parameters. Cadmium was found to correlate significantly with HCl and oxalate-extractable iron but not total iron. The apparent association of cadmium with poorly-ordered (extractable) hydrous iron oxides rather than total iron suggest that crystalline oxides may have low affinities for cadmium in general agreement with laboratory experiments. Cadmium also correlated with organic carbon and statistical filtering suggested that the humic fraction of organic carbon was the important substrate. Cadmium correlated with total manganese content and grain size but since iron, organic carbon and grain size are all intercorrelated it was not possible to separate the relative importance of these parameters in an unequivocal way. The results are generally in very substantial agreement with the predicted partitioning on the basis of model phase studies.

Luoma and Bryan (1981) found that copper tended to correlate strongly with organic carbon and even more strongly with the humic (base-extractable) content of sediments. In sediments of low organic content the copper correlated very strongly with extractable iron. These results suggest copper is mostly associated with organics, particularly humics, and iron oxides, thus again providing confirmation of the partitioning model.

The overall agreement of the predictions of the partitioning model and the results of the selective extraction studies discussed above is encouraging. Apparently the model can be used to predict trends in geochemical associations. Whether the model can be used in a quantitative way is not yet certain but for an adequate test a refined approach to characterizing sediments is required. Some suggestions for improved methods arise out of the above discussion and particularly Luoma and Bryan's study:

1) Characterization of the nature of hydrous iron oxides in sediments as well as analyses of total concentrations is required. Ammonium oxalate and dilute HCl

are probably useful extractants of ferrihydrite (Schwertmann and Taylor, 1977) in oxidized sediments but these reagents would also extract ferrous sulphides (other than pyrite) in anaerobic sediments. An estimate of sulphide iron can be obtained by analysis of total sulphides (Williamson and Bella, 1975) but this involves assumptions about the (variable) stoichiometry of the iron sulphides present (for example: FeS, mackinawite; Fe_3S_4, greigite; Berner, 1971).

2) Luoma and Bryan (1981) have suggested that ammonium acetate may be a useful reagent for extraction of manganese oxides as distinct from manganese carbonates and sorbed manganese in sediments.

3) Organic content of sediments can be usefully characterized in terms of "humic" (base-extractable) and non-humic content.

4) HCl (about 1 M) may be a useful extractant for operationally-defining the non-crystalline trace metal content of oxidized sediments and thus the potentially bioavailable content (Luoma and Jenne, 1976).

5) It is highly desirable that solution phase trace metal concentrations (pore waters or overlying waters) be measured in studies of metals in sediments to enable method (2) above to be applied to test application of the partitioning model.

It should be mentioned that efficient extraction of humic-carbon and ferrihydrite-iron according to the above characterization scheme may be problematical in some sediments since iron and humic polymers interact strongly (Chapter 4). Luoma and Bryan (1981) found that pretreatment of sediments with acid ammonium oxalate substantially increased humic extractability suggesting intimate association of these components.

The methods of pretreatment and storage of sediments prior to extraction are of critical importance in obtaining meaningful data

(Thompson *et al*, 1980). Freezedrying may well be the preferred method of storage (Adams, 1980).

7.2.3 Cadmium Uptake by Natural Estuarine Sediments

Two studies of cadmium uptake by natural estuarine sediments employing Cd-109 as a tracer have been performed in this department. Bleriot (1980) studied both oxidized surface sediments (sampled with a diver-operated scraper which took a 1 cm slice of the surficial sediment) and anaerobic sediments (taken from cores) obtained at five locations in Yaquina Bay, Oregon (Figure 4.1). Table 7.3 lists characteristics of the sediment samples. Kulm and Byrne (1966) have reported studies on the general nature of the sediments of this estuary.

Adsorption studies were performed on the unfractionated sediment samples suspended in seawater ($32^{o}/oo$ salinity natural seawater from the Oregon Coast, filtered through a 0.2 μm membrane) and with total solids concentrations adjusted to give about 50% adsorption of Cd-109. Methodology was very similar to that used in Chapter 5 except that an N_2 atmosphere was maintained over anaerobic sediments. Linear partition coefficients at pH 8 were calculated by interpolation of the fractional adsorption data.

Table 7.4 lists the values of the linear partition coefficients obtained by Bleriot. K_{tot} correlated strongly with sediment parameters, notably iron, volatile solids and grain size, however these correlations are in part spurious because of intercorrelations among parameters. Only oxidized sediments will be considered henceforth because of the uncertainty about partitioning in anaerobic sediments (which contain sulphides) and the probability that the *status quo* with respect to free sulphides was not maintained in Bleriot's experiments.

The linear partition coefficients predicted from the data in Table 7.3 taking into account the lower salinity of the natural seawater are also shown in Table 7.4. The agreement between predicted and measured coefficients is encouragingly close when all the assumptions involved are considered. In three out of four cases the

Table 7.3

CHARACTERISTICS OF SEDIMENTS FROM YAQUINA BAY, OREGON
(refer Figure 4.1 for sample locations)

Sample	VS	SSC	MGS	TS	RSC	Fe_T	Mn_T
A (an)	1.12	86:14:0	185	35	100	0.495	38
B	2.12	80:16:4	180	10	1378	1.233	117
B (an)	1.50	85:15:0	200	36	795	0.538	66
C	3.14	44:50:6	60	0	1176	1.350	95
C (an)	5.61	25:66:9	33	412	1620	2.014	128
D	3.21	16:76:8	36	0	2066	1.582	108
D (an)	4.38	19:73:8	31	18	343	1.716	90
E	6.02	26:67:7	40	0	1645	1.878	115
E (an)	7.01	26:64:10	40	456	724	1.462	90

(an) denotes anaerobic (core) samples at greater than 20 cm depth.

VS = volatile solids (%, 400°C, 6 hr, Luoma and Bryan, 1981).

SSC = % sand:% silt:% clay

MGS = mean grain size (μm)

TS = total sulphides ($\mu g.g^{-1}$, Standard Methods, 1975)

RSC = reduced sulphide capacity ($\mu g.g^{-1}$, Williamson and Bella, 1975)

Fe_T = iron (%, EPA, 1974)

Mn_T = manganese ($\mu g.g^{-1}$, EPA, 1974)

Table 7.4

MEASURED AND PREDICTED LINEAR PARTITION COEFFICIENTS FOR SEDIMENTS FROM YAQUINA BAY, OREGON

	K_{tot} ($L.g^{-1}$, 32°/oc salinity, pH 8)			
	Measured		Predicted	O:Fe:Mn
Sample	Anaerobic	Aerobic	Aerobic	
A	1.00	-	-	-
B	1.70	0.11	0.28	9:85:6
C	11.7	0.96	0.33	12:84:4
D	1.23	0.69	0.38	10:85:5
	(After H_2O_2	0.75)		
	(After C/D	0.04)		
E	4.69	1.10	0.48	16:80:8

O:Fe:Mn Represents the percentage contributions (P_n values of Organics, Iron and Manganese.

C/D denotes citrate-dithionate extraction (of oxides).

predicted K_{tot} values are lower than measured. Some of the scatter may well be due to the presence of sulphides in the oxidized samples (sulphides were actually measured in sample B - refer Table 7.3) which would tend to increase apparent cadmium uptake if dissolution of sulphides occurred. It is also possible that sites for cadmium adsorption exist in sediments C, D and E which are not associated with iron, manganese or organic matter. It might be speculated that aluminosilicates could be involved but these would either have to be present at much higher concentrations than expected or have higher affinity for cadmium than the synthetic aluminosilicate studied in Chapter 5. It is also possible that the affinity of the sediment-iron for cadmium may actually be higher than predicted on the basis of experiments with fresh precipitates since recent work by Anderson (Civil Engineering Department, University of Washington, pers. comm.) has shown that the adsorption of cadmium on synthetic hydrous iron oxides increases with aging.

Figure 7.7 shows a plot of log K_p(pH) values calculated from Bleriot's data for sediment D compared with the predicted line. The measured data appear to fall somewhat above the line but the difference is not significant. The slope of the predicted line (0.65) closely matches that of the data confirming that iron is the dominant phase (manganese and organics have much lower pH dependence than iron as is shown in Figures 7.1 and 7.2).

Bleriot (1980) also studied the effect of extraction of components of the tidal flat sediment D on K_{tot}. Extraction with H_2O_2 (which destroys manganese oxides and organics) slightly *increased* K_{tot} (Table 7.4). Further extraction with citrate-dithionate (to remove iron) greatly decreased K_{tot}, indicating that iron was the most important sink for cadmium in this sediment as predicted by the partitioning model.

A second study of cadmium uptake by natural estuarine sediments was made by Nivault (1981). Samples of surficial deposits were obtained from Stations 8 and 9 (see Nelson, 1980 for locations) in Coos Bay, Oregon, by scraping a uniform layer from the surface of a box core. Nivault's methodology was similar to that of Bleriot (1980)

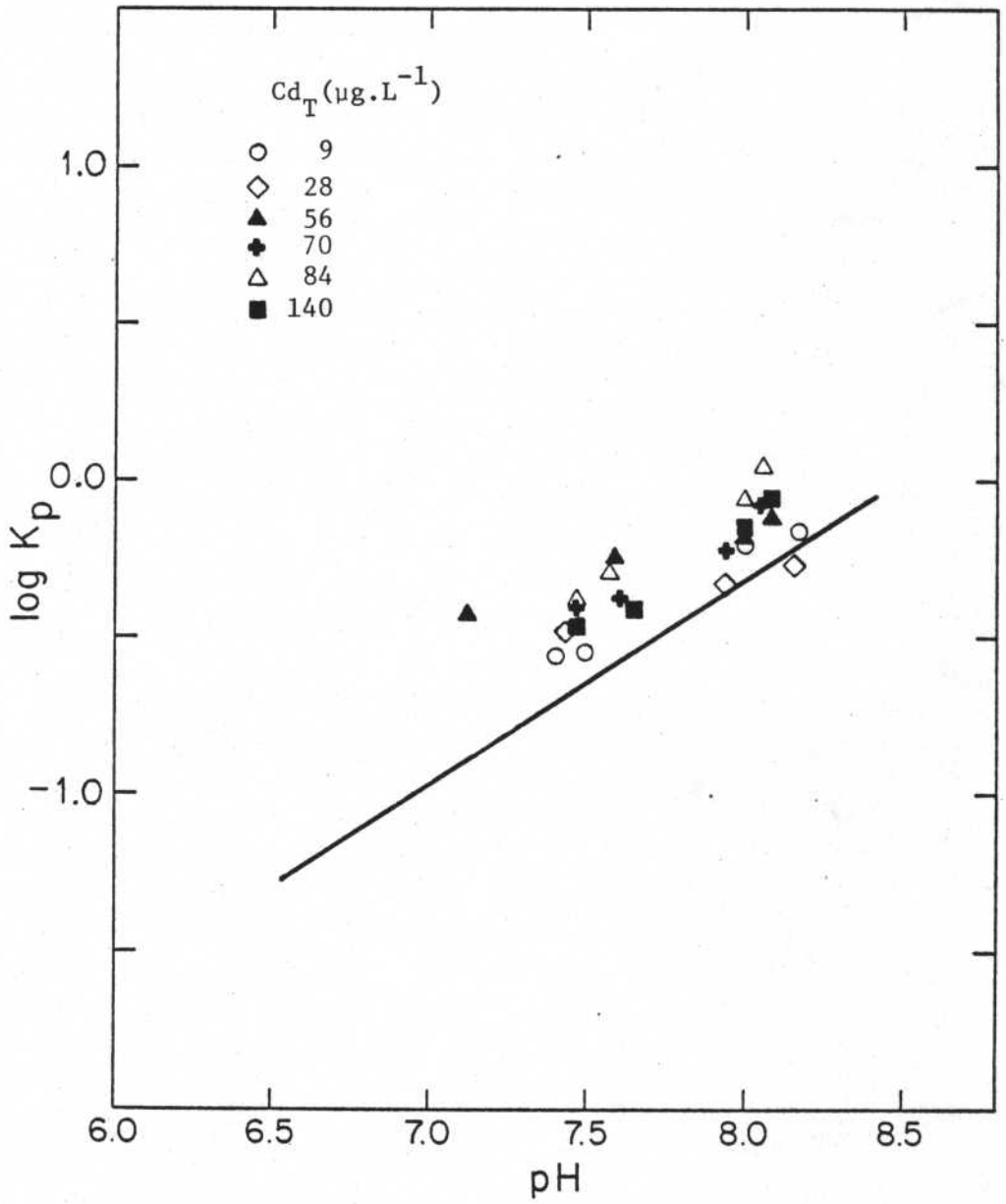


Figure 7.7. Cadmium Uptake by Sediment D from Yaquina Bay, Oregon, in Natural Seawater.

except that artificial seawater (35°/oo salinity) was used as a medium rather than natural seawater. Partly because of the interest in size distribution of cadmium binding sites and partly to avoid the problems encountered by Bleriot with dispersion of sandy sediments, the mud and sand fractions were treated separately. Nivault used a sequential selective extraction scheme and measured K_{tot} after each extraction step in an attempt to estimate values of K_p for the extracted material from the changes in the linear partition coefficient. Unfortunately, the data obtained by Nivault are not suitable as a quantitative test of the partitioning model because of problems with selectivity and efficiency of extraction and probable changes in configuration of sedimentary phases within the sediments during extractions.

Table 7.5(a) shows the values of parameters characterizing the sediment samples. Nivault did not report separate values of these parameters for the sand and mud fractions, however, it is still possible to compare the K_{tot} values calculated:

$$K_{tot} = (K_p \cdot F)_{sand} + (K_p \cdot F)_{mud}$$

with predicted values (Table 7.5(b)). In this case the partitioning model *overestimates* K_{tot}. It is possible that a greater proportion of iron in the Coos Bay sediments was present as crystalline detrital oxides than in the Yaquina Bay samples. Indeed Nivault found that only 30 - 60% of total sediment iron was oxalate-extractable. Thus the partitioning model calibrated with data for fresh hydrous iron oxides may overestimate the sink represented by iron in the Coos Bay sediments.

It is of considerable interest that the specific affinity of the sand was only slightly less than that of the mud fractions (Table 7.5(b)). Intuitively the sand would be expected to contribute a negligibly low metal sink compared with mud because of the vastly greater specific surface of the latter fraction. The results suggest two possibilities: either the "sand" is composed of coarse aggregates of finer particles or the sand is heavily coated with materials of high affinity for cadmium. Ultrasonication of the sediment did not appear to increase the proportion of mud (< 64 μm esd) and did not decrease

Table 7.5

CADMIUM UPTAKE BY SEDIMENTS FROM COOS BAY, OREGON

(a) Characteristics of Sediment Samples

Sample	*VS(TOC)	S:S:C	MGS	TS	RSC	Fe_T	Mn_T
8	6.30(2.84)	53:19:28	119	65	2596	1.41	180
9	10.57(5.27)	31:39:30	61	83	3505	2.42	333

* Parameters measured as in Table 7.3 except TOC (total organic carbon, %) by dry combustion and IR analyzer.

(b) Measured and Predicted Linear Partition Coefficients

	$K_p (L.g^{-1})$		$K_{tot} (L.g^{-1})$		
Sample	Sand	Mud	Measured	Predicted	O:Fe:Mn
8	0.11	0.24	0.171	0.288	20:73:7
9	0.14	0.35	0.278	0.495	20:73:7

cadmium uptake by the sand. However, extraction with ammonium oxalate decreased K_p of the sand fraction by a factor of 3 - 5. These observations and optical examination of the sand under a petrological microscope which revealed brown colored grains, are consistent with the presence of iron oxide coatings which were responsible for cadmium binding. In the mud fraction, as expected, the clay-sized particles had a greater specific affinity for cadmium than the silt.

In summary, results of studies of metal binding in natural sediments are consistent with the predictions of the partitioning model. Hopefully in future it will be possible to apply more adequate tests of the model using more refined data than is presently available for natural sediments.

7.3 ANAEROBIC SEDIMENTS

7.3.1 Introduction

While no experimental work was performed in the present study with simulation of reducing sediments it is of considerable interest to place conceptual bounds on "oxidized" sediments by considering redox processes known to be occurring in estuarine benthic systems (refer to Figure 3.1). Such consideration also yields estimates for the solubility of sulphide mineral phases which may be controlling toxic metal concentrations in the pore waters under reducing conditions.

Since the most important diagenetic processes in estuarine sediments are those involving sulphate reduction and iron mineral transformations (Berner, 1971), in as much as these reactions determine the physico-chemical environment in pore waters, this discussion will commence with a consideration of the thermodynamics of the relevant redox reactions.

7.3.2 Control of Free Sulphide Concentrations in Anaerobic Sediments

Sulphides are produced in estuarine sediments by bacterially-mediated coupling of sulphate reduction with oxidation of organics

(Bella, 1975). *Desulfovibrio* species are commonly involved in production of sulphides which can then be used as an oxidizable energy source by autotrophic bacteria such as *Thiobacteriaceae* (Cline and Richards, 1969). Sulphide oxidizers are known to store elemental sulphur in lipid droplets and can also deposit this sulphur in colloidal form outside the cell (Trudinger, 1979). Boulegue (1977) suggests that this colloidal sulphur may be considerably less thermodynamically stable than well-crystallized (orthorhomic) sulphur (Table 7.6). Reaction of sulphides (S(-II)) with elemental sulphur yields a series of polysulphide ions (S_n^{2-}, n ranges from 2 to 6) which are thought to be the electroactive species (along with HS^-) in sulphidic waters. The speciation diagram of Boulegue and Michard (1979) for the system: H_2S - S_8 - H_2O is useful for conceptualizing the relative importance of sulphide and polysulphide species at different pH values. A similar diagram could be derived from free energy values in Table 7.6. At pH's between 7 and 8.7 (a range which includes most estuarine pore waters) HS^- is the dominant species. At pH's below the $pK_a(H_2S) = 7.02$ H_2S dominates while about pH 8.7 polysulphides dominate.

Sulphides and/or polysulphides can react with iron and manganese oxides (some steps in this process may also be bacterially mediated) to produce solid sulphide minerals. These sulphides are typically poorly-ordered and fine grained and give reducing sediments their characteristic black color (Berner, 1967). Berner (1967, 1969) has suggested that the important diagenetic reactions can be summarized by the overall reaction:

$$2\ FeOOH_{(s)} + 3\ H_2S^o = 2\ FeS_{(s)} + S^o_{(s)} + 4\ H_2O_{(1)} \qquad (7.8)$$

It is immediately seen that the coexistence of iron oxides, iron sulphides and elemental sulphur will control the concentration of sulphides in estuarine sediment pore waters. Those estuarine sediments in this intermediate state have available sulphide capacity (ASC) (Williamson and Bella, 1975) which probably corresponds to the ferrihydrite content, because the initial ratio of "reactive" iron to labile organics in the sediments was relatively high. Bella (1975) has proposed a classification scheme for estuarine sediments based on

Table 7.6

SELECTED FREE ENERGY VALUES FOR AQUEOUS SPECIES AND SOLID PHASES OCCURRING IN ESTUARINE SEDIMENTS

Species	ΔG_f^o (Kcal.mol^{-1})	Source
Solids		
FeOOH (fresh precipitate)	-112.6	a,b
FeOOH ("soil iron")	-113.6	a,b
α-FeOOH (goethite)	-116.7	a
γ-FeOOH(lepidocrocite)	-115.5	b
S^o (orthorhombic, standard state)	0	a
S^o (colloidal)	0.5	c
FeS (fresh precipitate)	-21.3	d
FeS (mackinawite)	-22.3	d
FeS (troilite)	-24.2	d
Fe_3S_4 (greigite)	-69.4	d
FeS_2 (marcasite)	-37.8	a
FeS_2 (pyrite)	-38.3	a
CuS (covellite)	-11.7	a
Cu_2S (chalcocite)	-20.7	a
CdS (greenockite)	-34.8	a

Species	ΔG_f^o (Kcal.mol^{-1})	Source
Aqueous Species		
H_2O (liquid)	-56.64	a
H^+ (standard state)	0	a
Cu^+	11.94	a
Cu^{2+}	15.64	a
Cd^{2+}	-18.53	a
HS^-	2.89	a
H_2S	-6.67	b
S^{2-}	20.5	a
S_2^{2-}	22.7 ± 3	e
S_3^{2-}	21.0 ± 3	e
S_4^{2-}	16.3	e
S_5^{2-}	16.0	e
S_6^{2-}	16.4	e
$Cu(S_4)_2^{3-}$	13.4	e
$CuS_4S_5^{3-}$	14.4	e

a Robie *et al* (1978)
b Lindsay (1979)
c Boulegue *et al* (1977)
d Berner (1971)
e Cloke (1963 a,b)

the ratio of inorganic sedimentation rate (expressing the concentration of iron and, to a lesser extent, manganese) to organic sedimentation rate.

More recently Bella and Williamson (1977) have classified sediments according to the ratio of the available sulphide capacity (ASC) to the reduced sulphide capacity (RSC = ASC + solid sulphides) and have referred to a "biochemical succession" in sediments ranging from oxidizing conditions (no sulphides) to strongly reducing conditions (with free sulphides present).

An approximate calculation of free sulphides (symbolized: $\Sigma S(-II)$) can be made using free energy data in Table 7.6. With ΔG_f^o values for "soil iron" (ferrihydrite and/or iron-hydroxy interlayers in chloritic clays), mackinawite and colloidal sulphur we obtain:

$$\Delta G_r^o = -23.5 \text{ kcal.mol}^{-1}$$

from which:

$$-3 \log(H_2S^o) = \log K^o = \frac{-\Delta G_r^o}{1.364} = 17.2$$

thus:

$$\log(H_2S^o) = -5.7.$$

Since

$$S(-II) = [H_2S^o] + [HS^-] + [S^{2-}] + \sum_{n=2}^{6} [S_n^{2-}] = \frac{(H_2S^o)}{\gamma_o \, \alpha_{H_2S}(pH)} \qquad (7.9)$$

where γ_o = activity coefficient for an uncharged specie and the distribution coefficient for H_2S (a function of pH) is given:

$$\alpha_{H_2S}(pH) = \frac{[H_2S^o]}{\Sigma S(-II)} \qquad (7.10)$$

it is possible to calculate S(-II) poised by the coexistence of the solids. For a typical marine sediment at pH 7.5 (γ_o = 1.2 and α_{H_2S} = 0.16) the value of $\Sigma S(-II)$ controlled by coexistence of the phases considered above is about 10^{-5} M.

Since the free energies of possible coexisting solids in reaction (7.8) range widely in value (Table 7.6) it is possible that $\Sigma S(-II)$ controlled by the reaction could also range widely. A higher stability (lower or more negative ΔG_f^o value) for the iron oxide phase and lower stabilities for the elemental sulphur and ferrous sulphide phases results in a higher calculated $\Sigma S(-II)$. However, the value of $\Sigma S(-II)$ computed above is probably close to a maximum for a system of coexisting phases in equilibrium since iron oxides of higher stability than ferrihydrite would be expected to be unreactive towards sulphides. Well-crystallized oxides such as goethite would not contribute to the available sulphide capacity as measured in the short-term test developed by Williamson and Bella (1975) and this may in part explain the apparent poor correlation between sulphide capacity and total sediment iron. It would seem a reasonable generalization that in sediments with free sulphide concentrations higher than about 10^{-5} M the available sulphide capacity has been essentially reduced to zero and any iron oxides persisting metastably in these sediments are probably highly crystalline detrital minerals such as goethite, haematite or magnetite which dissolve relatively slowly.

$\Sigma S(-II)$ concentrations lower than 10^{-5} M may be controlled by coexistence of sulphides of higher stability than mackinawite with reactive hydrous iron oxides. As pointed out by Berner (1971) the reaction:

$$FeS + S^o = FeS_2 \text{ (pyrite or marcasite)} \qquad (7.11)$$

proceeds with a considerable free energy change (using ΔG_f^o values for mackinawite, colloidal sulphur and pyrite in Table 7.6, $\Delta G_r^o = -20$ kcal.mol^{-1}). Thus the products in reaction (7.8) further react (together with additional elemental sulphur) to produce pyrite. This reaction occurs rather slowly in estuarine sediments (over a time scale of years according to Berner, 1970) and results in an eventual lightening of the sediment color to grays as the black sulphides are pyritized. Again, using free energy values in Table 7.6 we can calculate that when iron oxides and pyrite coexist (as in a sediment buried below the turnover depth for many years) $\Sigma S(-II)$ would be of

the order of 10^{-14} M, at which concentration trace metal behavior is unlikely to be controlled by sulphide solubility.

Of course free sulphide concentrations in estuarine sediments, rather than being in true *equilibrium*, are more likely to represent a *steady state* which expresses a balance point of the rates of the competing reactions: ferrous sulphide precipitation (probably largely dependent on the rate of solubilization of forms of iron providing the available sulphide capacity), sulphide oxidation and sulphate reduction, together with the effects of vertical diffusional fluxes of free sulphides. Considerable insight into these processes was gained from the computer simulation studies of Gardner (1979) and Bella and Williamson (1980).

In the light of the above discussion it is now possible to qualitatively explain the commonly observed sediment concentration profiles with depth of sulphate, free sulphides and solid sulphides and pyrite (for example, Bella and Williamson, 1977). When appreciable free sulphides occur, say greater than 10^{-5} M (in sediments with no readily available sulphide capacity) concentrations usually peak at a small depth (few cm) into the sediments and thereafter decrease gradually in the downward direction, sometimes to immeasurably low values below 1-2 m (Berner, 1971). The peak represents the zone of most rapid sulphate reduction; above that level upwards diffusing free sulphide species are rapidly chemically or biochemically oxidized to elemental sulphur, thiosulphate, sulphite and, eventually, to sulphate (Cline and Richards, 1967; Chen and Morris, 1972). Sulphides diffusing in the downwards direction may be consumed by slow reactions with any remaining detrital crystalline iron oxides in the deep-buried sediments.

For the purposes of consideration of trace metal behavior we can define two general classes of sediments:

1) *Sediments in which (readily) available sulphide capacity has been largely depleted.* In these sediments free sulphide concentrations are determined by the balance of diffusional losses and rates of sulphate reduction (given a steady supply of organics and no

sulphate limitation) and may rise to 10^{-3} or even 10^{-2} M (Table 2.2).

2) *Sediments in which available sulphide capacity exists.* In these sediments S(-II) must be less than about 10^{-5} M and is usually considerably lower. There are two sub-classes: (a) Sediments in which the black metastable ferrous sulphides coexist with ferrihydrite. Free sulphide may range from about 10^{-5} M down to essentially immeasurably low values. (b) Sediments, usually deep-buried, in which pyritization has proceeded undisturbed for considerable time. In these sediments free sulphides are reduced to very low levels, assuming coexistence of iron oxides, and the trace metals would be expected to behave similarly as in oxidized sediments.

7.3.3 Behavior of Copper and Cadmium in Anaerobic Sediments

In the presence of free sulphides both copper and cadmium may precipitate as solid sulphides which then control the solubility of these metals. Since under reducing conditions Cu(II) is reduced to Cu(I) ($p\varepsilon^o = + 2.7$, $E_h = 0.16$ V, Table 7.7) we need to consider cuprous copper in anaerobic sediments. Both cuprous copper and cadmium are Class B metal ions (Stumm and Morgan, 1970) and their sulphides have very low solubility products. On the other hand, again as Class B "soft sphere" (polarisable) metals, both cuprous copper and cadmium have a strong tendency to form soluble complexes with "soft sphere" ligands such as bisulphides or polysulphides. Of the major anionic species occurring in sediment pore waters chloride is also expected to be an important ligand.

Solubilities of both cadmium and cuprous copper have been computed using the equilibrium constants given in Table 7.7 for a typical sediment pH of 7.5 and seawater ionic strength. The approach used was somewhat similar to that of Leckie and Nelson (1975), however, these workers used $p\varepsilon$ as a master variable. An essentially identical study

Table 7.7

THERMODYNAMIC CONSTANTS USED IN CALCULATIONS OF SPECIATION IN PORE WATERS OF ANAEROBIC ESTUARINE SEDIMENTS.

SOLIDS/AQUEOUS	LOG K (I = 0, 25°C)	SOURCE
$Cu_2S + H^+ = 2Cu^+ + HS^-$ (chalcocite)	-38.4	a
$CuS + 1/2H^+ = Cu^+ + 1/2HS^- + 1/2S^o$ (covellite)	-18.4	a
$Cu_2S + 5HS^- + H^+ = 2Cu(HS)_3^{2-}$ (chalcocite)	1.0	b
$2CuS + S_3^{2-} + 3S_4^{2-} = 2Cu(S_4)_2^{3-} + S^{2-}$ (covellite)	-1.30	c
$2CuS + 3S_4^{2-} + S_5^{2-} = 2CuS_4S_5^{3-} + S^{2-}$ (covellite)	-6.44	c
$CdS + H^+ = Cd^{2+} + HS^-$	-14.03	a

a Robie *et al* (1978)
b Snellgrove and Barnes (1974) cited in Emerson *et al* (in press, 1981)
c Cloke (1963 a,b)
d Smith and Martell (1976)
e Sposito and Mattigod (1981) GEOCHEM DATA
f Stumm and Morgan (1970)

AQUEOUS	LOG K (I = 0, 25°C)	SOURCE
$Cd^{2+} + HS^- = Cd(HS)^+$	8.14	d
$Cd^{2+} + 2HS^- = Cd(HS)_2^o$	15.37	d
$Cd^{2+} + 3HS^- = Cd(HS)_3^-$	17.18	d
$Cd^{2+} + 4HS^- = Cd(HS)_4^{2-}$	19.17	d
$Cd^{2+} + Cl^- = CdCl^+$	2.00	e
$Cd^{2+} + 2Cl^- = Cd(Cl)_2^o$	2.60	e
$Cd^{2+} + 3Cl^- = CdCl_3^-$	2.40	e
$Cd^{2+} + 4Cl^- = CdCl_4^{2-}$	2.50	e
$Cu^+ + 2S_4^{2-} = Cu(S_4)_2^{3-}$	22.77	c,a
$Cu^+ + S_4^{2-} + S_5^{2-} = CuS_4S_5^{3-}$	21.81	c,a
$Cu^+ + 3HS^- = Cu(HS)_3^{2-}$	17.9	b,a
$Cu^+ + Cl^- = CuCl^o$	2.31	d
$Cu^+ + 2Cl^- = CuCl_2^-$	5.5 (20°C)	d
$Cu^+ + 3Cl^- = CuCl_3^{2-}$	5.7 (20°C)	d
$2S^o + HS^- = S_3^{2-} + H^+$	-13.28	c,a
$3S^o + HS^- = S_4^{2-} + H^+$	-9.82	c,a
$4S^o + HS^- = S_5^{2-} + H^+$	-9.59	c,a
$5S^o + HS^- = S_6^{2-} + H^+$	-9.87	c,a
$S^{2-} + H^+ = HS^-$	13.9	d
$HS^- + H^+ = H_2S^o$	7.02	d
$H_2S_{(g)} = H_2S^o$	-0.99	d
$Cu^+ + e^- = Cu^+$	2.7(pe^o = 2.7)	f

was made by Emerson *et al* (1981) except that species activities were plotted as a function of log $[(HS^-)/(SO_4^{2-})]$ and the system was constrained to a constant total sulphur content (equal to SO_4^{2-} - sulphur in 35°/oo seawater, about 10^{-2} M). This constraint seems a spurious requirement to the present author given that much of the sulphur in sediments is bound in solid phases (particularly pyrite, Berner, 1967, 1971) and that diffusional fluxes of both sulphate and sulphides occur in response to vertical concentration gradients in sediments. For this reason log (HS^-) was used as a master variable in the present study. Bisulphide is the predominant species over the pH range of most estuarine sediments and its activity can be readily related to the analytical concentration of free sulphides:

$$\Sigma S(-II) = [H_2S^o] + [HS^-] + [S^{2-}] + \sum_{n=2}^{6} [S_n^{2-}] \qquad (7.12)$$

Using formation constants, in terms of (HS^-) from Table 7.7 we obtain:

$$\Sigma S(-II) = (HS^-) \left[\frac{(H^+)}{K_{a1}\ \gamma_o} + 1 + \frac{K_{a2}}{(H^+)\ \gamma_{\pm 2}} + \Sigma \frac{\beta_n}{(H^+)\ \gamma_{\pm 2}}\right] \qquad (7.13)$$

The value of the bracketed term is about 1.7 (pH 7) and 2.2 (pH 8) in seawater and is even closer to unity at lower salinities.

The thermodynamic constants given in Table 7.7 were taken in the main from Smith and Martell (1976) or were derived from the free energy tabulation of Robie *et al* (1978). The polysulphide constants were derived from free energy values reported by Cloke (1963a) which are similar to those of Boulegue (1977) but differ somewhat from those of Maronny (1959) and Giggenbach (1972, 1974), neither of whom considered the formation of S_6^{2-}. The constants for cuprous polysulphide complex formation were derived from free energy values given by Cloke (1963b). Although the assumed stoichiometry and speciation may not be entirely accurate (these complexes were assumed by analogy with acanthite - AgS - solubility) the *total* predicted solubility should be accurate since the analysis was performed on actual solubility measurements for covellite in polysulphide solutions. The constants for the cuprous bisulphide complex, $Cu(HS)_3^{2-}$, were taken directly from

Emerson *et al* (1981) (the original source was not checked) and a few other constants were obtained from Stumm and Morgan (1970) or from the data set of Mattigod and Sposito's (1979) GEOCHEM computer equilibrium program. The constants reported in Table 7.7 may not be internally consistent because of the variety of sources consulted.

Pure sulphides were assumed to control solubilities. Greenockite (CdS) was an obvious choice for cadmium but two sulphides of copper could conceivably exist. Chalcocite (Cu_2S) solubilities are usually given in terms of cuprous copper but many thermodynamic compilations (including Smith and Martell, 1976) report covellite (CuS) solubility in terms of cupric copper. However, polysulphide and bisulphide complexes which form on dissolution of covellite are known to involve only cuprous copper (these complexes are pale yellow-colored rather than blue or green like cupric complexes, Crerar and Barnes, 1976). Thus, following Emerson *et al* (1981), the solubility of covellite was recomputed from free energy data assuming cuprous copper. Rickard (1972) showed that covellite is the sulphide phase produced on reaction of sulphides with cupric solutions, and suggested that covellite may be the common phase in estuarine sediments.

Since sulphide precipitation of copper and cadmium may occur nearly simultaneously with that of iron in estuarine sediments the question arises whether solid solutions of trace metal sulphides in ferrous sulphides may control solubilities. Leckie and Nelson (1975) showed that the ratio of activity of the free (trace) metal ion (M^{m+}) in equilibrium with a solid solution of its sulphide in ferrous sulphide to that in equilibrium with the pure sulphide phase $(M^{m+})_o$ is given:

$$\frac{(M^{m+})}{(M^{m+})_o} = (\gamma X)_{MS_n} \qquad (7.14)$$

where γ is the activity coefficient and X is the mole fraction of MS_n in the solid solution. Since X is necessarily very small this equation predicts much lower trace metal solubilities for a solid solution than for a pure phase even while the activity coefficient may be considerably larger than unity (Leckie and Nelson, 1975). An analysis

of the possibility of CdS solubility in FeS by Framson and Leckie (1978) suggested that cadmium sulphides would be unlikely to dissolve in crystalline ferrous sulphides because of "lattice stresses" but the author is not aware of any similar consideration of cuprous sulphides.

The speciation diagrams for cadmium and cuprous copper are given for a pH of 7.5 and seawater ionic strengths in Figures 7.8 and 7.9. Activities are plotted rather than concentrations (except for total solubility which must be given as a concentration) so that the speciation will be independent of ionic strength except for the degree of chloride complexation. The present lack of good understanding of the true nature of the solid phases controlling Cu(I) and Cd(II) solubilities is a major limitation, thus the diagrams should be considered as speculative rather than predictive in an accurate quantitative sense. It is encouraging, however, that cadmium and copper analyses in a range of natural sulphidic waters (Table 7.8) plot reasonably closely (within an order of magnitude in most cases) to predicted solubilities.

Over most of the $p(HS^-)$ range considered $Cd(HS)_2^o$ is predicted to be the dominant complex, and concentrations of this specie, being uncharged, are only slightly dependent on salinity (ionic strength). No polysulphide data are available for cadmium thus no assessment of possible enhancement of solubility in the presence of elemental sulphur can be made. The speciation diagram for chalcocite has the same shape as that of covellite but all species have activities about one log unit higher. For cuprous copper the two polysulphide species reported by Cloke (1963b) predominate and thus determine solubility. Since both complexes are highly charged, solubility will be greatly dependent on ionic strength. The solubility curves are given for $35^o/oo$ seawater but would be significantly lower at lower salinities as encountered in estuaries. This may explain in part why some of the copper analyses tend to fall below the line for covellite which is probably the controlling phase if a pure sulphide exists. It should be noted that the activity correction is of dubious accuracy for such a highly charged species at such a high ionic strength as occurs in

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Table 7.8

COPPER, CADMIUM AND FREE SULPHIDE DATA FOR NATURAL SULPHIDIC WATERS AND SEDIMENTS

Source of Sample (PW = pore water)	$p\Sigma S(-II)$	pCu_{TS}	pCd_{TS}	ref.
Bridgeport, CT (PW)	2-2.2	6.5-7.3	6.5-7.4	a
Saanich Inlet (water)	4.4	8.7	10	b
Saanich Inlet (PW)	3	6.2-8.1	-	c
Marine Sediments off S. California				
Core TII (PW)	2.5-3	7.4-7.7	7.7-8.3	d1
Santa Barbara box core (PW)	3.1-3.7	7.1-7.5	7.5-8.3	d2
Beppa Bay, Japan	3.1	8.2	-	e
Black Sea	3.4-3.7	8.3	-	f
Enghien les Bains, France (sulphidic spring waters)	2.4	7.15	8.3	g
Lake Nitinat, British Columbia	4.0	8.7-9.0	-	h
Los Angeles Harbor (laboratory incubation of natural sediments)				
Silty sand	3-3.3	8.9	9.0	i1
Silty clay	3-3.3	9.8	9.3	i2

a Brannon *et al* (1976)
b Emerson *et al* (1981 in press)
c Presley *et al* (1972)
d Brooks *et al* (1972)
e Shiozuma *et al* (1977)
f Spencer and Brewer (1971)
g Boulegue (1977)
h Lieberman (1979)
i Lu and Chen (1977)

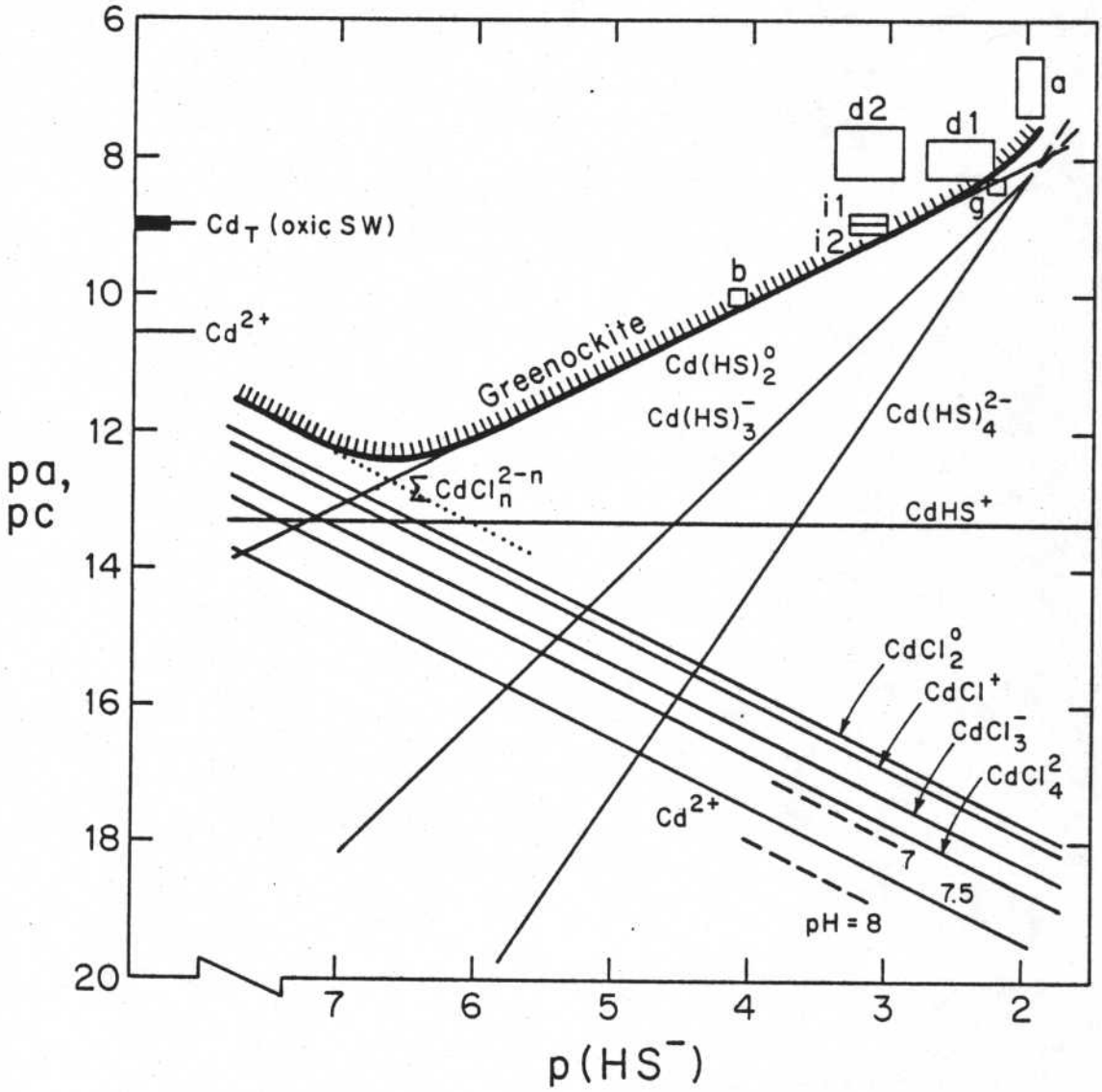

Figure 7.8. Cadmium Solubility at pH 7.5 in Sulphidic Seawater Assuming Greenockite (CdS) Exists.

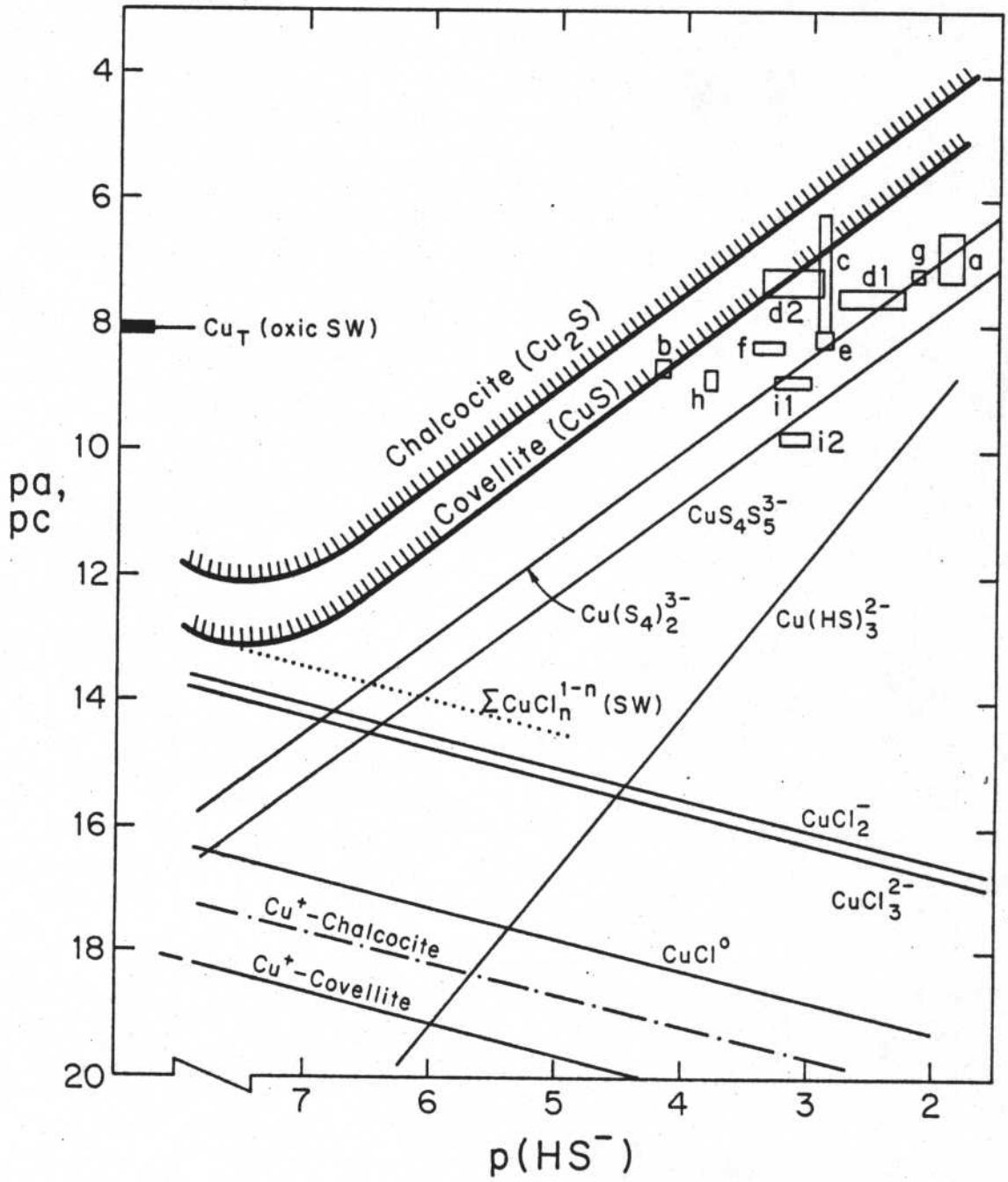

Figure 7.9. Copper Solubility at pH 7.5 in Sulphidic Seawater Assuming Chalcocite (Cu_2S) or Covellite (CuS) Exist.

seawater, however, the activity correction error is probably considerably smaller than the uncertainty regarding the controlling solid phase.

This analysis neglects the probable presence of metastable sulphur species other than polysulphides and elemental sulphur (such as $S_2O_3^{2-}$ or SO_3^{2-}). However, based on the complete sulphur speciation reported by Boulegue (1977) for natural sulphidic spring waters at Enghien les Bains, France (in which such intermediates were present at small concentrations) and on consideration of the relatively moderate formation constants for metal complexes of these ligands reported by Smith and Martell (1976), it is unlikely that they could affect overall solubility of copper or cadmium. A further limitation to the analysis may be the assumption that thermodynamically stable elemental sulphur ($\Delta G_f^o = 0$) exists rather than colloidal sulphur ($\Delta G_f^o \simeq 0.5$ Kcal.mol^{-1}, Boulegue, 1977) which would increase the yield of polysulphides and thus cuprous solubility.

Since the speciation is dependent on pH (Table 7.7) the solubility will also be dependent on pH. Solubility of cadmium (dominated by $Cd(HS)_2^o$ will *decrease* by one log unit per unit increase in pH while cuprous solubility (dominated by $Cu(S_4)_2^{3-}$) and $CuS_4S_5^{3-}$) will *increase* by 1.5 log units per unit pH increase. Both metals are predicted to have a solubility minimum, being about 10^{-13} M at $p(HS^-) = 7.5$ for covellite and less than 10^{-12} M at $p(HS^-) = 6.5$ for greenockite. These minimum solubilities are many orders of magnitude lower than total concentrations in typical oxic seawater (also shown on the figures, concentrations from Brewer and Spencer, 1975) and suggest that where (HS^-) is controlled by the coexistence of ferrihydrite and the less stable (black) ferrous sulphides (refer last section) trace metal solubilities will be very low in sediment pore waters. Under these conditions diagenetic fluxes from the overlying aerobic sediments may continually withdraw metals from the water column, that is the sediments will act as an ultimate metal sink. However, if available sulphide capacities are depleted in the sediments resulting in rise of free sulphide to 10^{-3} M or even higher concentrations, solubility of both metals is likely to rise to levels approximating or

exceeding those in typical open ocean water, whereupon the reducing sediments could conceivably act as a metal source (for example, Elderfield and Hepworth, 1975). At very low bisulphide activities as may occur in deep-buried sediment at an advanced stage of pyritization, chloride complexation dominates. In these sediments the partitioning of trace metals and control of their pore water concentrations is likely to be similar to aerobic sediments, although of course the hydrous iron and manganese oxide content may be significantly reduced. Note though, that even at extremely low $\Sigma S(-II)$ levels $p\varepsilon$ may still be sufficiently low that cuprous copper predominates over cupric since $p\varepsilon$ is strongly buffered by the 8 e^- transfer in the SO_4^{2-}/HS^- couple.

8. SUMMARY AND CONCLUSIONS

8.1 SUMMARY AND DISCUSSION

8.1.1 Summary of the Research

A review of the relevant literature suggested that our lack of knowledge of the physico-chemical forms and associations of toxic heavy metals in sediments (being the major environmental compartment) is the largest deficiency in our understanding of the environmental hazard posed by metal contamination in estuaries. This study was designed with the major goal of developing a method for predicting partitioning of metals in sediments that can be used as a basis for assessing the significance of such contamination.

A simple adsorption model was developed to describe metal uptake by sedimentary solids for quantitative comparison of metal binding by various sedimentary components. The model requires knowledge of the speciation of metals in seawater, however, while a computer equilibrium program (UMDEQ) can successfully predict the speciation of cadmium there is considerable uncertainty about the speciation of copper, thus the model was not used in its complete form in this study.

Several solid phases were selected to model those components of estuarine sediments of likely significance in binding of toxic metals: hydrous iron and manganese oxides, montmorillonite clay, a synthetic aluminosilicate gel and a humic extract from a natural estuarine sediment. The model phases were prepared by carefully defined procedures and were characterized by a variety of physical and chemical techniques to ensure reproducibility of the metal binding studies. The affinities of the model solid phases for the heavy metals cadmium and copper were quantified by simple adsorption experiments using artificial seawater media of different salinities and Cd-109 or Cu-64 as tracers. The binding of copper by estuarine humic substances was measured using a titration technique in which a copper specific ion electrode was employed to monitor unbound copper.

Uptake of cadmium was greatly decreased by increase in salinity, mainly because of complexation of cadmium by chloride. Copper adsorption was less sensitive to salinity. pH dependence of metal uptake varied greatly among the various phases. The order of affinity of the model phases for cadmium was: hydrous manganese oxide > hydrous iron oxide > estuarine humic substances > aluminosilicate > montmorillonite. The order for copper was: hydrous manganese oxide > estuarine humic substances > hydrous iron oxide > aluminosilicate > montmorillonite.

With a view to gaining some insight into the possible effects on metal binding of phase interactions occurring in sediments three types of "phase complex" were synthesized: a) hydroxy-iron interlayered montmorillonite, b) humic-coated hydrous iron oxide, and c) a ternary clay-iron-humic complex. Adsorption studies with these solid phase complexes suggested that interactions between sedimentary phases may not greatly affect equilibrium metal partitioning and total metal binding capacity of natural sediments.

A model of metal partitioning among competing solid phases in a sediment, analogous to metal speciation in a solution of competing ligands, was developed. This model predicts that cadmium partitioning in estuarine sediments of typical composition is dominated by hydrous iron oxides (about 80% or more of sediment capacity for cadmium) while manganese oxides and humics are of much lesser importance (contributing, typically, about 10% each). Copper binding is dominated by humic and iron phases. Clay minerals may be of less importance as heavy metal sinks than as substrates for the sedimentary components of higher metal affinity. Results of selective extraction studies on metal partitioning and studies in this department on cadmium binding by natural estuarine sediments are in substantial agreement with predictions of the partitioning model and provide a semiquantitative verification of this model.

Theoretical consideration of copper and cadmium in sulphidic waters using available thermodynamic data suggests that precipitation of solid sulphides in equilibrium with bisulphide and/or polysulphide complexation may determine the behavior of trace metals in anaerobic

sediments. Anaerobic sediments may act either as metal sources or sinks depending on free sulphide concentrations.

8.1.2 Discussion

This study has shown that the behavior in estuaries of two toxic metals, copper and cadmium, can be predicted on the basis of adsorption experiments used to calibrate a simple partitioning model. Concentrations of copper and cadmium in the solution phase (water column or pore water) are dependent on the identity and concentrations of adsorbent phases in the sediments and can be estimated using derived linear partition coefficients for the total sediment.

In principle the approach should apply in any situation where the solid/solution partitioning is linear for all contributing adsorbents in the sediment. Thus it should be possible to predict the equilibrium water column concentrations in the vicinity of a dredge spoil disposal site where sediments are present as dispersed slurries. Tidally-averaged metal concentrations in estuaries should express a steady state related to both the equilibrium concentrations (as predicted from the partitioning model) and the flushing time of the estuary. In metal-contaminated estuaries steady-state concentrations of copper and cadmium could be significantly higher than in pristine estuaries thus posing an environmental hazard to biota.

When the speciation of copper in seawater can be predicted with more certainty it will be possible to express the partitioning coefficients in terms of free metal ion concentrations (rather than total solution metal concentrations). This will allow the use of the constants together with other thermodynamic data in computerized chemical equilibrium model programs such as UMDEQ (Chapter 3). Thus it will be possible to interface modelling of metal partitioning in sediments with modelling of solution phase speciation.

The phase association of copper and cadmium and other toxic metals in sediments greatly affects bioavailability and thus toxicity to benthic organisms, particularly non-selective deposit feeders. This phase association can also be predicted by the partitioning model

which then becomes a basis for assessing bioassay results for such organisms.

Although this study has been experimentally limited to copper and cadmium the results have implications for the partitioning of other heavy metals in estuarine environments. For example, because mercury (II) is strongly complexed by organics and by chloride (MacNaughton, 1973) we would expect organics to dominate or at least be of great importance in mercury uptake by sediments and that this uptake would be strongly influenced by salinity. Zinc might be expected to behave somewhat similarly to cadmium because of chemical similarities although the rather different speciation of zinc in seawater (Zirino and Yamamoto, 1972) suggests adsorption of this metal would not be as strongly dependent on salinity as is the case with cadmium.

There seems to be no good reason why the basic approach used in this study could not be extended to other toxic metals such as zinc, mercury and lead or to other materials of nutrient or toxic interest such as phosphate and PCB's. Certainly the method could be used for prediction of the behavior of metals in non-saline aquatic systems such as freshwater lakes or wastewaters.

This study has identified iron (and to much lesser extent manganese) and organics as being the sedimentary components of greatest significance with regard to behavior of trace metals in estuaries. In aerobic sediments iron and organics (primarily humics) are the major metal adsorbents, organics being somewhat more important for copper while iron is the dominant sink for cadmium. In anaerobic sediments iron and organics are significantly although indirectly involved in that these components determine the concentrations of free sulphides which in turn determine trace metal distributions.

8.2 CONCLUSIONS

(1) Equilibrium cadmium and copper partitioning and total uptake by estuarine sediments may not be significantly affected by interactions of component sedimentary solids.

(2) Cadmium binding by aerobic estuarine sediments is dominated by iron oxides which typically account for 80% of the total sediment binding capacity. Organics, primarily humic substances, and manganese oxides typically contribute 10% each of the total binding capacity. The relative importance of the sedimentary phases in cadmium partitioning depends somewhat on pH but is almost independent of salinity.

(3) Organics (humic substances) and iron oxides are the most important contributors to binding of copper by aerobic estuarine sediments. In typical estuarine sediments organics are somewhat more important than iron oxides while the contribution of manganese oxides is only about 1%. The partitioning of copper is insensitive to pH and salinity.

(4) Clay minerals are not significant trace metal sinks although they may be important in metal transport processes in that they act as substrates for the sedimentary components of higher metal affinity. Amorphous aluminosilicates are probably not significant metal sinks except in sediments containing large quantities of recently-deposited volcanic ash.

(5) Cadmium uptake by estuarine sediments is very dependent on salinity. Increase in degree of chloride complexation is the primary factor responsible for the decrease in cadmium binding as salinity increases as in moving seawards through an estuary. Copper binding is only slightly influenced by salinity. Uptake of both metals increases with increase in pH.

(6) In anaerobic estuarine sediments in which free sulphides occur, thermodynamic calculations show that trace metal distributions are controlled by chemical equilibria between solid sulphides and soluble bisulphide and polysulphide complexes. Soluble metal concentrations are very low at low free sulphide concentrations as exist in "high-iron" sediments but may equal or even exceed those in oxic seawater at high free sulphides (of the order of 10^{-3} M) as occur in "low-iron" sediments.

(7) Methods for predicting trace metal distributions in sediments that can be used as a basis for assessing the environmental significance of metal contamination in estuaries have been developed. These methods have potential application in predicting the environmental impact of metals in dredge spoils and for estimating the bioavailability of sediment-bound metals to estuarine organisms, particularly benthic deposit feeders.

8.3 SUGGESTIONS FOR FURTHER RESEARCH

In spite of the clear importance of iron and organics from the point of view of metal cycling as shown in this and other studies and in spite of a considerable research effort the geochemistry of these materials is rather poorly known. In the case of iron some of the factors inhibiting the advancement of understanding include: the insolubility of ferric iron which presents severe analytical problems with the extremely low levels of soluble Fe(III) at environmental pH's and which allows several metastable iron minerals to persist, the range of thermodynamic stabilities and spectrum of degrees of ordering of iron phases in the environment and the severe interactions of iron oxides with aluminosilicates and organics. In the case of organics the research effort tends to be frustrated by the chemical complexity of these materials (hence the need for lumping terms like "geopolymers" and "humic substances") and the continual exchanges with living organisms which occur in the natural environment. In spite of the above-mentioned problems it is the author's opinion that renewed effort to elucidate the geochemistry and environmental significance of iron and organics is warranted. Some specific areas relevant to the estuarine environment where further study is suggested are as follows.

1) Comprehensive investigation of the iron minerals formed in laboratory experiments under conditions simulating those in estuaries.
2) Similarly comprehensive study of the chemical nature of both base-extractable and non-extractable (by difference) organic matter in estuarine sediments.

3) Investigation of the expected correlation of ammonium-oxalate extractable iron and available sulphide capacity in estuarine sediments.

4) Quantification of the nature and extent of interaction of organics and poorly-ordered iron oxides in sediments with further laboratory studies on natural sediments using extraction procedures.

With regard to the more specific problem of trace metals in estuaries the following areas are suggested for further study.

1) Examination of trace metal binding by bacterial products (precursors of humics). Some work in this area has been performed with regard to biological waste treatment but less attention has been devoted to the involvement of bacteria in trace metal cycling in the natural environment.

2) Experiments similar to those performed in this study could be applied to other trace metals of toxic concern (lead, mercury, zinc) and to some other materials of environmental interest such as phosphates.

3) The approach could be extended to consideration of fresh water and wastewater systems.

4) An extension of this type of approach may be applicable to persistent organic materials of environmental concern such as the PCB's.

5) Experiments should be designed to examine trace metal behavior under anaerobic conditions of differing free sulphide concentrations/redox potentials, initially as a test of the equilibrium solubility predictions presented in Chapter 7.

6) Further and more fundamental investigation of the kinetic factors involved in trace metal partitioning is warranted since reactions may be considerably slower in the complex assemblages of phases known as "sediments" than in simple laboratory systems.

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APPENDICES

APPENDIX A

FORMATION CONSTANTS IN THE THERMODYNAMIC DATA FILE OF GEOCHEM
USED FOR SEAWATER SPECIATION CALCULATIONS WITH UMDEQ.

		LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
CA																					
1	CO3	3.20	1	1	0	11.40	1	1	1												
2	SO4	2.30	1	1	0																
3	CL	.60	1	1	0																
4	F	1.00	1	1	0																
48	B(OH)4	1.80	1	1	0																
99	OH	-12.60	1	0	-1																
MG																					
1	CO3	2.90	1	1	0	11.30	1	1	1												
2	SO4	2.20	1	1	0																
3	CL	.50	1	1	0																
4	F	1.80	1	1	0																
48	B(OH)4	1.60	1	1	0																
99	OH	-11.80	1	0	-1	-39.70	4	0	-4												
SR																					
1	CO3	2.50	1	1	0	10.90	1	1	1												
2	SO4	2.20	1	1	0																
3	CL	.70	1	1	0																
4	F	.60	1	1	0																
48	B(OH)4	1.60	1	1	0																
99	OH	-13.30	1	0	-1																
K																					
1	CO3	.90	1	1	0	10.20	1	1	1	.70	2	1	0								
2	SO4	.90	1	1	0	1.90	1	1	1	1.50	2	1	0								
3	CL	-.30	1	1	0																
4	F	-2.20	1	1	0																
48	B(OH)4	0	1	1	0																
99	OH	-14.50	1	0	-1																

APPENDIX A (cont'd)

		LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
NA																					
1	CO3	.60	1	1	0	10.50	1	1	1	-.70	2	1	0								
2	SO4	1.10	1	1	0	2.00	1	1	1	1.50	2	1	0								
3	CL	-.10	1	1	0																
4	F	-1.70	1	1	0																
48	B(OH)4	.20	1	1	0																
99	OH	-14.20	1	0	-1																
CU+2																					
1	CO3	6.70	1	1	0	9.80	1	2	0	14.60	1	1	1								
2	SO4	2.40	1	1	0	1.10	1	2	0	-3.90	1	3	0	3.00	1	1	1				
3	CL	.40	1	1	0	-.40	1	2	0	-1.00	1	3	0	-4.00	1	4	0	-8.50	1	1	-1
4	F	1.30	1	1	0																
5	BR	1.10	1	1	0																
48	B(OH)4	7.10	1	1	0	12.40	1	2	0	15.20	1	3	0								
99	OH	-8.00	1	0	-1	-17.30	1	0	-2	-27.80	1	0	-3	-39.60	1	0	-4	-10.40	2	0	-2
CO																					
1	CO3	4.10	1	1	0	4.60	1	2	0	12.40	1	1	1								
2	SO4	2.50	1	1	0	2.90	1	2	0	1.90	1	3	0	2.90	1	1	1				
3	CL	2.00	1	1	0	2.60	1	2	0	2.40	1	3	0	2.50	1	4	0	-8.50	1	1	-1
4	F	1.10	1	1	0																
5	BR	2.20	1	1	0	3.00	1	2	0	3.00	1	3	0	2.90	1	4	0				
48	B(OH)4	3.80	1	1	0	10.60	1	4	0												
99	OH	-10.10	1	0	-1	-20.40	1	0	-2	-33.30	1	0	-3	-47.40	1	0	-4	-9.40	2	0	-1
H																					
1	CO3	10.30	0	1	1	16.70	0	1	2												
2	SO4	2.00	0	1	1	-8.30	0	1	2												
3	CL	-8.40	0	1	1																
4	F	3.00	0	1	1																
48	B(OH)4	9.20	0	1	1																

APPENDIX B

DATA FROM CADMIUM ADSORPTION EXPERIMENTS WITH MODEL PHASES IN ISOLATION

Cadmium Uptake by Hydrous Iron Oxide ({Fe} = 0.2043 $g.L^{-1}$)
(Artificial Seawater, $35^{o}/oo$)

Cd_T	pH	f	$logK_p$
2.8	8.30	0.878	1.547
2.8	7.91	0.751	1.169
2.8	7.65	0.605	0.875
2.8	6.97	0.207	0.106
7.0	8.32	0.870	1.515
7.0	7.94	0.742	1.149
7.0	7.66	0.590	0.848
7.0	6.98	0.178	0.025
28	8.34	0.874	1.531
28	7.91	0.728	1.117
28	7.63	0.567	0.807
28	6.98	0.199	0.085
56	8.52	0.904	1.664
56	8.05	0.773	1.222
56	7.68	0.570	0.812
56	6.96	0.162	0.024
*84	8.64	0.916	1.727
*84	8.07	0.770	1.215
*84	7.68	0.554	0.784
*84	6.94	0.170	0.001
*140	8.61	0.902	1.654
*140	8.09	0.761	1.193
*140	7.66	0.526	0.735
*140	6.67	0.090	0.315

$logK_p = 1.08pH - 7.42$ ($r = 0.997$, $n = 24$)
* Not included in regression

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Cadmium Uptake by Hydrous Iron Oxide ({Fe} = 0.2043 $g.L^{-1}$)
(Natural Seawter, $32^{o}/oo$)

Cd_T	pH	f	$logK_p$
2.8	8.25	0.89	1.598
2.8	7.88	0.80	1.292
2.8	7.77	0.77	1.215
2.8	7.31	0.55	0.777
7.0	7.88	0.78	1.239
7.0	7.78	0.74	1.144
7.0	7.42	0.58	0.830
28	8.13	0.84	1.410
28	7.98	0.77	1.215
28	7.77	0.74	1.144
28	7.46	0.59	0.848
56	7.96	0.79	1.265
56	7.76	0.74	1.144
56	7.46	0.58	0.830

$$logK_p = 0.85pH - 5.50 \quad (r = 0.981,\ n = 14)$$

Effect of Salinity on Cadmium Uptake by Hydrous Iron Oxide
(Artificial Seawater of Varying S^{o}/oo) ({Fe} = 0.0511 $g.L^{-1}$)
Salinity = $1.4^{o}/oo$

28	8.51	0.961	2.683
28	7.76	0.839	2.009
28	7.24	0.618	1.500
28	7.64	0.799	1.891
28	6.66	0.302	0.928

$$logK_p = 0.95pH - 5.38 \quad (r=0.999,\ n = 5)$$

Cd_T	pH	f	$\log K_p$
Salinity = $5^o/oo$			
28	8.67	0.965	2.732
28	8.55	0.946	2.535
28	7.91	0.863	2.091
28	7.16	0.532	1.347
28	7.60	0.704	1.668
28	7.02	0.334	0.992

$\log K_p = 0.98pH - 5.74$ ($r = 0.991$, $n = 6$)

Salinity = $9.3^o/oo$			
28	8.44	0.914	2.318
28	7.94	0.774	1.826
28	7.30	0.440	1.187

$\log K_p = 0.99pH - 6.06$ ($r = 0.999$, $n = 3$)

Salinity = $15^o/oo$			
28	8.44	0.883	2.169
28	7.93	0.703	1.666
28	7.49	0.440	1.187

$\log K_p = 1.03pH - 6.54$ ($r = 0.999$, $n = 3$)

Effect of Chloride Complexation on Cadmium Uptake by Hydrous Iron Oxide ($\{Fe\} = 0.0511 g.L^{-1}$)

0.55M Cl^-, 0.15M NO_3^-			
28	8.77	0.90	2.246
28	6.59	0.06	0.097
28	8.80	0.94	2.487
28	7.41	0.24	0.791

$\log K_p = 1.06pH - 6.93$ ($r = 0.995$, $n = 4$)

Cd_T	pH	f	$\log K_p$
0.7M NO_3^-			
28	7.90	0.93	2.415
28	6.47	0.29	0.903
28	7.24	0.72	1.702

$\log K_p = 1.06pH - 5.94$ ($r = 0.999$, $n = 3$)

Effect of Temperature on Cadmium Uptake by Hydrous Iron Oxide (Results of Experiment at 5^oC, Artificial Seawater $35^o/oo$) ($\{Fe\} = 0.2043\ g.L^{-1}$)

2.8	8.39	0.88	1.555
2.8	8.04	0.72	1.100
2.8	7.71	0.63	0.921
2.8	7.06	0.22	0.140
7	8.41	0.89	1.598
7	7.96	0.74	1.144
7	7.72	0.62	0.902
7	6.90	0.19	0.060
28	8.51	0.86	1.478
28	8.17	0.78	1.239
28	7.58	0.56	0.795
28	6.45	0.21	0.114
56	8.49	0.86	1.478
56	8.09	0.74	1.144
56	7.73	0.55	0.777
56	6.64	0.15	-0.064

$\log K_p = 0.83pH - 5.53$ ($r = 0.978$, $n = 16$)

Cadmium Uptake by Hydrous Manganese Oxide
(Artificial Seawater, $35^{o}/oo$) ($\{Mn\}$ = 29.6 $mg.L^{-1}$)

Cd_T	pH	f	$\log K_p$
2.8	8.20	0.81	2.158
2.8	7.88	0.73	1.961
2.8	7.50	0.66	1.817
2.8	8.12	0.80	2.131
2.8	7.78	0.70	1.897
2.8	7.14	0.61	1.723
7	8.85	0.84	2.249
7	8.31	0.80	2.131
7	7.91	0.74	1.983
7	7.44	0.70	1.897
7	8.68	0.83	2.217
7	8.05	0.74	1.983
7	7.79	0.73	1.961
7	6.95	0.57	1.651
28	8.81	0.82	2.187
28	8.28	0.75	2.006
28	7.93	0.67	1.836
28	7.48	0.67	1.836
28	8.62	0.78	2.078
28	8.18	0.74	1.983
28	7.82	0.65	1.798
28	7.05	0.58	1.669
140	8.79	0.66	1.817
140	7.66	0.31	1.181
140	7.45	0.20	0.927
140	8.53	0.60	1.705
140	7.51	0.26	1.074
140	7.45	0.18	0.892

$$\log K_p = 0.33pH - 0.59 \quad (r = 0.969,\ n = 14)$$

Cadmium Uptake by Hydrous Manganese Oxide
(Artificial Seawater, $5^{o}/oo$) ($\{Mn\}$ = 6.97 $mg.L^{-1}$)

Cd_T	pH	f	$logK_p$
2.8	7.89	0.90	3.11
2.8	8.38	0.92	3.22
2.8	7.07	0.88	3.02
7	7.78	0.86	2.95
7	7.51	0.86	2.95

$$\log K_p = 0.35pH + 0.39 \ (r = 0.89, \ n = 5)$$

Cadmium Uptake by Montmorillonite ($\{SWy\text{-}1\}$ = 35 $g.L^{-1}$)
(Artificial Seawater, $35^{o}/oo$)

2.8	8.25	0.028
2.8	7.78	0.018
2.8	7.44	0
2.8	7.14	0
7	8.26	0.012
7	7.80	0
7	7.47	0
7	7.18	0
140	7.95	0.029
140	7.51	0.015

Cadmium Uptake by Montmorillonite ($\{SWy\text{-}1\}$ = 6.29 $g.L^{-1}$)
(Artificial Seawater, $5^{o}/oo$)

2.8	7.81	0.275	-1.220
2.8	7.20	0.110	-1.707
2.8	6.88	0.085	-1.831
2.8	6.78	0.040	-2.179

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Cd_T	pH	f	$\log K_p$
28	7.78	0.230	-1.323
28	7.35	0.135	-1.605
28	6.97	0.060	-1.994
28	6.73	0.035	-2.239

$$\log K_p = 0.90pH - 8.28 \ (r = 0.993, n = 7)$$

Cadmium Uptake by Fischer Bentonite Reagent Clay
(Artificial Seawater, $35^o/oo$) ($\{Clay\} = 4.33\ g.L^{-1}$)

5	8.0±0.3	0.23	-1.161
12.5	8.0±0.3	0.19	-1.266
50	8.0±0.3	0.11	-1.545
100	8.0±0.3	0.16	-1.337
150	8.0±0.3	0.16	-1.357
250	8.0±0.3	0.15	-1.390

Cadmium Uptake by Amorphous Aluminosilicate Gel
(Artificial Seawater, $35^o/oo$) ($\{Al_2O_3 + SiO_2\} = 4.99\ g.L^{-1}$)

2.8	8.11	0.66	-0.410
2.8	7.65	0.36	-0.948
2.8	7.19	0.12	-1.563
2.8	6.80	0.064	-1.863
7	7.96	0.53	-0.646
7	7.48	0.26	-1.152
7	7.20	0.18	-1.357
28	7.94	0.52	-0.663
28	7.54	0.25	-1.175
28	7.21	0.13	-1.524
28	6.67	0.058	-1.909

Cd_T	pH	f	$\log K_p$
140	7.88	0.47	-0.750
140	7.61	0.30	-1.066
140	7.24	0.15	-1.451
140	6.86	0.072	-1.808

$$\log K_p = 1.05pH - 9.01 \ (r = 0.991, \ n = 16)$$

Cadmium Uptake by Amorphous Aluminosilicate Gel
(Artificial Seawater, $5^o/oo$) ($\{Al_2O_3 + SiO_2\} = 0.713 g.L^{-1}$)

28	7.96	0.52	0.182
28	7.50	0.38	-0.066
28	7.18	0.22	-0.403
28	7.88	0.62	0.360
28	7.60	0.44	0.042
28	7.45	0.33	-0.161
28	6.74	0.090	-0.858

$$\log K_p = 1.11pH - 8.36 \ (r = 0.997, \ n = 8)$$

Cadmium Uptake by EHS (Ultrafiltration Method)
(Artificial Seawater, $35^o/oo$) ($\{EHS\} = 1.383 \ g.L^{-1}$)

2.8	7.65	0.60	0.035
56	7.92	0.47	-0.193
56	6.50	0.46	-0.211
56	6.78	0.46	-0.211
714	6.78	0.43	-0.193
714	6.72	0.30	-0.368
714	7.96	0.55	-0.054

$$\log K_p = 0.13pH - 1.12 \ (r = 0.65, \ n = 7)$$

Cadmium Uptake by EHS (Ultrafiltration Method)
(Artificial Seawater, $5^{o}/oo$) ($\{EHS\} = 0.449\ g.L^{-1}$)

Cd_T	pH	f	$logK_p$
28	7.04	0.86	1.136
28	6.73	0.80	0.950
28	7.96	0.88	1.213
28	8.54	0.90	1.302

$$logK_p = 0.17pH - 0.11 \quad (r = 0.93,\ n = 4)$$

Cadmium Uptake by EHS (Direct Electrode Method)
(Artificial Seawater, $35^{o}/oo$)

$\{EHS\} = 1.936\ g.L^{-1}$

500	8.00	0.63	-0.056
500	8.00	0.63	0.001
500	8.00	0.66	0.001

$\{EHS\} = 1.100\ g.L^{-1}$

286	7.24	0.495	-0.050
286	6.90	0.368	-0.276
286	6.34	0.304	-0.401
286	6.81	0.333	-0.343
286	7.52	0.400	-0.219
286	7.86	0.465	-0.102

Cadmium Uptake by EHS (Direct Electrode Method)
(Artificial Seawater, $5^{o}/oo$) ($\{EHS\} = 0.2205\ g.L^{-1}$)

137	6.80	0.667	0.962
137	7.57	0.732	1.093
137	7.23	0.784	1.217
137	7.50	0.744	1.120
137	7.21	0.791	1.237

APPENDIX C

DATA FROM COPPER ADSORPTION EXPERIMENTS WITH MODEL PHASES IN ISOLATION

Copper Uptake by Hydrous Iron Oxide ({Fe} = 0.818 $mg.L^{-1}$)
(Artificial Seawater, $35^{o}/oo$)

Cu_T	pH	f	$logK_p$
2.8	8.69	0.490	3.070
2.8	8.17	0.494	3.077
2.8	7.38	0.411	2.931
2.8	6.67	0.255	2.622
7	8.67	0.784	3.346
7	8.20	0.781	3.338
7	7.30	0.710	3.175
7	6.63	0.567	2.903
28	8.62	0.865	3.593
28	8.18	0.835	3.490
28	7.26	0.761	3.289
28	6.77	0.620	2.999
140	8.69	0.878	3.643
140	8.23	0.888	3.690
140	7.33	0.770	3.311

Copper Uptake by Hydrous Iron Oxide ({Fe} = 1.636 $mg.L^{-1}$)
($5^{o}/oo$ Artificial Seawater)

2.8	7.96	0.835	3.394
2.8	6.81	0.634	2.928
2.8	6.39	0.678	3.013

Cu_T	pH	f	$\log K_p$
7	6.82	0.708	3.171
7	8.51	0.783	3.344
7	7.15	0.734	3.227

Copper Uptake by Hydrous Manganese Oxide
(Artificial Seawater, $35^o/oo$) ($\{Mn\} = 0.211\ g.L^{-1}$)

2.8	8.38	0.521	3.713
2.8	8.31	0.535	3.737
2.8	7.26	0.666	3.976
2.8	6.72	0.688	4.020
7	8.51	0.693	4.030
7	8.00	0.615	3.880
7	7.48	0.634	3.915
7	6.70	0.689	4.022
28	8.49	0.665	3.974
28	8.14	0.688	4.020
28	7.39	0.431	3.556
28	6.78	0.546	3.757
140	8.60	0.628	3.904
140	8.18	0.567	3.793
140	7.27	0.382	3.467

$$\log K_p = 0.018pH + 3.714\ (r = 0.07,\ n = 15)$$

Further Data ($\{Mn\} = 0.0843\ mg.L^{-1}$):

2.8	8.70	0.251	3.599
2.8	8.15	0.372	3.847
2.8	7.43	0.335	3.776
2.8	6.67	0.466	4.015
7	8.76	0.462	4.008
7	8.29	0.401	3.900
7	7.46	0.366	3.836

Cu_T	pH	f	$\log K_p$
28	8.72	0.393	3.885
28	8.22	0.443	3.975
28	7.45	0.340	3.786
114	8.75	0.323	3.753
114	8.25	0.316	3.739
114	7.46	0.401	3.900
114	6.68	0.394	3.887

$$\log K_p = -0.013pH + 3.95 \quad (r = -0.06,\ n = 29)$$

Copper Uptake by Hydrous Manganese Oxide
(Artificial Seawater, $5^o/oo$) ($\{Mn\} = 0.0843\ mg.L^{-1}$)

7	7.91	0.591	4.234
7	8.55	0.695	4.322
7	7.52	0.639	4.322
7	6.46	0.653	4.349

$$\log K_p = 0.020pH + 4.183 \quad (r = 0.21,\ n = 4)$$

Copper Uptake by Montmorillonite ($\{SWy\text{-}1\} = 250\ mg.L^{-1}$)

2.8	8.60	0.563	0.712
2.8	7.97	0.473	0.555
2.8	7.24	0.447	0.510
7	8.62	0.544	0.679
7	7.99	0.488	0.581
7	6.64	0.406	0.437
28	8.67	0.720	1.012
28	8.07	0.466	0.543
28	7.36	0.464	0.539
28	6.52	0.396	0.419

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Cu_T	pH	f	$\log K_p$
140	8.77	0.679	0.927
140	8.09	0.501	0.927
140	7.38	0.342	0.318
140	6.65	0.204	0.011

$\log K_p = 0.253pH - 1.40$ ($r = 0.82$, $n = 14$)

Copper Uptake by Aluminosilicate
(Artificial Seawater, $35^o/oo$) ($\{Al_2O_3 + SiO_2\} = 17.9\ mg.L^{-1}$)

2.8	8.40	0.771	2.275
2.8	8.13	0.553	1.841
2.8	7.32	0.496	1.741
2.8	6.63	0.355	1.489
7	8.48	0.934	2.899
7	8.17	0.730	2.180
7	7.28	0.729	2.178
7	6.85	0.525	1.792
28	8.26	0.841	2.472
28	8.14	0.788	2.318
28	7.27	0.603	1.930
28	6.59	0.441	1.645
112	8.45	0.933	2.892
112	8.13	0.795	2.337
112	7.26	0.576	1.881
112	6.81	0.408	1.587

$\log K_p = 0.523pH - 1.907$ ($r = 0.85$, $n = 16$)

Copper Titration of EHS, Scatchard Analysis
(Artificial Seawater, 35°/oo) ({EHS} = 20.03 mg.L^{-1})

Cu_T	E(mV)	Cu_{TS}	[CuL]	[CuL] /Cu_{TS}
pH = 6.3±0.1, Titration 1				
10	*-32.8	1.095	8.905	8.13
20	-35.0	0.965	19.04	19.73
40	-20.8	2.185	37.81	17.31
70	-0.2	7.153	62.85	8.79
100	13.1	15.38	84.62	5.50
200	39.2	69.10	130.9	1.894
400	61.3	246.6	153.4	0.622
700	75.2	548.9	151.1	0.275
1000	83.0	860.0	140.0	0.163
pH = 7.0±0.1, Titration 2				
10	*-61.2	0.4032	9.597	23.80
20	-58.3	0.478	19.52	40.84
40	-43.2	1.164	38.84	33.36
70	-22.8	3.87	66.13	17.09
100	-8.9	8.78	91.22	10.39
200	18.1	43.07	156.9	3.64
400	42.1	177.07	222.9	1.26
700	56.3	408.7	291.3	0.713
1000	63.8	635.7	364.3	0.573
2000	76.4	1335.4	664.6	0.498

* indicates that potential was still drifting (downwards) when read

Cu_T	E(mV)	Cu_{TS}	[CuL]	[CuL] /Cu_{TS}
pH = 7.7±0.1, Titration 3				
10	*-55.4	-		
20	*-57.7	0.309	19.69	63.73
40	-48.5	0.524	39.48	75.33
70	-34.4	1.180	68.82	58.32
100	-20.1	2.688	97.31	36.20
200	11.7	16.78	183.2	10.92
400	40.2	86.50	313.51	3.62
700	57.0	227.5	472.5	2.08
1000	65.6	373.4	626.7	1.68

* indicates that potential was still drifting (downwards) when read

APPENDIX D

DATA FROM ADSORPTION EXPERIMENTS WITH SOLID PHASE COMPLEXES

Cadmium Uptake by Iron-Hydroxy Interlayered Montmorillonite (Artificial Seawater, $35^{o}/oo$) ($\{Fe\} = 0.0511 g.L^{-1}$)

Cd_T	pH	f	$logK_p$
Iron in Isolation			
2.8	8.57	0.73	1.724
2.8	8.06	0.47	1.239
2.8	7.45	0.18	0.633
2.8	7.06	0.09	0.286
7	8.41	0.64	1.541
7	7.95	0.42	1.151

$$logK_p = 0.95pH - 6.44 \quad (r = 0.999,\ n = 6)$$

Iron-Clay Complex: 16 meq-$Fe.g^{-1}$Clay			
2.8	8.28	0.56	1.396
2.8	7.95	0.41	1.133
2.8	7.73	0.34	1.004
2.8	7.30	0.22	0.742
7	8.13	0.47	1.239
7	7.90	0.38	1.079
7	7.36	0.21	0.716

Iron-Clay Complex: 4 meq-$Fe.g^{-1}$Clay			
2.8	8.63	0.73	1.723
2.8	8.17	0.50	1.291
2.8	7.54	0.21	0.716
2.8	7.07	0.09	0.286

Cd_T	pH	f	$\log K_p$
7	8.51	0.66	1.579
7	7.92	0.38	1.079
7	6.99	0.11	0.383
7	6.70	0.03	-0.219
Iron-Clay Mixture: 4 meq-Fe.g^{-1}Clay			
2.8	8.68	0.79	1.867
2.8	8.05	0.50	1.291
2.8	7.09	0.12	0.426
2.8	6.88	0.10	0.337
7	8.49	0.71	1.680
7	7.95	0.45	1.204
7	7.08	0.09	0.316
7	6.48	0.02	-0.400
Iron-Clay Complex: 1 meq-Fe.g^{-1}Clay			
2.8	8.51	0.73	1.723
2.8	8.11	0.52	1.326
2.8	7.44	0.19	0.661
2.8	6.91	0.09	0.286
7	8.04	0.45	1.204
7	7.85	0.33	0.984

Copper Uptake by Iron-Hydroxy Interlayered Montmorillonite (Artificial Seawater, $35^o/oo$) ($\{Fe\}$ = 1.636 mg.L^{-1})

Iron-Clay Complex: 4 meq-Fe.g^{-1}Clay			
7	8.38	0.812	3.422
7	7.97	0.769	3.309
7	7.17	0.671	3.096
7	6.67	0.602	2.966

Cd_T	pH	f	$\log K_p$
28	8.47	0.907	3.775
28	8.01	0.768	3.306
28	7.22	0.727	3.212
28	6.74	0.616	2.991
Iron-Clay Complex: 1 meq-Fe.g^{-1}Clay			
7	8.40	0.856	3.560
7	8.01	0.773	3.318
7	7.20	0.723	3.203
7	6.73	0.601	2.964
28	8.43	0.873	3.623
28	8.21	0.865	3.593
28	7.22	0.741	3.243
28	6.77	0.626	3.010

Cadmium Uptake by Humic-Coated Hydrous Iron Oxide (Artificial Seawater, $35^o/oo$) ({Fe} = 0.1023 $g.L^{-1}$)

Iron in Isolation			
2.8	8.61	0.843	1.720
2.8	7.92	0.600	1.166
2.8	7.32	0.326	0.675
2.8	6.92	0.154	0.250
7	8.17	0.696	1.350
7	7.67	0.439	0.884
7	6.75	0.120	0.125
7	6.98	0.166	0.289

$$\log K_p = 0.87pH - 5.74 \quad (r = 0.998,\ n = 8)$$

Cd_T	pH	f	$logK_p$
Iron-Humic Complex: Organic-C:Fe, 1:12			
2.8	8.19	0.687	1.328
2.8	7.53	0.361	0.729
2.8	7.22	0.238	0.463
2.8	6.91	0.138	0.156
7	7.51	0.348	0.704
7	7.45	0.333	0.675
7	7.03	0.167	0.260
7	6.81	0.126	0.107
Iron-Humic Complex: Organic-C:Fe, 1:2			
2.8	7.85	0.554	1.056
2.8	7.47	0.355	0.672
2.8	6.95	0.167	0.139
2.8	6.74	0.120	-0.105
7	7.34	0.300	0.548
7	7.26	0.261	0.449
7	6.92	0.170	0.154
7	6.68	0.132	-0.022
Iron-Humic Complex: Organic-C:Fe, 3:1			
2.8	7.80	0.677	1.204
2.8	6.89	0.296	-0.153
2.8	6.66	0.226	-
7	7.13	0.406	0.480
7	6.96	0.350	0.252

Cadmium Uptake by Ternary Clay-Iron-Humic Complexes
(Artificial Seawater, $35^{o}/oo$) ({Fe} = 0.1023 $g.L^{-1}$)

Cd_T	pH	f	$logK_p$
Iron-Clay Complex (Uncoated) 4 meq-Fe.g^{-1}Clay			
7	8.36	0.71	1.379
7	7.67	0.37	0.759
7	7.39	0.23	0.465
Iron-Clay Complex (Uncoated) 1 meq-Fe.g^{-1}Clay			
7	8.35	0.74	1.444
7	7.45	0.29	0.601
7	7.08	0.15	0.237

$$logK_p = 0.93pH - 6.37 \ (r = 0.997, n = 6)$$

Ternary Complex, 4 meq-Fe.g^{-1}Clay, Org-C:Fe, 1:2			
7	8.42	0.78	1.528
7	7.42	0.28	0.495
7	7.07	0.19	0.227
Ternary Complex, 1 meq-Fe.g^{-1}Clay, Org-C:Fe, 1:2			
7	8.26	0.78	1.529
7	7.27	0.23	0.357
7	6.99	0.14	0.000
Ternary Complex, 4 meq-Fe.g^{-1}Clay, Org-C:Fe, 3:1			
7	8.22	0.78	1.470
7	8.19	0.76	1.413
Ternary Complex, 1 meq-Fe.g^{-1}Clay, Org-C:Fe, 3:1			
7	8.33	0.79	1.498
7	7.87	0.62	1.055