AN ABSTRACT OF THE THESIS OF

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Title: THE GEOCHEMICAL PARTITIONING AND BIOAVAILABILITY OF TRACE

METALS IN MARINE SEDIMENTS

Abstract approved: *Redacted for Privacy*

Kenneth J. Williamson

Trace metals in the aquatic environment are generally concentrated on the surface of solid geochemical phases which eventually become incorporated into estuarine and marine sediments. The mechanism of trace metal concentration is believed to be adsorption with various geochemical phases such as hydrous metal oxides, clays, and organic matter. Metals in estuarine or marine sediments can thus be expected to be partitioned between different phases, depending on the concentration of the phase and the strength of the adsorption bond.

The bioavailability of sediment-bound metals to deposit-feeding organisms will depend on trace metal partitioning and the kinetics of biological metal uptake from each geochemical phase. The present study was undertaken to develop models for trace metal partitioning and bioavailability in marine sediments.

An equilibrium adsorption model was developed that can be used to predict the partitioning of trace metals between different geochemical phases in aquatic sediments from laboratory studies. The model uses conditional equilibrium constants determined from the linear portion of an adsorption isotherm. Conditional equilibrium constants deter-

mined for the adsorption of Cu and Cd on bentonite clay, $Fe(OH)_3$, MnO_2, and humic acid in seawater show that the model is applicable for trace metal concentrations existing in the natural environment. Based on the laboratory results, the model predicts that the clay fraction may be a major sink for Cu and Cd in marine sediments.

A kinetic bioavailability model was then developed which can be used to estimate the relative bioavailability of trace metals from both different sediment phases and seawater under short-term laboratory conditions. This model was used to determine the bioavailability of Cu and Cd from several sediment phases (bentonite clay, humic acid, $Fe(OH)_3$) and seawater to the deposit-feeding polychaete worm, Abarenicola pacifica. The results suggest that, under natural conditions similar to those used in this study, the bioavailability of sediment-bound Cu and Cd to A. pacifica can be much more significant than that of seawater.

The Geochemical Partitioning and Bioavailability
of Trace Metals in Marine Sediments

by

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CHAPTER 1

INTRODUCTION

Trace metals in the aquatic environment are generally concentrated

on the surface of solid geochemical phases which, after transport

through river systems, become incorporated into estuarine and marine

sediments. The mechanism of trace metal concentration is believed to

be adsorption with various geochemical phases such as hydrous metal

oxides, clays, and organic matter. Metals in estuarine or marine sedi-

ments can thus be expected to be partitioned between different phases,

depending on the concentration of the phase and the strength of the

respective adsorption bond.

Because the concentrations of metals in sediments are usually

several orders of magnitude higher than those in the water column, and

because marine organisms are known to accumulate high concentrations of

trace metals in their tissues, it is important to assess the bioavaila-

bility of sediment-bound metals to benthic organisms. Since there is

little evidence in the literature to suggest that trace metals are bio-

magnified in food chains, the bioavailability of sediment-bound metals

should be most significant for non-selective deposit feeder organisms

which indiscriminately ingest sediment particles.

Although there have been studies in the literature which attempt

to assess the bioavailability of sediment-bound metals, the results have

either been contradictory or inconclusive. Since bioavailability will

depend upon trace metal partitioning, the kinetics of biological metal uptake from each geochemical phase, the species of organism, and the environmental conditions, it is necessary to utilize information both from chemical adsorption studies and biological studies to develop conceptual and mathematical models for assessing bioavailability to deposit-feeding organisms; the present study was undertaken in an attempt to fulfill these objectives.

The specific objectives of this study were:

1. To develop an adsorption and partitioning model for select geochemical phases in seawater.

2. To develop a kinetic bioavailability model for trace metal uptake from sediments and water.

3. To conduct laboratory studies in order to estimate parameters for the above models for several trace metals.

CHAPTER 2

THE ADSORPTION AND PARTITIONING OF TRACE METALS IN MARINE SEDIMENTS

Introduction

Trace metals are known to concentrate in the sedimentary material

of natural aquatic systems (1-4). This accumulation of metals is thought

to be caused by adsorption processes with various geochemical phases

such as hydrous metal oxides, clays, and organic matter (5-9). Since

the bioavailability to sediment-ingesting organisms and release of trace

metals to the water column after changes in the chemical environment

depend on the geochemical phase with which a metal is associated (10),

the partitioning of metals between geochemical phases is the most impor-

tant factor influencing their overall environmental behavior. Trace

metal partitioning is a function of metal type and species, the concen-

trations of the geochemical phases present, and the chemical environment

of the ambient water.

Current data on metal partitioning are based on empirical analy-

tical methods in which metals are selectively extracted from environmen-

tal samples (11-15). Although these extraction methods have given some

valuable insight, they are often plagued with difficulties, such as non-

selectivity, that raise serious questions as to their reliability (16,17).

Recently several authors have introduced new methods that attempt

to overcome the difficulties of selective extraction. Luoma and Bryan

(18) have used statistical correlations to define chemical relationships

between total trace metal concentrations and geochemical phase concen-

trations. Pilkington and Warren (19) used a density gradient technique

to separate geochemical phases which allowed separate analysis for trace

metal concentrations. These methodologies offer promise in overcoming the inherent difficulties of selective chemical extractions.

Although empirical studies can give valuable information that is directly applicable to natural systems, there is also a need to develop a theoretical base for understanding and predicting trace metal behavior. In this way, the results of empirical studies can be interpreted in a much more meaningful way. There are several models in the literature dealing with the adsorption of metals (20-26), but only a few of these consider partitioning among competing surfaces (25), and most deal with simple electrolyte systems using a single solid phase (usually an oxide). These models are limited in their ability to predict adsorption and partitioning in complex systems (e.g., seawater and several solid phases) because of the number of parameters that need to be measured (26).

In this paper a simple conditional equilibrium model is proposed that can be used to describe and predict the partitioning of trace metals between any number of sediment phases. Previous studies have shown that the kinetics of partitioning are rapid (within several days) (27), thus it seems reasonable to assume equilibrium as a first approximation. The value of this type of model is that trace metal partitioning can be theoretically calculated from conditional equilibrium constants derived from simple adsorption experiments. The results of the model then can be compared with field data to give further insight into trace metal behavior.

Copper (Cu) and cadmium (Cd) were the two metals chosen for study. These metals are both important aquatic pollutants (4), and are also useful for comparative study because of their widely different complex-

ation behavior; Cu shows a high preference for organics whereas Cd does not (28). The geochemical phases chosen were amorphous iron and manganese oxides, humic acid, and bentonite clay. These phases represent the principle types of adsorbents in aquatic sediments (9). The hydrous metal oxides have long been indicated as the major sink for trace metals in aquatic sediments (7). Humic acid represents the main component of organic matter in marine sediments (29,30). Although the clay type in a sediment can vary widely, bentonite (montmorillonite) was chosen as a representative clay. Seawater was chosen as the solution medium.

The specific objectives of this study were to:

1. Develop a theoretical model for trace metal partitioning between different geochemical phases based on conditional equilibrium adsorption constants derived from adsorption isotherms.

2. Determine conditional equilibrium adsorption constants for Cu and Cd from adsorption isotherms for the geochemical phases in marine sediments.

3. Use the model to predict metal partitioning and determine the important sinks for different geochemical phase concentrations in marine sediments.

Theory

Adsorption

In this model, it is assumed that the mechanism for trace metal association with sediment phases is an adsorption reaction. The adsorption of a soluble free metal ion, Me, with an available solid phase, S, can be conceived as a reversible equilibrium reaction that

is dependent on the bulk concentration of both metal species and solid phase. Thus:

$$Me + S \overset{K_{eq}}{=} MeS \tag{1a}$$

$$K_{eq} = \frac{[MeS]}{[Me][S]} \frac{\gamma_{MeS}}{\gamma_{Me}\gamma_{S}} \tag{1b}$$

where [MeS] is the amount of surface covered by metal Me, K_{eq} is the thermodynamic equilibrium constant, and γ's are the respective activity coefficients (brackets signify concentration in terms of moles/l). This equation is conceptually equivalent to solution equilibria such as complex formation.

Likewise, the adsorption of soluble metal-ligand complexes (which may be more important than adsorption of the free metal ion) on surface S is:

$$MeL_i(j) + S \overset{K_{eq}(i,j)}{=} MeL_i(j)S \tag{2a}$$
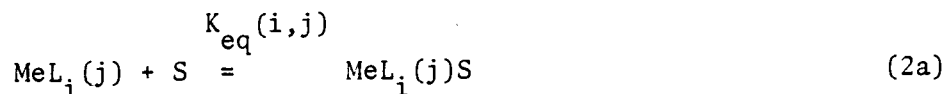
$$K_{eq}(i,j) = \frac{[MeL_i(j)S]}{[MeL_i(j)][S]} \frac{\gamma_{MeL_i(j)S}}{\gamma_{MeL_i(j)}\gamma_S} \tag{2b}$$

where L is a soluble ligand of type j and i represents system stoichiometry.

There are several operational difficulties in applying Equations 1b or 2b. First, the concentration units for S, MeS, and $MeL_i(j)S$ should be, from a thermodynamic view, in terms of moles per liter. For simple systems containing solid phases with well characterized surfaces, it is possible to express [S] in terms of moles of surface sites per

liter of solution (22,23). However, poorly characterized surfaces such
as humic acids and metal oxide-coated clays may preclude accurate deter-
mination of the number of surface sites even in simple systems.

Second, since [S] represents the equilibrium concentration of avail-
able (uncomplexed or unbound) surface sites in equations 1b and 2b, it
is necessary to know the concentration of all metal-ligand complexes
and their respective adsorption equilibrium constants. This information
would have to be known for all metal species, both major and minor. At
present, there are incomplete adsorption data to use for complex systems
such as seawater environments.

Equations 1b or 2b can be more readily applied if some simplifying
assumptions are made. In a seawater environment, the concentrations of
all major species, pH, pE, and ionic strength can be assumed to be fixed.
Thus the trace metal of interest can be studied by using a conditional
equilibrium constant approach. In this case, the adsorption reaction
can be written as:

$$Me_T + S_T \overset{K_{AD}}{=} MeS \tag{3a}$$

$$K_{AD} = \frac{[MeS]}{[Me_T]\{S_T\}} \tag{3b}$$

$$[Me_T] = \overset{i}{\Sigma} \overset{j}{\Sigma} [MeL_i(j)] \tag{4}$$

$$[MeS] = \overset{i}{\Sigma} \overset{j}{\Sigma} [MeL_i(j)S] \tag{5}$$

where $[Me_T]$ is the total soluble trace metal concentration for metal Me
in moles/1, $\{S_T\}$ is the total concentration of the solid phase in g/1,

[MeS] is the concentration of metal-solid complex in moles/l, and K_{AD} is the conditional equilibrium adsorption constant in l/g for metal Me and solid phase S (where [ ] denotes moles/l and { } denotes g/l).

Equation 3b contains mixed units, but is conceptually equivalent to Equations 1b or 2b. The advantage of using mixed units can be seen if Equation 3b is arranged as follows:

$$\frac{[MeS]}{\{S_T\}} = K_{AD}[Me_T] \tag{6}$$

Equation 6 is identical to a linear adsorption isotherm since:

$$\frac{[MeS]}{\{S_T\}} = \Gamma \tag{7}$$

where Γ is the adsorption density of a metal on a solid surface in moles/g. In this case, the conditional equilibrium constant, K_{AD}, is identical to the distribution coefficient and is equal to the slope of a straight line on a Γ versus Me_T plot (Figure 1).

From Figure 1, it can be seen that Equation 6 only applies in the region where $\lambda\{S_T\} \gg [MeS]$, where λ is the mass occupied by each mole of adsorbent. That is, the adsorption of the trace metal must have only negligible effect on the total concentration of available surface sites.

By combining Equations 2b, 3b, 4, and 5, the relationship between the conditional equilibrium constant, K_{AD}, and the thermodynamic equilibrium constants, $K_{eq}(i,j)$, for metal Me and surface S can be expressed as
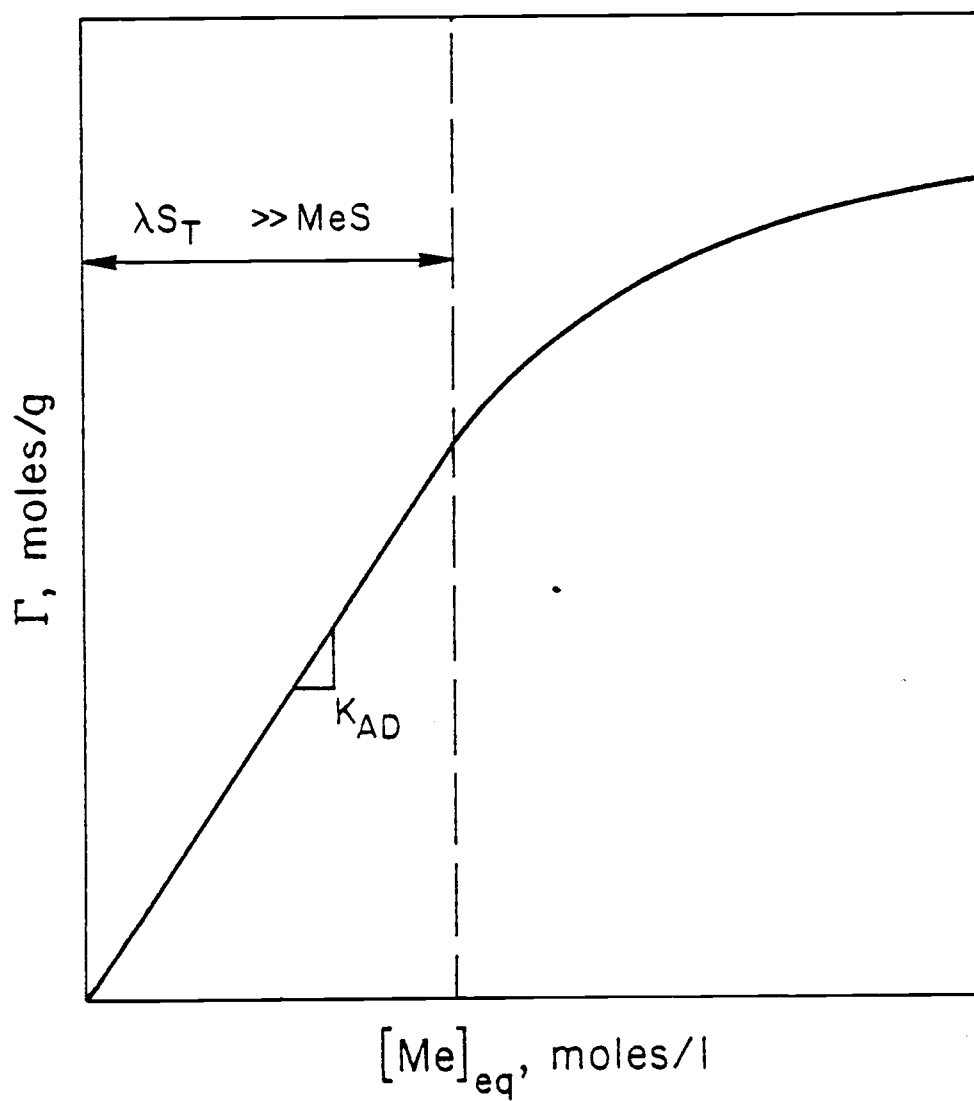
Figure 1. A Theoretical Adsorption Isotherm

$$K_{AD} = \left[\sum_i^{} \sum_j^{} \left(\frac{K_{eq}(i,j) \; \gamma_{MeL_i}(j) \; \alpha(i,j)}{\gamma_{MeL_i}(j)S} \right) \right] \frac{\gamma_S}{\lambda} \tag{8}$$

where

$$\alpha(i,j) = \frac{[MeL_i(j)]}{[Me_T]} \quad \text{and} \quad \lambda = \{S\}/[S]$$

From Equation 8, K_{AD} is seen to be a linear combination of the individual $K_{eq}(i,j)$ for all metal-ligand species. It thus can be considered as an integrative or overall adsorption parameter with the inherent advantages and limitations the simplification necessarily implies.

Metal Partitioning

If the linear assumption of Equation 6 is valid for typical environmental concentrations of trace metals, it can be assumed that there is negligible competition in the adsorption between different trace metals. Thus, adsorption and partitioning systems of trace metals in the linear range can be studied individually without considering competing equilibria as long as all other factors are constant (major cation species, pH, pE, ionic strength).

The partitioning of a given metal Me between various competing surfaces will be a function of their respective concentrations and conditional equilibrium constants for adsorption. For a given solid phase, $S_T(k)$, the concentration of adsorbed metal species is:

$$[MeS(k)] = K_{AD}\{S_T(k)\}[Me_T] \tag{9}$$

The total concentration of metal in the system, both soluble and ad-

sorbed is:

$$[Me_{ST}] = [Me_T] + [MeS(k)] \tag{10}$$

$$[Me_{ST}] = [Me_T] + K_{AD}\{S_T(k)\}[Me_T] \tag{11}$$

For k surfaces:

$$[Me_{ST}] = [Me_T] + \sum^k K_{AD}(k)\{S_T(k)\}[Me_T] \tag{12}$$

$$[Me_{ST}] = [Me_T] (1 + \sum^k K_{AD}(k)\{S_T(k)\}) \tag{13}$$

The fraction of metal adsorbed on a particular solid phase is then:

$$\frac{[MeS(k)]}{[Me_{ST}]} = \frac{K_{AD}(k)\{S_T(k)\}[Me_T]}{[Me_T](1 + \sum^k K_{AD}(k)\{S_T(k)\}} = \frac{K_{AD}(k)\{S_T(k)\}}{1 + \sum^k K_{AD}(k)\{S_T(k)\}}$$

$$\tag{14}$$

Values of K_{AD} can be determined for different solid phases from laboratory adsorption experiments. If the linear range of the isotherm is within the environmental range of interest, then Equation 14 can be used to predict the equilibrium partitioning of a given trace metal between different solid phases. Equation 14 is independent of soluble trace metal concentration as long as the concentration is within the linear portion of the isotherm.

Mathematically, this model is identical to those of complexation and distribution of soluble trace metals among dissolved ligands (31). It should be emphasized that this model is, however, conditional upon

the experimental conditions for which the values of K_{AD} are determined.

Experimental

Reagents and Glassware

All laboratory glassware used was washed with 50 percent nitric acid and rinsed twice with double-distilled water. Polyethylene bottles were used for the storage of all liquid solutions.

Stock metal solutions were prepared by dissolving the reagent grade metal with redistilled nitric acid and diluting to the desired volume with double-distilled water.

Seawater (salinity = 32 o/oo) was collected from Oregon coastal waters, filtered sequentially through a sand filter and 0.2 μm membrane filter (Ultipor), and stored at 4°C in polyethylene bottles. The dissolved organic carbon concentrations ranged from 2 to 3 mg/l in the seawater samples.

Preparation of Solids

Bentonite clay (Fisher Scientific) was washed with double-distilled water and seawater.

Amorphous iron oxide $(Fe(OH)_3)$ was prepared by adding a stock ferric nitrate solution to double-distilled water and adjusting to pH 8.0 with sodium hydroxide. The resulting suspension was washed several times with seawater and aged for 24 hours before use.

Hydrous manganese oxides (MnO_2) were prepared using the technique of Morgan and Stumm (32). Briefly, a solution of manganese sulfate was added to a requisite solution of potassium permanganate at pH 8.0. The resulting suspension was also washed with seawater and aged for 24 hours

before use.

Humic acid (K & K Chemical) was washed with 1 N nitric acid, then rinsed with double-distilled water and seawater. The final ash content (550°C for 24 hrs) was 14 percent.

After washing and aging, all solids were stored as a stock slurry mixture in the filtered seawater. The concentration of solid in each slurry was determined by drying a known volume at 105°C for 24 hours. Because drying alters the surface characteristics of solids, only dilutions of stock slurry mixtures were used for adsorption experiments.

Adsorption Experiments

Adsorption experiments were carried out in 50 ml polyethylene centrifuge tubes in which a known amount of solid ($\simeq$ 10 mg) was added to 25 ml of seawater. A requisite amount of stock metal solution then was added and the pH adjusted to 8.0 $\pm$ 0.1 with NaOH or HNO_3. The tubes then were agitated for 24 hours on a wrist shaker; preliminary studies had shown that the kinetics of adsorption are rapid, and that equilibrium appears to be reached within one hour. The solid/liquid separation for the clay and hydrous metal oxides was achieved by centrifuging the tubes at 1500 g for 30 minutes; the supernatant solution showed no visible Tyndall cone indicating that colloidal material was effectively removed.

Although in the natural environment, humic acid adsorbs on clays (33,34) and other surfaces (35,36), in a simple system of humic acid and seawater a stable sol is formed that cannot be removed by centrifugation (38). Therefore the humic acid was separated by ultrafiltration using a methodology similar to those used by Wheeler (38) and

MacFarlane (30). A UM-2 ultrafilter (Amicon Corp.) that had been stored in seawater for several days to equilibrate its surfaces was used for the separation. This filter removed the visible colloidal material, but did not appear to alter the dissolved organic carbon content of the seawater. The equilibrated filter did not significantly adsorb metal concentrations of Cu or Cd down to 10 μg/l if the first 10 ml of filtrate was discarded.

Analysis

The soluble metal concentrations of Cu and Cd were measured using a Perkin Elmer Model 360 atomic absorption spectrophotometer equipped with a HGA-2100 graphite furnace. The settings utilized on the graphite furnace for seawater samples were adopted from Segar and Cantillo (39). Direct injection volumes of 10 μl and 50 μl gave detection limits of ·1 μg/l and 5 μg/l for Cd and Cu, respectively.

The quantity of metal adsorbed on the solid was calculated by difference from the amount of metal added and the final soluble concentration. Adsorption on the walls of the centrifuge tubes was found to be negligible for the concentrations used.

Results and Discussion

Adsorption Isotherms

Figures 2 through 9 show the adsorption isotherms obtained for Cu and Cd for each of the four solid phases. All of the isotherms exhibit a linear portion in which the assumptions of Equation 6 are valid. Although these data could be fitted to a Langmuir or Freundlich equation, this is not necessary if the region of interest is confined to the
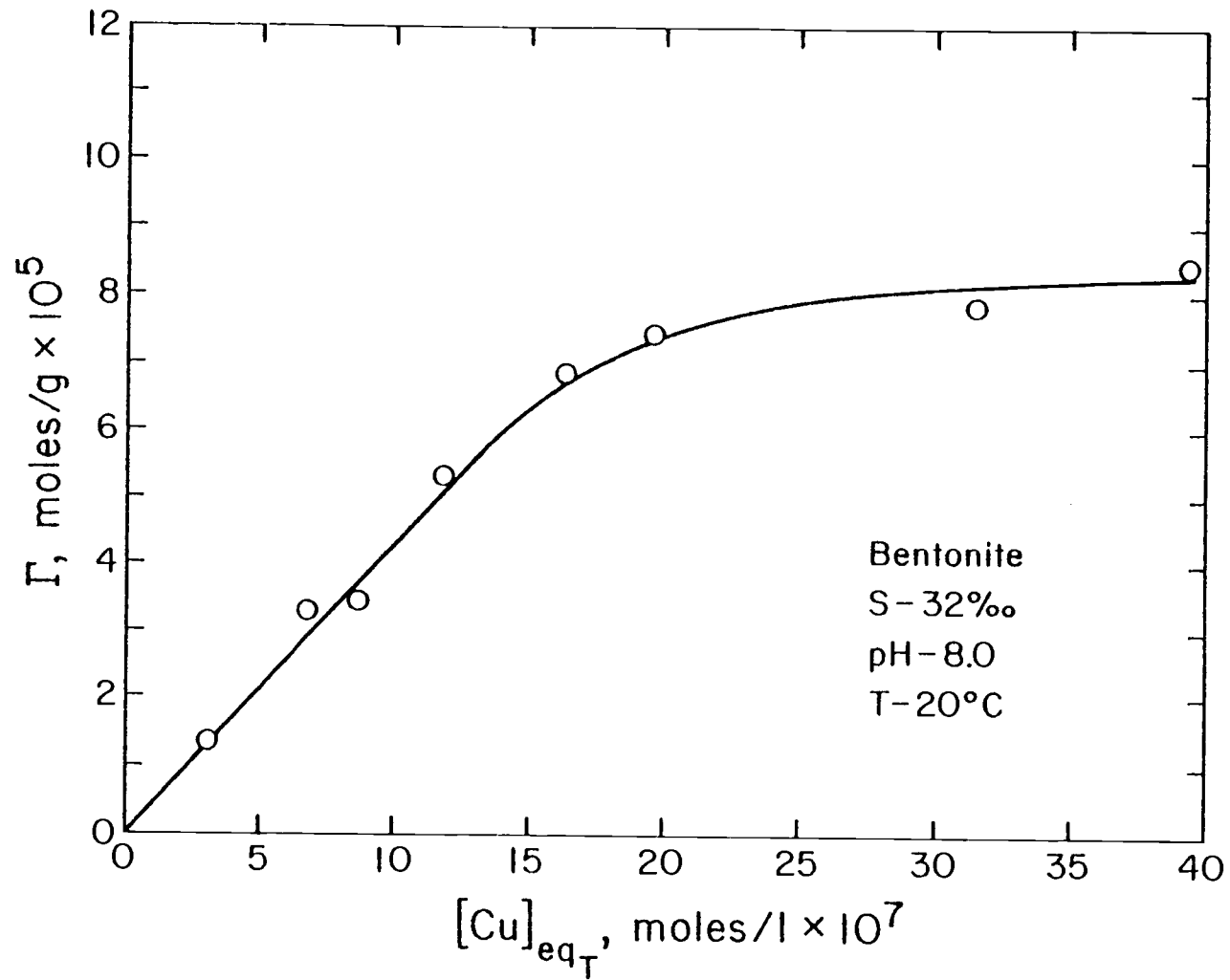
Figure 2. Adsorption Isotherm for Cu on Bentonite in Seawater
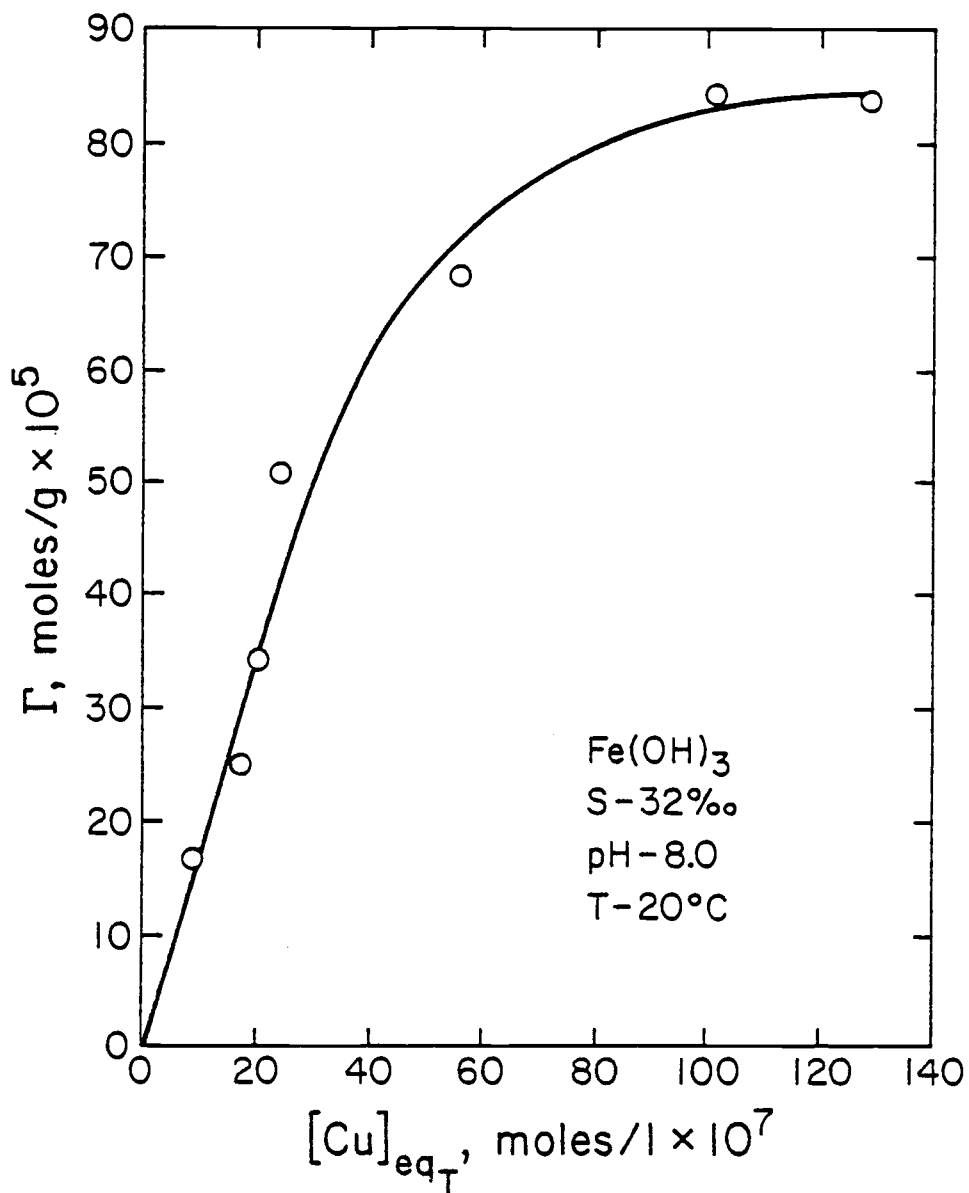
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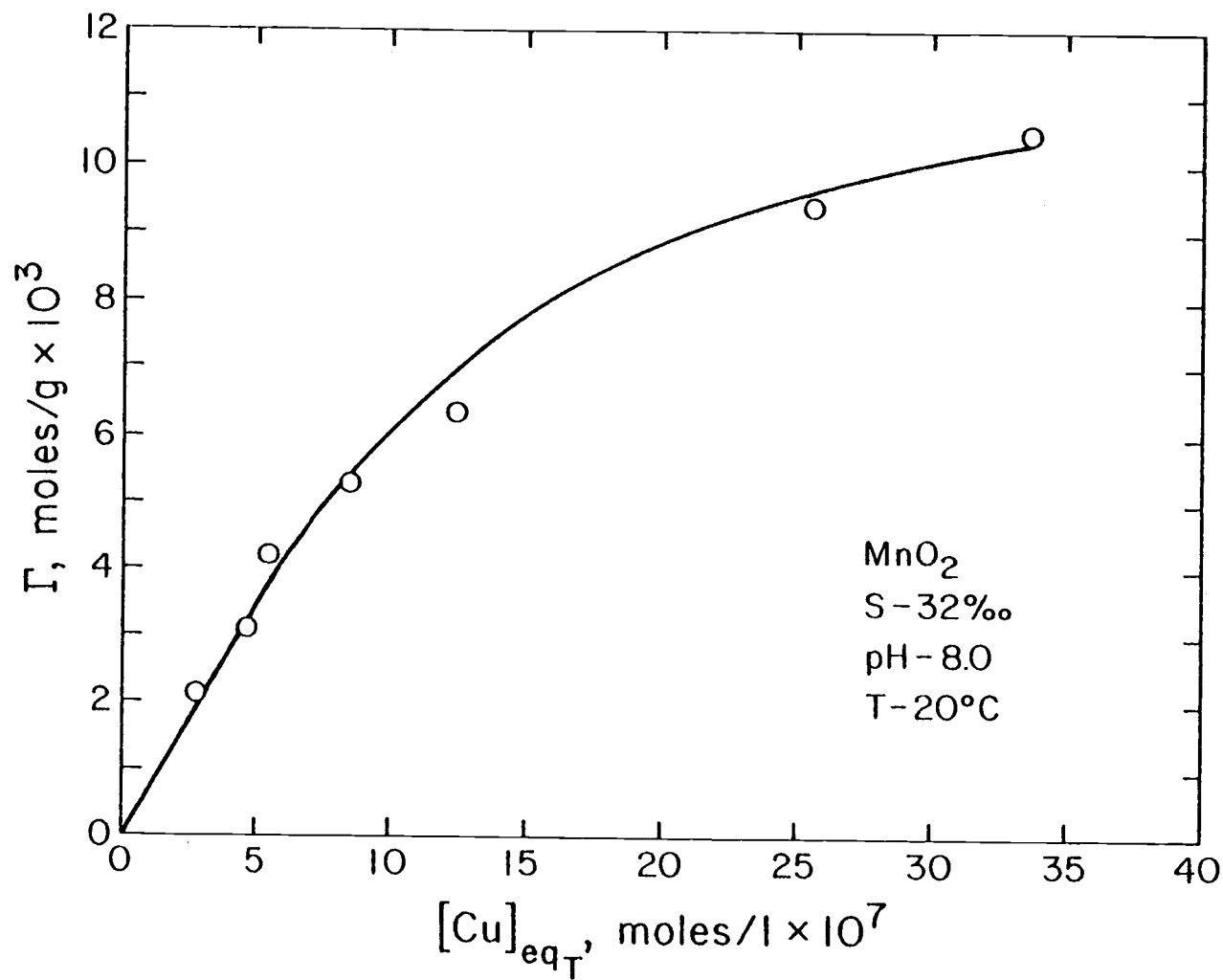
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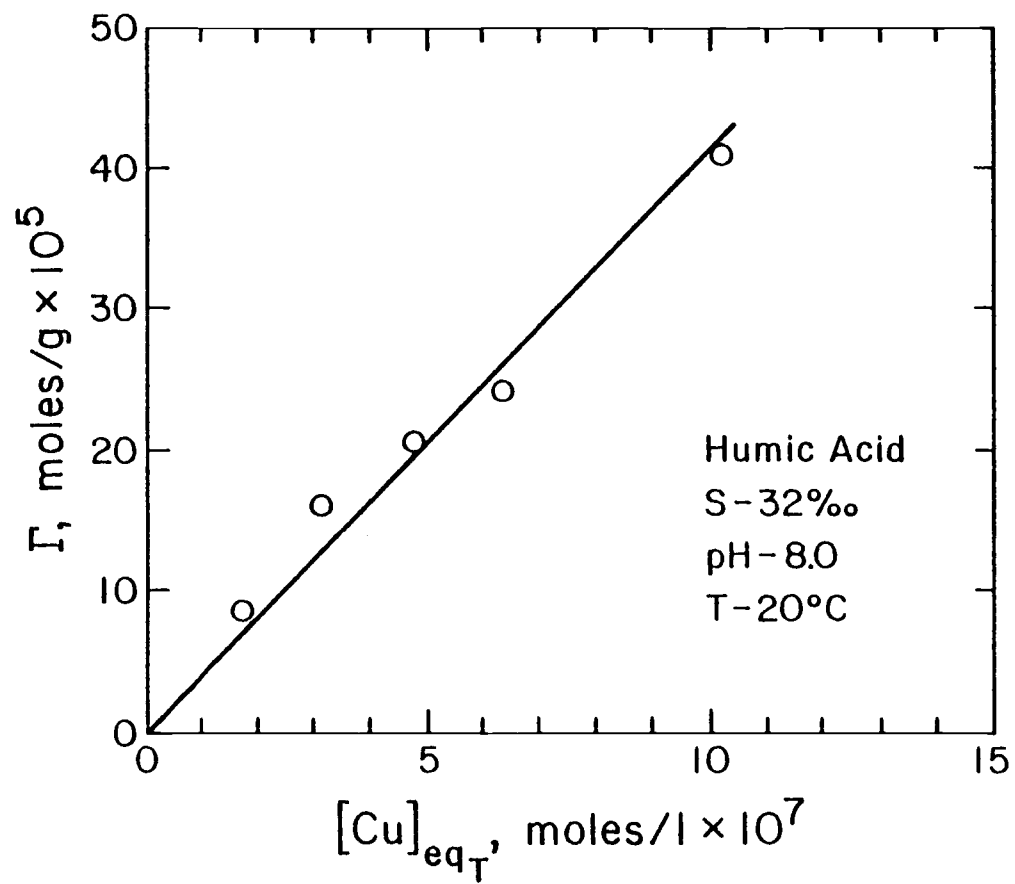
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in Seawater
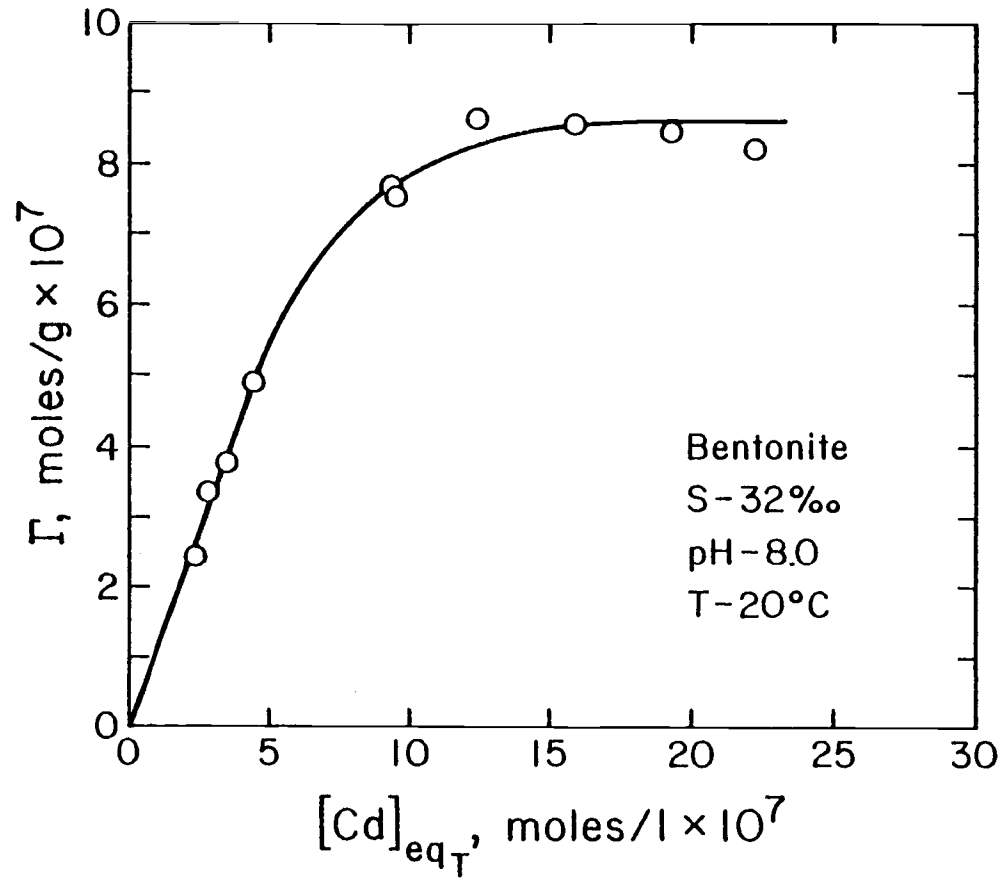
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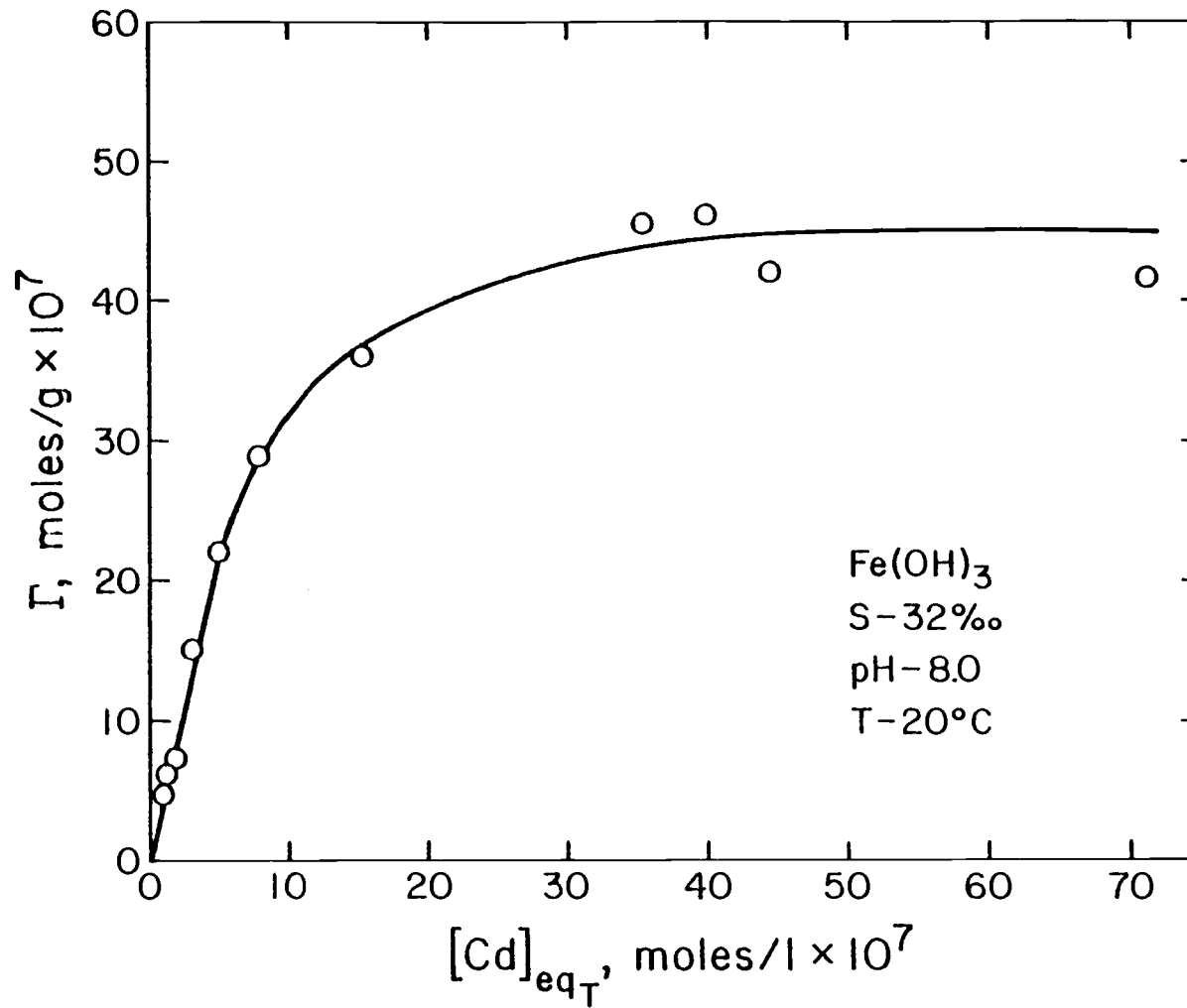
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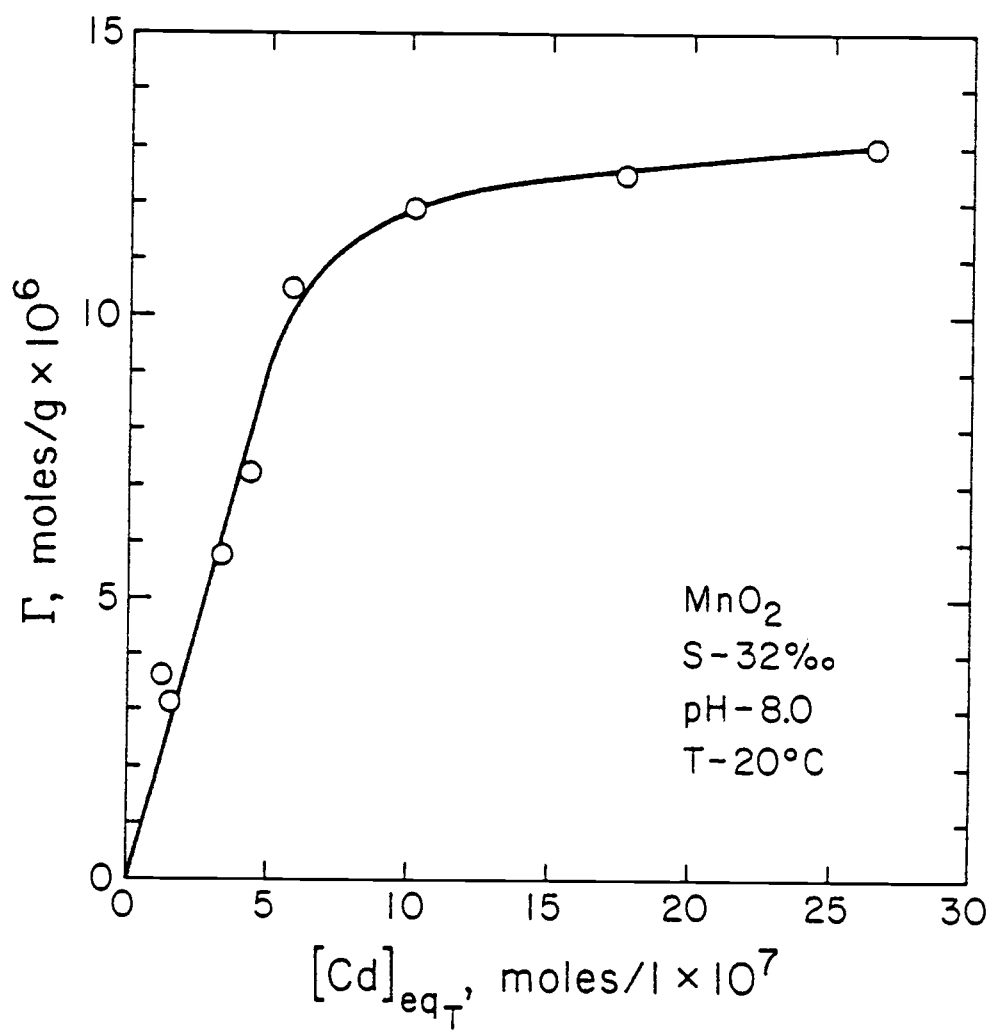
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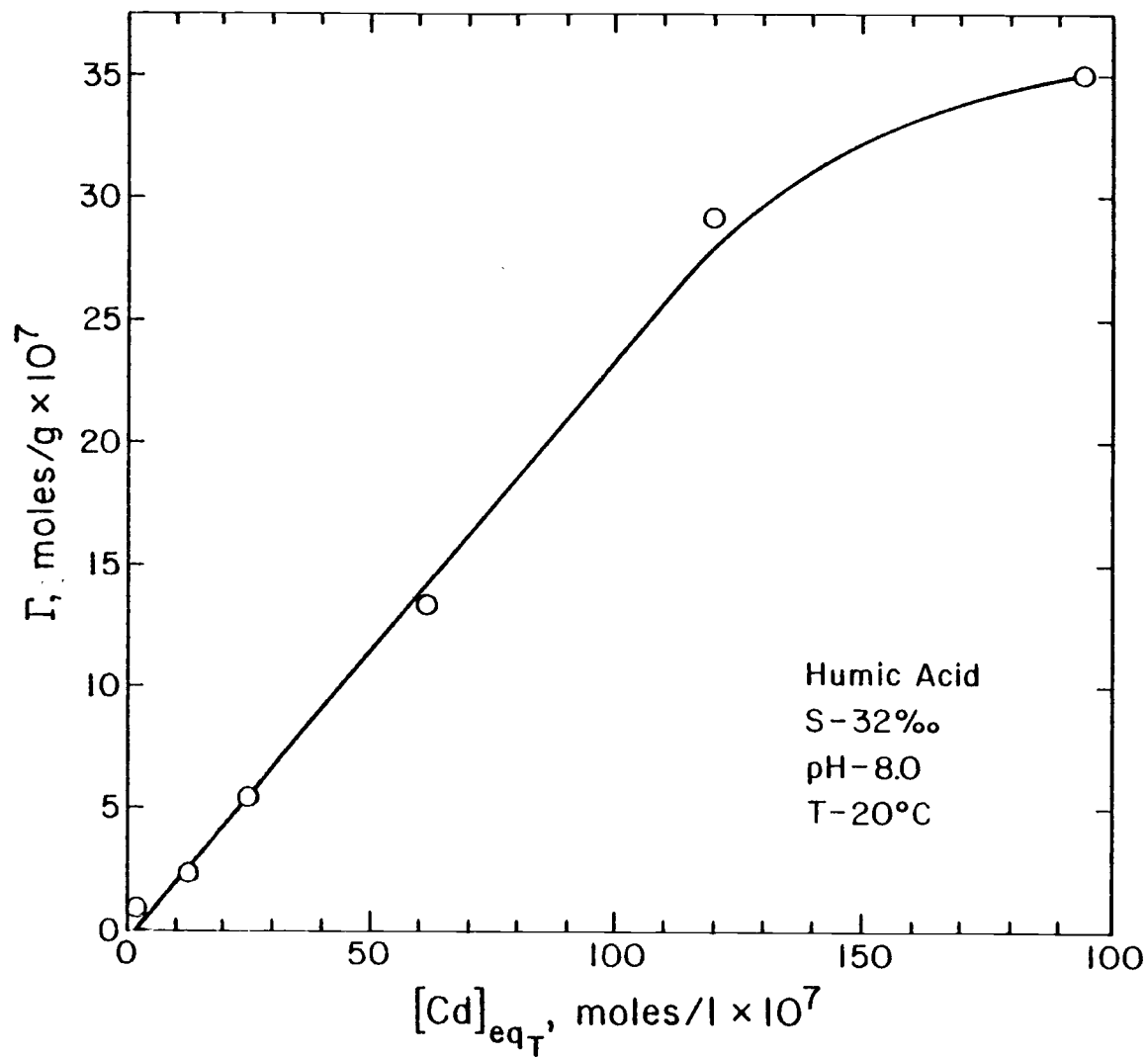
Figure 9. Adsorption Isotherm for Cd on Humic Acid in Seawater

linear portion.

The linear portions of the isotherms are plotted in Figures 10 and 11. These data show that the equilibrium soluble metal concentrations within the linear range are well above those typically measured in estuaries and coastal waters. Thus, the application of Equation 6 appears valid for concentrations of Cu and Cd likely to be encountered in the natural environment.

The conditional equilibrium constants for each metal were calculated from the data in Figures 10 and 11 by simple linear regression and are listed in Table 1. Copper exhibits a much higher affinity than cadmium for all solid phases. Although the K_{AD} for humic acid for Cu is high relative to the other phases, it is the lowest for Cd; this is corroborated by evidence in the literature that shows Cu has a higher preference for organics than most other trace metals (28). The hydrous manganese oxides show the highest K_{AD} values for both Cu and Cd. Jenne (9) has stated that hydrous manganese oxides exhibit much more extensive isomorphic substitution than amorphous iron oxides, thus their high K_{AD} values are not surprising.

There are several limitations in the use of K_{AD} values obtained from these isotherms which must be recognized in order to avoid erroneous interpretation of results. First, the amorphous hydrous oxides utilized are not thermodynamically stable phases, but only metastable ones. Thus, true equilibrium is not attained. Nevertheless, these phases only slowly transform into stable ones and the experimental results represent reproducible phenomena within short time spans. Because most estuarine and near-shore sediments exhibit rapid turnover rates, it is plausible to assume that the metastable phases will be the
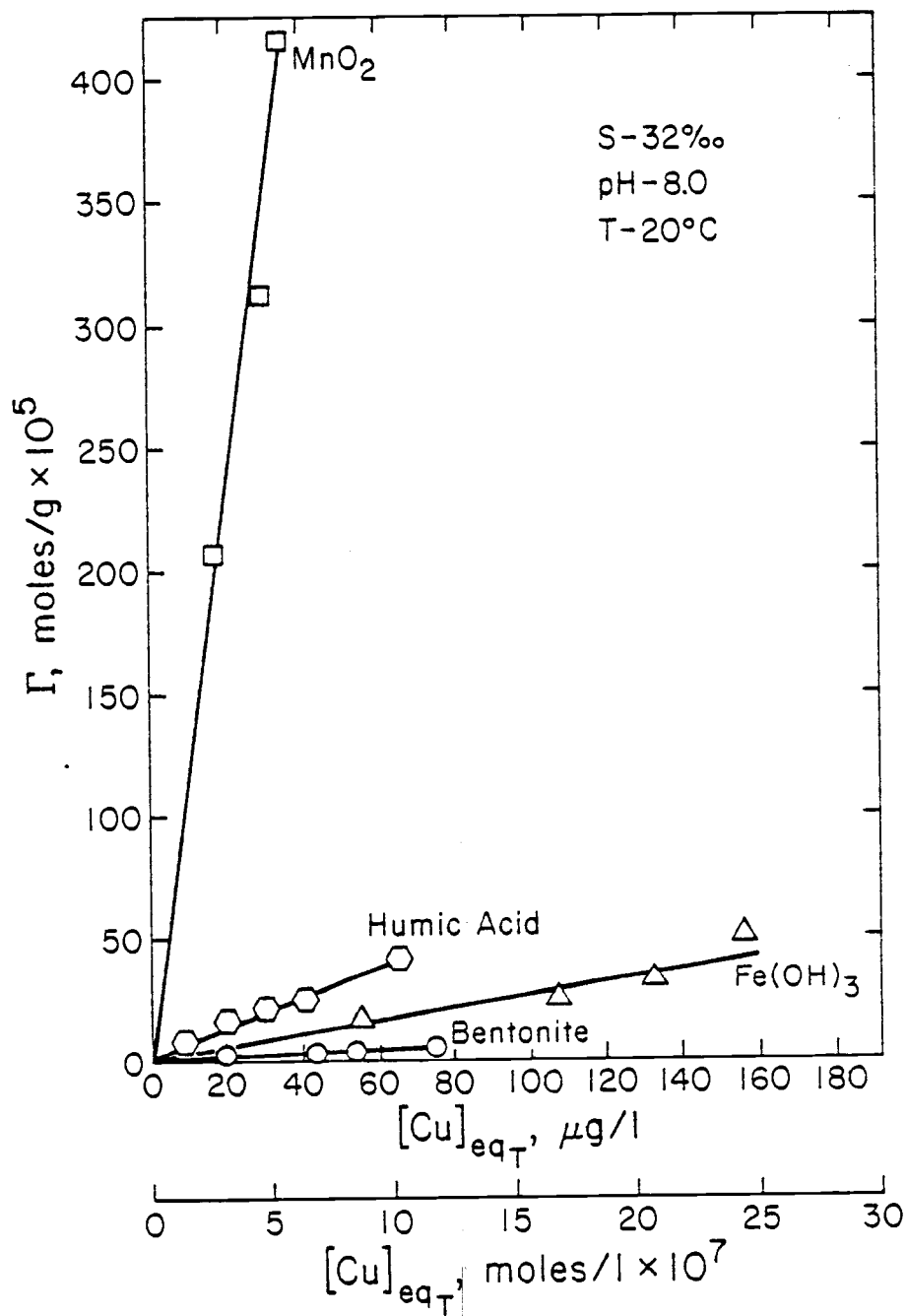
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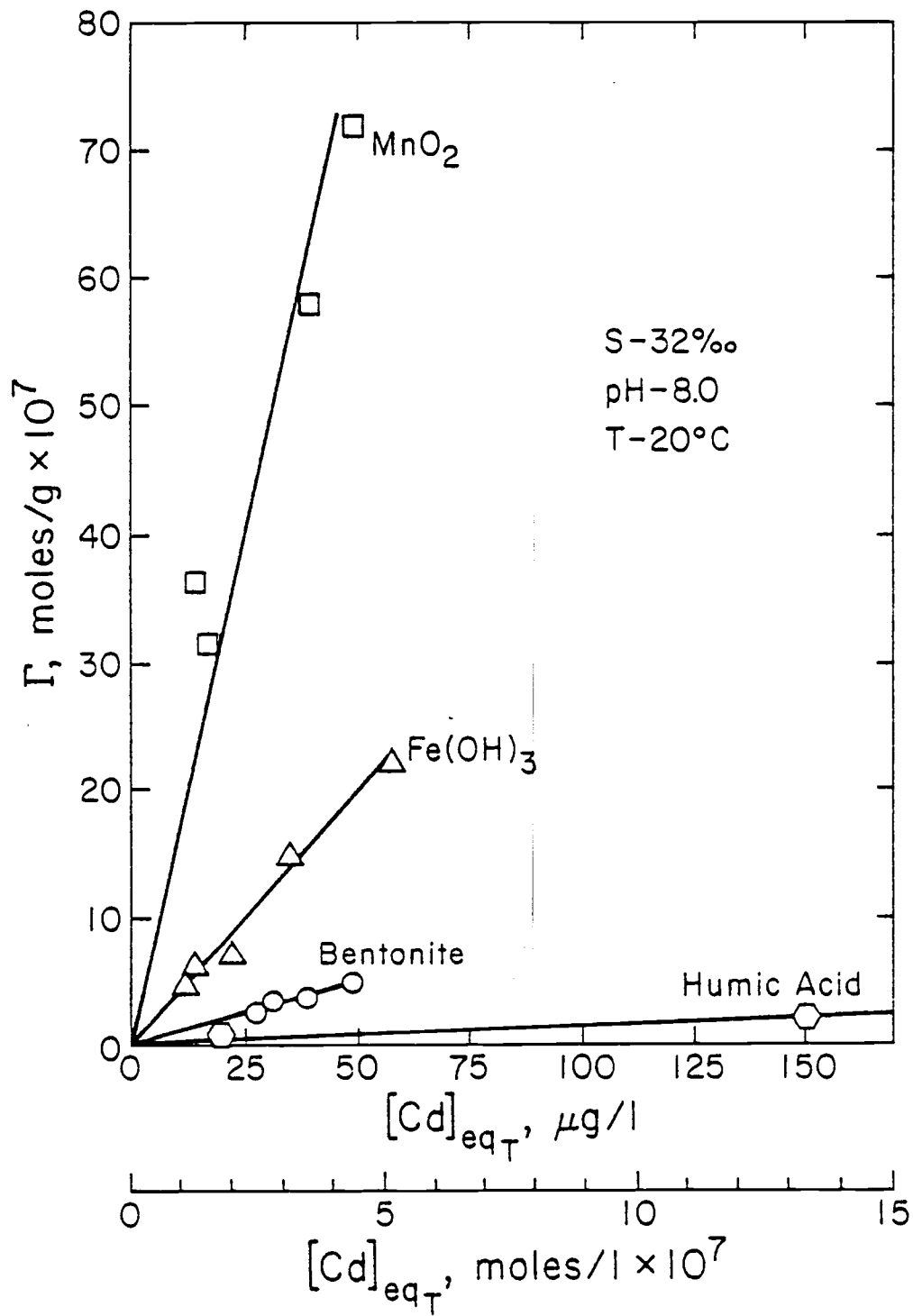
Figure 11. Linear Adsorption Isotherms for Cd in Seawater

Table 1. Conditional Equilibrium Constants for Cu and Cd in
Seawater. pH - 8.0; S - 32 o/oo; T - 20°C.

Solid Phase	Cu		Cd	
	K_{AD},1/g	R^2	K_{AD},1/g	R^2
Bentonite Clay	43	0.97	1.1	0.90
$Fe(OH)_3$	205	0.86	4.4	0.98
MnO_2	7339	0.95	15.0	0.96
Humic Acid	366	0.98	0.2	0.99

most important ones in many areas.

Second, the results with humic acid must be interpreted cautiously since the humic acid was removed by ultrafiltration rather than centrifugation. Humic acid in the natural environment probably adsorbs to some extent on other solids, thus the K_{AD} values obtained may be somewhat higher than would occur if a portion of the humic acid surface was bound to another solid.

Lastly, the results deal only with discrete particle phases as opposed to coatings. The effects of coatings cannot be ascertained until satisfactory separation techniques are developed so mixed solid phases (e.g., humic acid and clay, hydrous oxide coatings on clay) can be utilized in adsorption experiments.

Partitioning Among Solid Phases

The use of Equation 14 to predict the equilibrium partitioning of a trace metal between solid phases requires that the concentration (in g/1) of each solid phase be known. This information is difficult to estimate because of the high concentration of solids in sediments relative to the interstitial water. However, accurate information is available on the relative concentrations of the different solid phases in a sediment on a weight basis. The relative concentrations of solid phases can be used if $\sum^k K_{AD}(k)\{S_T(k)\}$ is much greater than 1 since Equation 14 reduces to:

$$\frac{[MeS(k)]}{[Me_{ST}]} = \frac{K_{AD}(k)\{S_T(k)\}}{\sum^k K_{AD}(k)\{S_T(k)\}} \qquad (15)$$

Based on the K_{AD} values in Table 1, and the fact that the true solution concentration of these solids phases in a typical sediment are within the high mg/l to g/l range, Equation 15 is valid. Thus, if the concentrations of solid phases in a sediment on a weight basis (in percent) are known or estimated, these percentage values can be directly incorporated into Equation 15.

Selected values of relative solid phase concentrations in sediments that have been cited in the literature are listed in Table 2. Although these values may not be representative of all geographical areas, they give an approximation of the orders of magnitude of concentrations that are reasonable to utilize in Equation 15.

Distribution plots of Cu and Cd for various combinations of hydrous oxides, clay, and humic acids within the range of concentrations listed in Table 2 are shown in Figures 12 through 19. To facilitate interpretation, the hydrous oxides and humic acid concentrations were fixed for each plot with the clay concentration chosen as the independent variable. This is an arbitrary convention and there are numerous others that could be used (e.g., three dimensional diagrams).

Figures 12 through 15 show that, except for cases where the humic acid concentration is high, clay is the dominant sink for Cu. Likewise, in Figures 16 through 19, the clay appears to be the dominant sink for Cd except for cases where the $Fe(OH)_3$ concentration is high. For both metals clay becomes the dominant sink at high clay concentrations (>60%). These results suggest that in sediments where bentonite is the major clay, it will also be the major sink for Cd and Cu if the concentrations of hydrous oxides and humic acids are low, or if the clay concentration is high. These results, of course, only pertain to systems

Table 2. Selected Values of Solid Phase Concentrations in Marine
or Estuarine Sediments Reported in the Literautre.

Solid Phase	Range of Concentrations (in weight percent)	References
Amorphous Fe(OH)$_3$	0.0 - 4.7	9
MnO$_2$	0.02 - 0.03	9
Clay (Montmoril- lonite)	0.08 - 75.5	13
Humic Acid	1.4 - 1.7	30
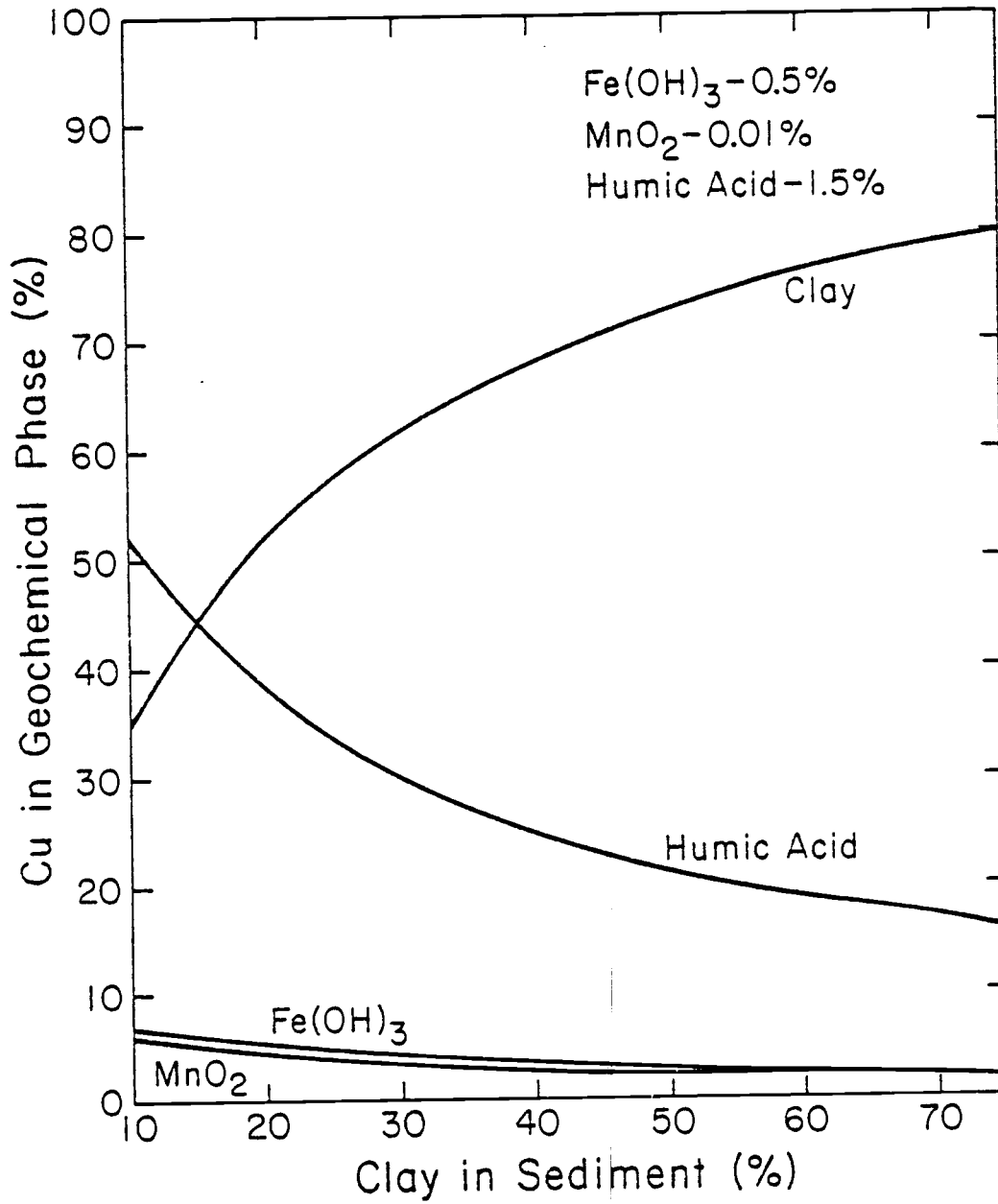
Figure 12. Partitioning of Cu as a Function of Clay Content for
Fe(OH)$_3$ - 0.5%; MnO$_2$ - 0.01%; HA - 1.5%
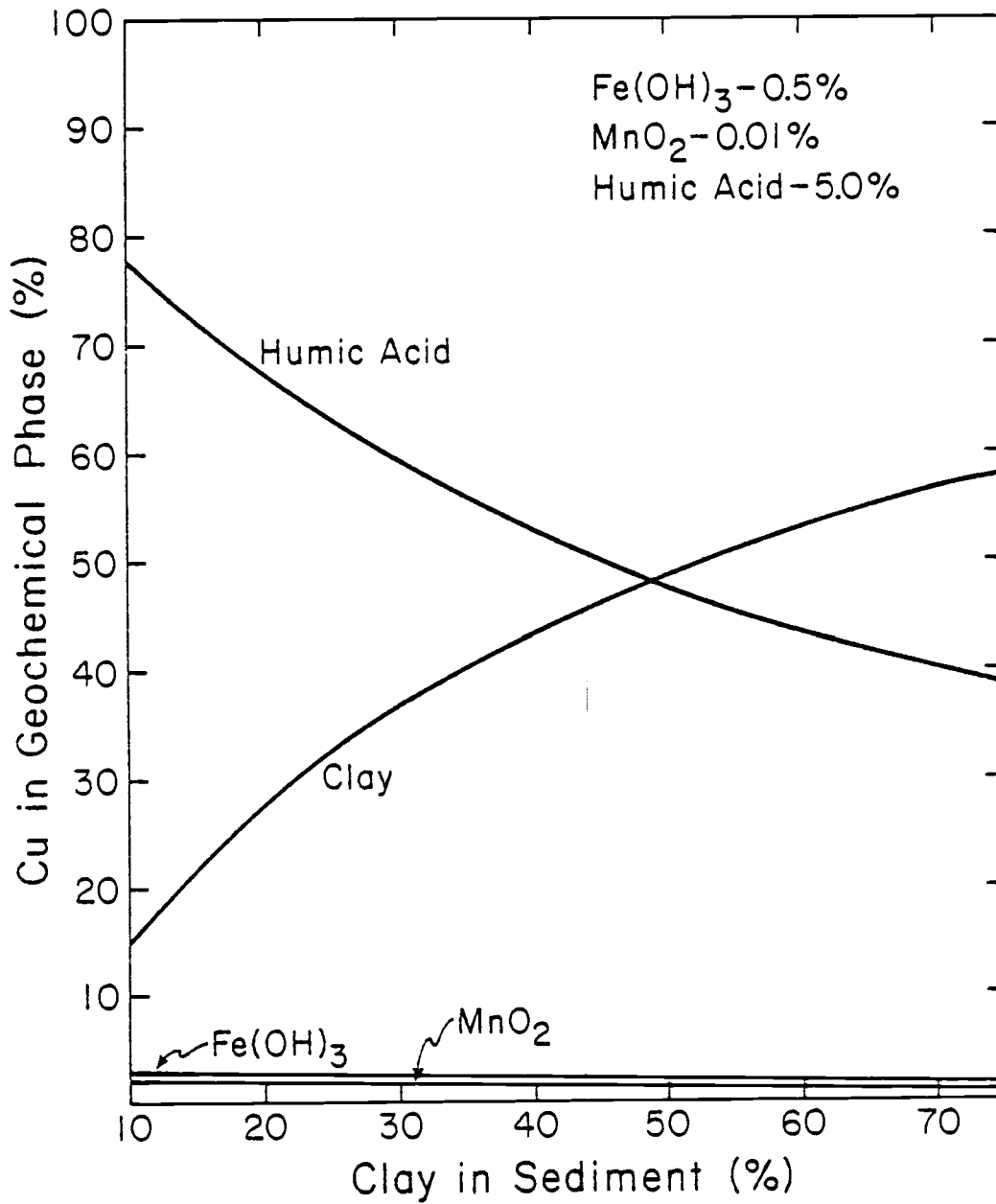
Figure 13. Partitioning of Cu as a Function of Clay Content for
Fe(OH)$_3$ - 0.5%; MnO$_2$ - 0.01%; HA - 5.0%
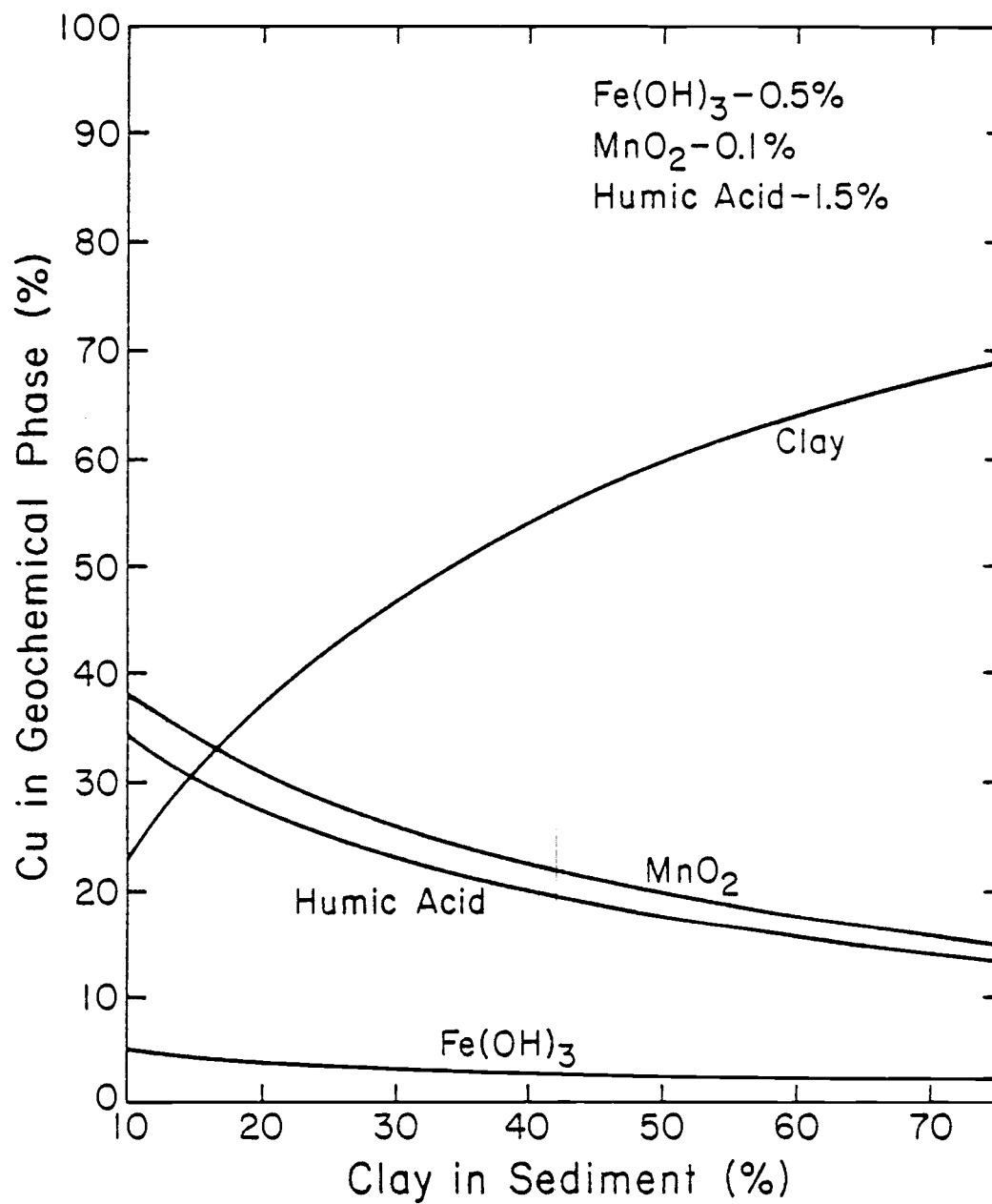
Figure 14. Partitioning of Cu as a Function of Clay Content for
Fe(OH)$_3$ - 0.5%; MnO$_2$ - 0.1%; HA - 1.5%
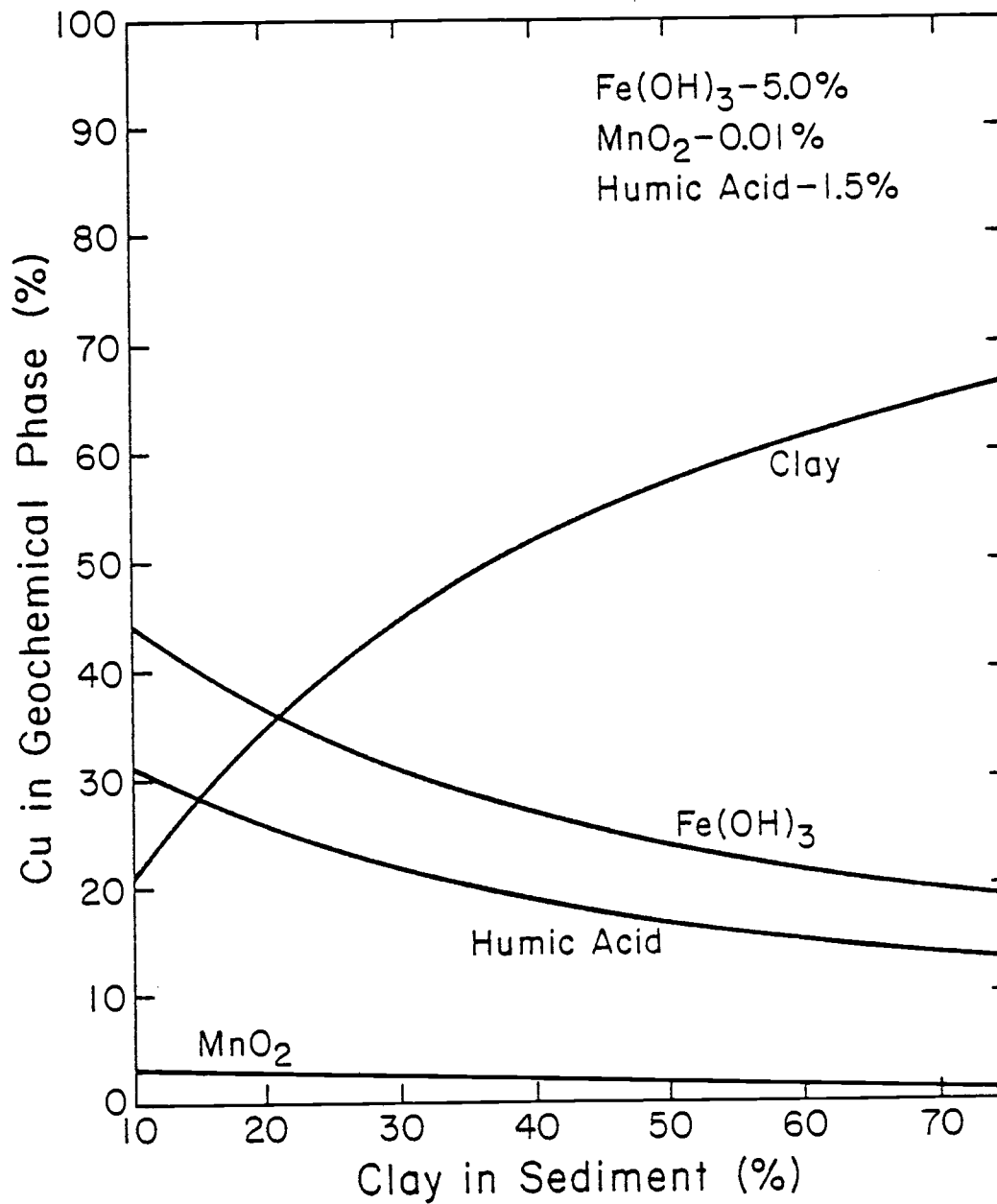
Figure 15. Partitioning of Cu as a Function of Clay Content for
Fe(OH)$_3$ - 5.0%; MnO$_2$ - 0.01%; HA - 1.5%
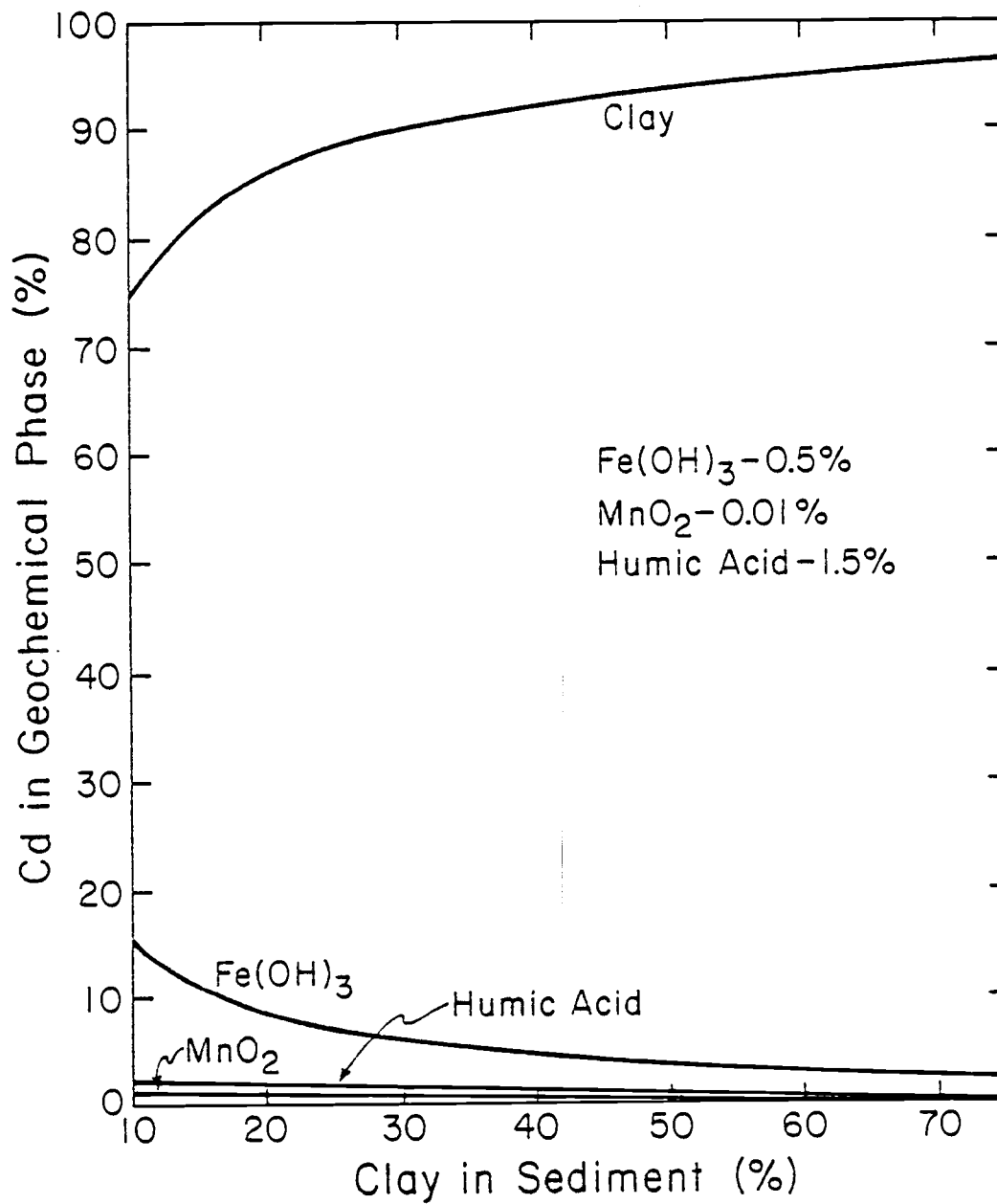
Figure 16. Partitioning of Cd as a Function of Clay Content for
Fe(OH)$_3$ - 0.5%; MnO$_2$ - 0.01%; HA - 1.5%
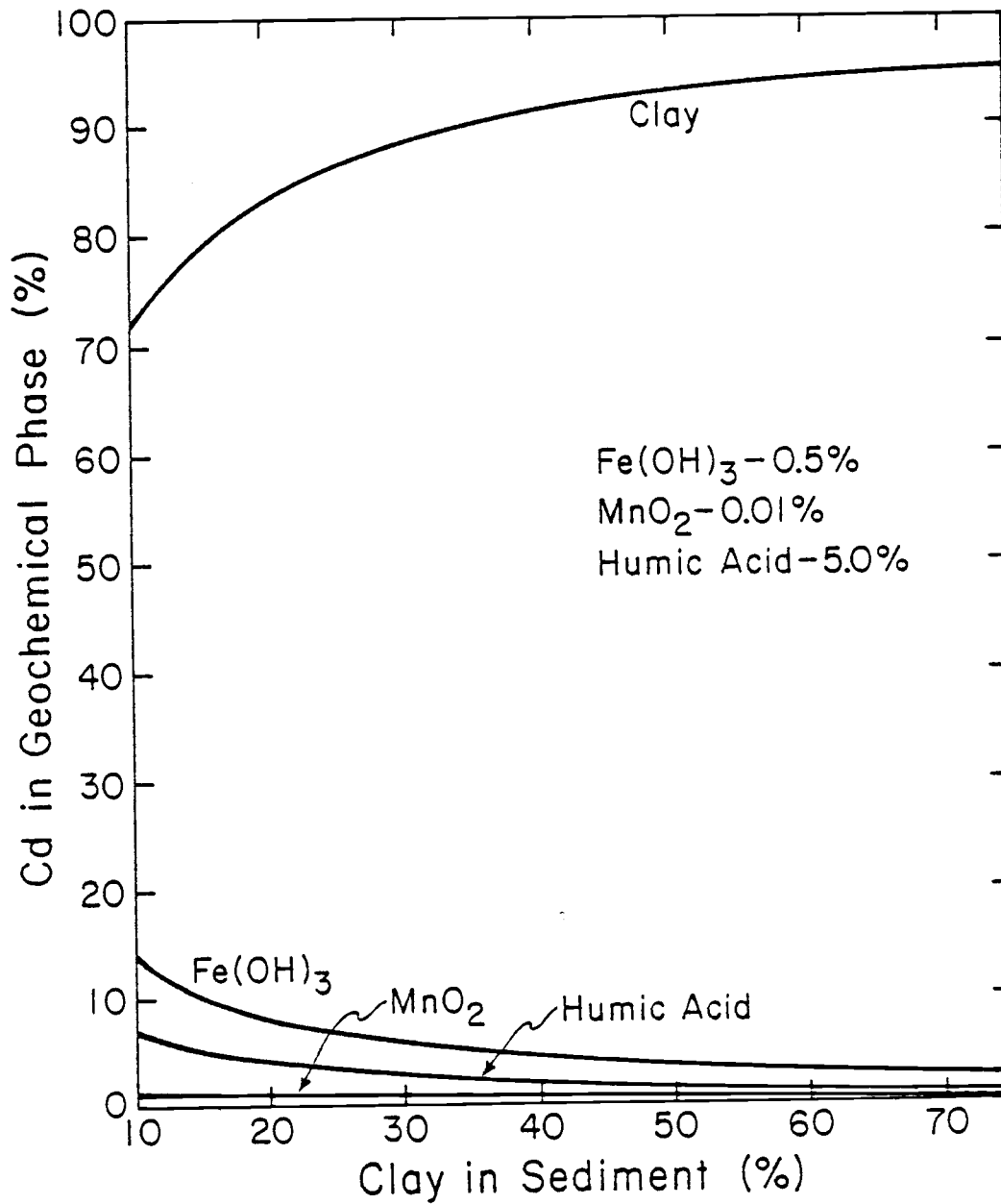
Figure 17. Partitioning of Cd as a Function of Clay Content for
$Fe(OH)_3$ - 0.5%; MnO_2 - 0.01%; HA - 5.0%
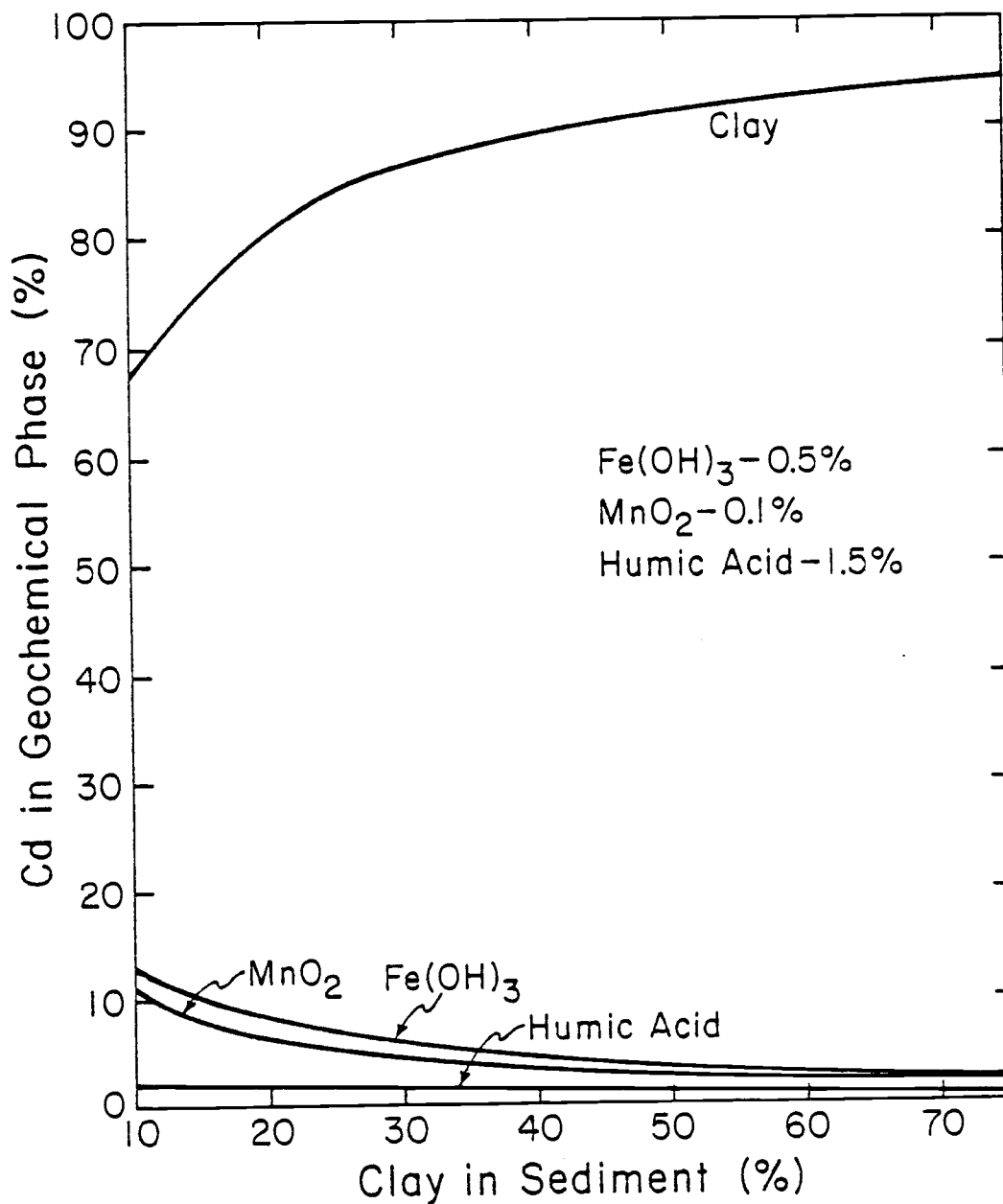
Figure 18. Partitioning of Cd as a Function of Clay Content for Fe(OH)$_3$ - 0.5%; MnO$_2$ - 0.1%; HA - 1.5%
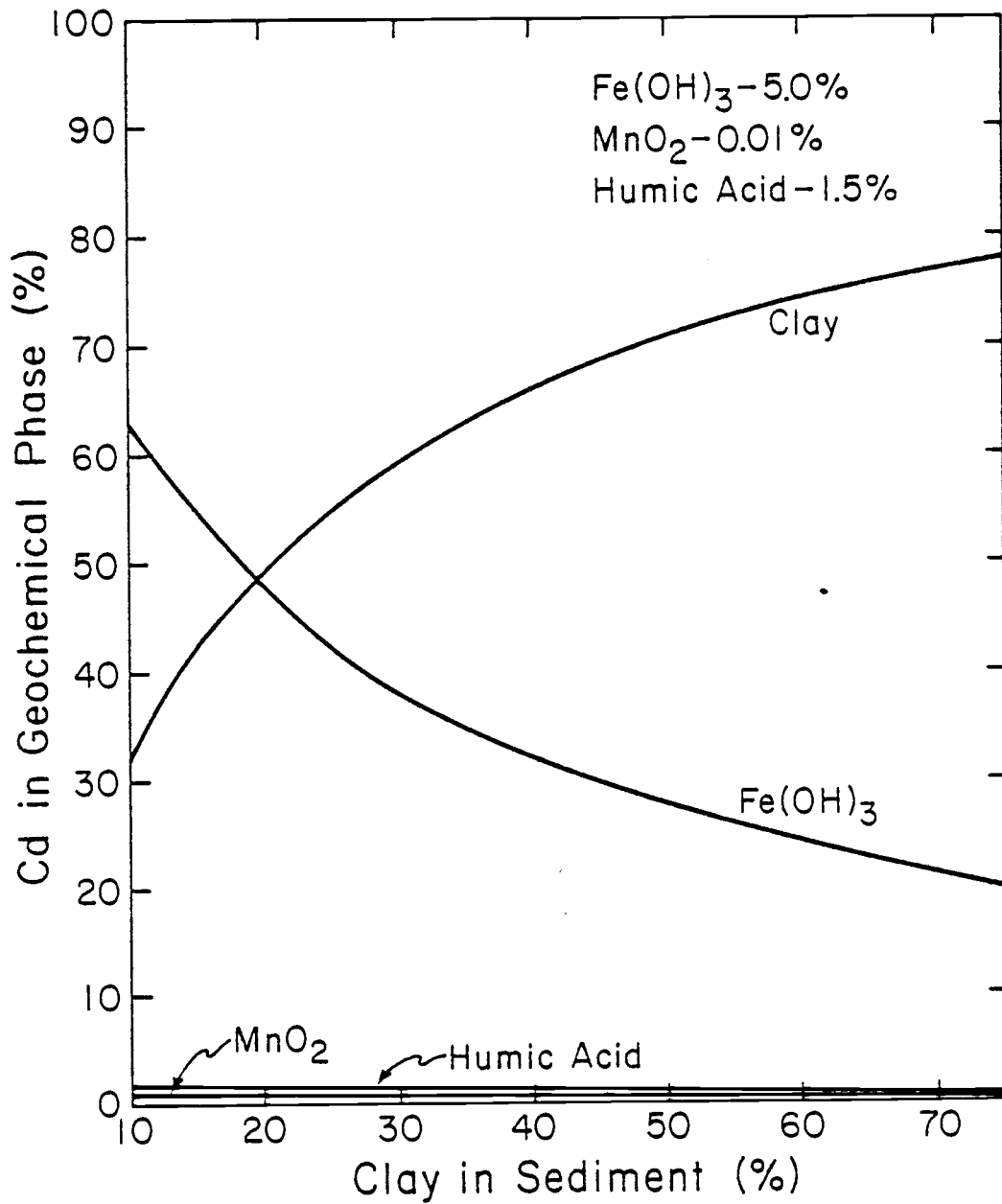
Figure 19. Partitioning of Cd as a Function of Clay Content for
$Fe(OH)_3$ - 5.0%; MnO_2 - 0.01%; HA - 1.5%

where the clay, humic acids, and hydrous oxides are the dominant adsorbents.

Jenne (7) has proposed that the hydrous oxides are the major sinks for trace metals in aquatic sediments. The results of this study appear to contradict that hypothesis. However, there is no doubt that most clays have some type of oxidic coating on their surfaces (9), although at present, it is extremely difficult to characterize the exact nature of the coating. Thus, the results may more accurately reflect the difference between adsorption and partitioning on clay/oxide coatings versus discrete oxide particles.

The results of this partitioning study are only suggestive of trace metal partitioning behavior in natural sediments. Although bentonite was chosen as the clay type, there are several other clay types that may be dominant in sediments depending on the soil type of the drainage basin and the age and extent of diagenesis that has occurred within the sediment. As mentioned previously, the effects of coatings may also influence partitioning although these results deal only with discrete particle phases. The hydrous oxides may, however, exist primarily as discrete particles in estuarine sediments where rapid turnover rates cause ferrous and manganous compounds from the anoxic zone to oxidize and form hydrous oxides.

No attempt was made to determine all the ranges of salinity, pH, and temperature within which the conditional equilibrium constants for each metal will be valid for the various solids. However, it is likely that for some metals and solids, the conditional equilibrium constants will not change significantly over a wide range of conditions. Figures 20 and 21 show the percent adsorption of Cu (within the linear range)
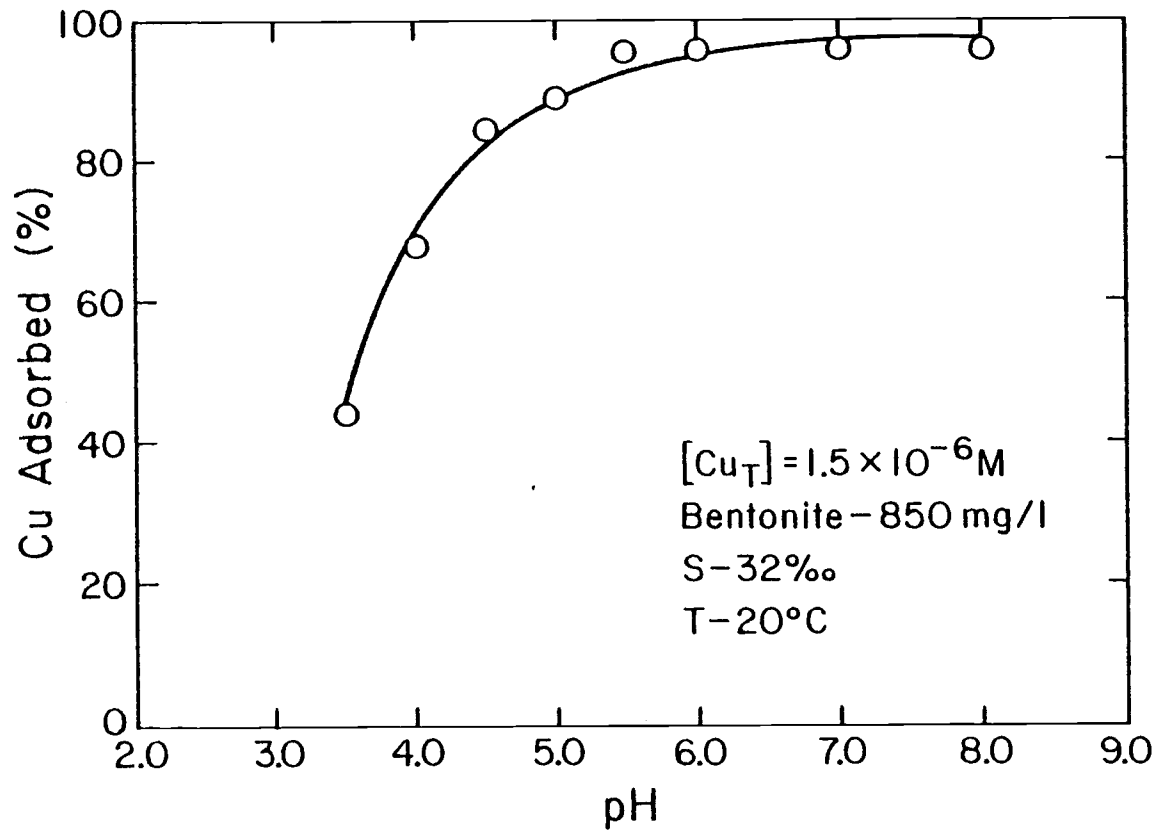
Figure 20. Adsorption of Cu on Bentonite in Seawater as a Function of pH
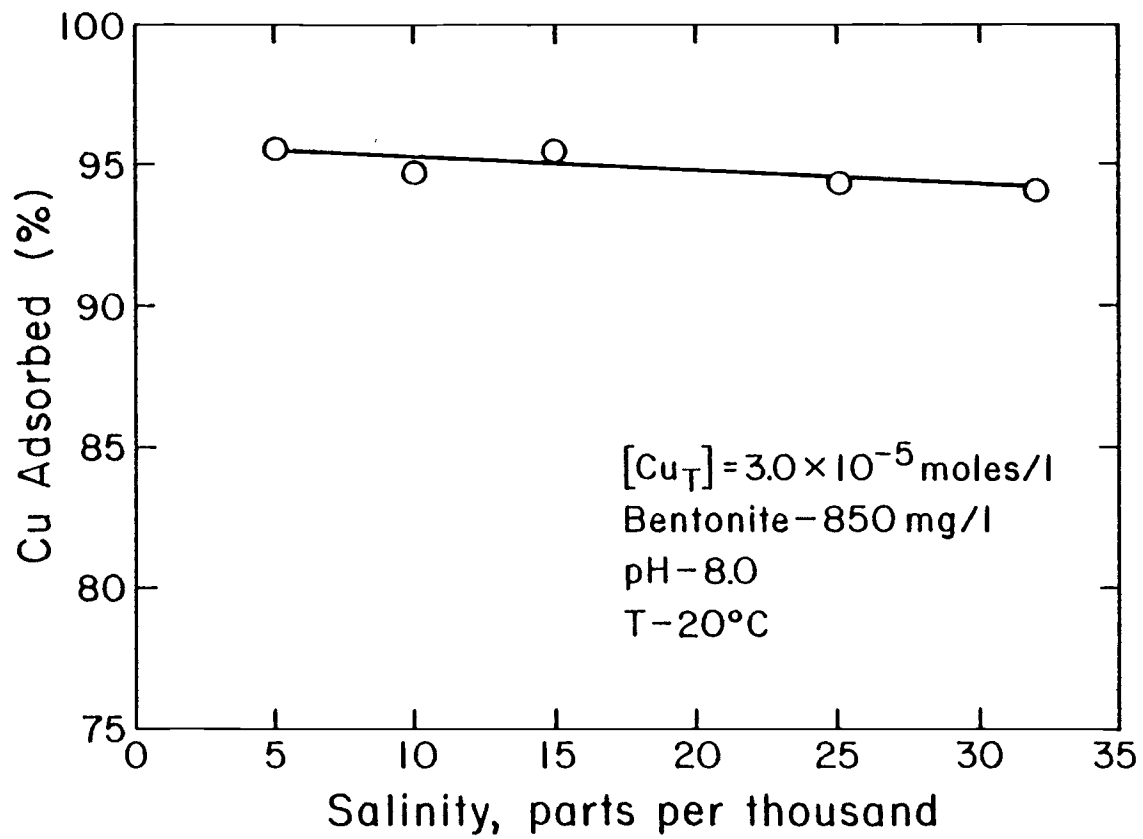
Figure 21. Adsorption of Cu on Bentonite as a Function of Salinity

on bentonite as a function of pH and salinity, respectively. The plots show that K_{AD} does not change significantly from pH 5.5 to 8.0 and for a salinity of 5 o/oo to 32 o/oo.

Although only trace metals were considered in this study, this model could also be used for the partitioning of organic compounds among different solid phases. Many organic compounds exhibit linear adsorption behavior (40,41), thus the assumptions of this model may apply equally well for organics also.

Conclusions

By developing a simple equilibrium adsorption model based on the linear portion of adsorption isotherms, it has been shown that trace metal partitioning can be predicted from laboratory studies with the use of conditional equilibrium adsorption constants. The constants determined for Cu and Cd adsorption on bentonite clay, $Fe(OH)_3$, MnO_2, and humic acid in seawater show that this model is applicable for trace metal concentrations existing in the natural environment. Based on the laboratory results, the model predicts that the clay fraction may be a major sink for Cu and Cd in marine sediments.

CHAPTER 3

THE BIOAVAILABILITY OF TRACE METALS FROM DIFFERENT GEOCHEMICAL PHASES

Introduction

Marine and estuarine organisms are known to accumulate high concentrations of trace metals in their tissues (4). Both Bower (42) and Polikarpov (43) have stated that marine animals satisfy their requirements for most metals by direct absorption from the surrounding water, and most early studies on trace metal uptake have assumed that uptake occurred largely from solution (44,45,46). Considerable evidence, however, supports the view that some marine organisms absorb trace metals chiefly from food (47,48,49); this fact may be significant for those organisms which depend on sediment as a food source, since trace metal concentrations in aquatic sediments are typically orders of magnitude higher than concentrations in the water column. Because many benthic organisms play a significant role in sediment turnover (50,51,52), it is important to assess the bioavailability of sediment-bound metals to these organisms.

Recently several investigators have conducted laboratory studies to assess the bioavailability of sediment-bound metals to benthic organisms (53-57). The results of Luoma and Jenne (53,55) suggested that sediment-bound metals can be readily bioaccumulated depending on the particular geochemical phase with which a metal is associated, while the results of Veda, et al. (54), Neff, et al. (56), and Ray, et al. (57) were either inconclusive, or showed uptake from sediments to be negligible as compared to water.

There are several limitations inherent in these past studies which

need to be overcome in order to unequivocally determine whether metal

uptake from sediments can be significant for benthic organisms. First,

as Jenne and Luoma (53,55) demonstrated, bioavailability will depend on

the particular geochemical phase with which a metal is associated. It

is therefore more useful to initially use artificial sediments consisting

of one geochemical phase in laboratory studies than natural sediments of

unknown characterization; this will eliminate any masking that may occur

in heterogeneous sediments if all of the metals are partitioned onto a

phase that exhibits low bioavailability.

Second, it is important to have adsorption isotherm data for each

metal-phase combination of interest. These data can be used to dose

sediment phases at metal concentrations (both solid and solution equili-

brium) likely to be encountered in the natural environment. The adsorp-

tion data can also be used in a partitioning model.

Third, although it is likely that the rate of metal uptake from

water is much higher than uptake from sediments, it is possible that

sediments are a much more important source of metals to certain organisms

because they contain much higher concentrations of metals on a weight

basis. It is necessary to utilize a mathematical model which estimates

the important kinetic parameters to quantitatively assess the relative

importance of various sediment phases or water.

Lastly, it is important to select a true deposit-feeding organism

which will indiscriminately ingest all of the important sediment phases.

Several investigators (54,56,57) have utilized organisms which are not

true deposit feeders, thus the results of their studies are inconclu-

sive insofar as bioavailability relates to organisms which are responsi-

ble for sediment turnover.

In an attempt to overcome these difficulties, a laboratory study was undertaken to determine the bioavailability of Cu and Cd both from different sediment phases and seawater. The adsorption results from Chapter 2 were used to dose bentonite clay, humic acid, and $Fe(OH)_3$ in seawater at equilibrium concentrations similar to those likely to be encountered in the natural environment. Metal uptake from the dosed sediment phases and water was monitored in the deposit feeding polychaete worm, Abarenicola pacifica. A mathematical model was developed which can be used to quantitatively estimate metal bioavailability both from different sediment phases and water.

Theory

Mathematical Model of Trace Metal Absorption

The available evidence for the process of trace metal absorption and elimination by an organism (whether from food or water) suggests that it can be approximated by a simple first-order compartment model (58-65). According to this model the concentration of metal in an organism's tissues will be a function of the mass of metal to which the tissue is exposed and the mass of metal in the tissue. For small organisms (where the metal concentration is expressed as the entire body burden) a three compartment model can be used to describe the kinetics of accumulation both from water and sediments as shown in Figure 22.

Figure 22 can be put into conventional mass balance equations as follows:

$$\frac{d(C\ M_o)}{dt} = k_w C_w V_w + k_s C_s M_s - k_e C\ M_o \tag{13}$$
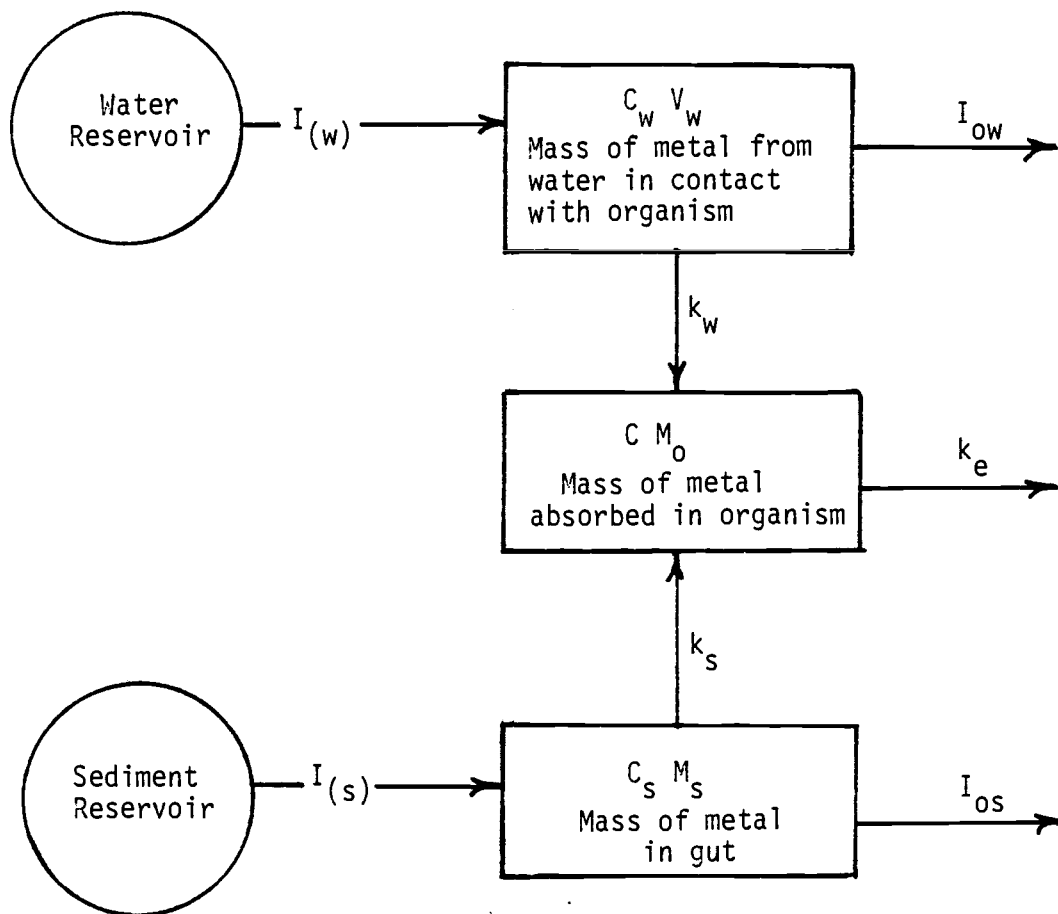
Figure 22. Three Compartment Model for the Absorption of Trace Metals from Sediment and Water by Organisms.

$I_{(w)}$ = metal respiration input rate, µg/t

C_w = metal concentration in water, µg/l

V_w = volume of water in contact with organisms, 1

I_{ow} = rate of unabsorbed metal elimination from water, µg/t

k_w = rate const. for metal absorption from water, 1/t

C_0 = conc. of metal in organism, µg/g

M_0 = mass of organism, g

k_e = rate const. for elimination, 1/t

$I_{(s)}$ = metal ingestion rate, µg/t

C_s = conc. of metal in sediment, µg/g

M_s = mass of sediment in gut, g

I_{os} = rate of unabsorbed metal elimination from gut, µg/t

k_s = rate const. for metal absorption from gut, 1/t

$$\frac{d(C_w V_w)}{dt} = I_w - I_{ow} - k_w C_w V_w \tag{14}$$

$$\frac{d(C_s M_s)}{dt} = I_s - I_{os} - k_s C_s M_s \tag{15}$$

Equation 13 shows that the relative importance of metal uptake from water or sediment will depend on the product of the rate constant, the medium concentration, and the mass of sediment or volume of water in contact with the absorbing tissues. In turn, as shown in Equations 14 and 15, the mass of sediment or volume of water in contact with the absorbing tissue will depend on the respiration rate (I_w) and ingestion rate (I_s) of the organism.

Equations 13-15 can be solved for the rate constants (k_w, k_s, k_e) if the other parameters can be measured experimentally. This is extremely difficult, however, for small benthic organisms, and some simplifying assumptions must be made.

If the mass of the organism, M_o, is considered constant, Equation 13 becomes

$$\frac{dC}{dt} = \frac{k_w C_w V_w}{M_o} + \frac{k_s C_s M_s}{M_o} - k_e C \tag{16}$$

Equation 16 can be rearranged as

$$\frac{dC}{dt} = k_w^* C_w + k_s^* C_s - k_e C \tag{17}$$

$$\text{where} \qquad k_w^* = \frac{k_w V_w}{M_o} \tag{18}$$

and $\qquad k_s^* = \dfrac{k_s M_s}{M_o}$ $\qquad\qquad\qquad$ (19)

Equation 17 is similar to other models that have been used in the literature (58-65) with the exception that it employs terms for both uptake from water and sediments.

Assuming that C_w and C_s are constants, the particular solution to Equation 17 becomes

$$C = \frac{k_w^* C_w + k_s^* C_s}{k_e} [1 - e^{-k_e t}] + C_o e^{-k_e t} \qquad\qquad (20)$$

where $C_o = C$ at $t = 0$.

If there are several different geochemical phases, i, on which a metal is partitioned, Equations 17 and 20 then become

$$\frac{dC}{dt} = k_w^* C_w + \sum^i k_s^*(i) C_s(i) - k_e C \qquad\qquad (21)$$

$$C = \frac{k_w^* C_w + \sum^i k_w^*(i) C_s(i)}{k_e} [1 - e^{-k_e t}] + C_o e^{-k_e t} \qquad\qquad (22)$$

where $\qquad C_s(i) = \alpha_i C_p(i)$ $\qquad\qquad\qquad$ (23)

where α_i is the fraction of phase i in the total sediment on a weight basis, and $C_p(i)$ is the concentration of metal adsorbed on phase i. Thus the relative importance of uptake from water or sediment will depend on the numerical values of $k_w^* C_w$ and $\sum^i k_s^*(i) C_s(i)$.

Because there are too many unknowns for the number of equations, Equations 21 and 22 must be further simplified in order to estimate the

parameters experimentally. This can easily be done if the uptake from each phase (water or sediment) is measured separately. If an organism is exposed only to an aqueous concentration of metal, the resulting equation is then

$$\frac{dC}{dt} = k_w^* \, C_w - k_e C \qquad (24)$$

$$C = \frac{k_w^* \, C_w}{k_e} \, [1 - e^{-k_e t}] + C_o e^{-k_e t} \qquad (25)$$

Equation 25 can be solved by nonlinear regression techniques (62).

Likewise, if an organism is exposed to only one sediment phase, and uptake from solution is either subtracted or negligible, the resulting equations are

$$\frac{dC}{dt} = k_s^* \, C_s - k_e C \qquad (26)$$

$$C = \frac{k_s^* \, C_s}{k_e} [1 - e^{-k_e t}] + C_o e^{-k_e t} \qquad (27)$$

An independent estimate of k_e can also be made if an organism that has accumulated a metal from either the water or sediment phase is placed in a clean environment for a depuration period, in which case (assuming M_o is constant)

$$\frac{dC}{dt} = -k_e C \qquad (28)$$

$$C = C_o e^{-k_e t} \qquad (29)$$

There are several limitations on the use of this model which must be recognized to avoid misinterpretation of results. Although the rate constants k_w, k_s, and k_e are treated as constants in Equation 13, they are in reality functions of the environmental conditions (physical, chemical, biological) under which the experiment was performed. The conditional rate constants k_w^* and k_s^* are in addition functions of the respiration and ingestion rates of the organism under study; an implicit assumption in the use of these conditional rate constants is that the respiration and ingestion rates, and the weight of the organism, do not change during the course of the experiment.

This model is also theoretically valid for only one individual organism. Since it is usually necessary to sacrifice animals over time, the variation between different individuals of the same species can make any parameter estimates deficient from a statistical point of view unless large numbers of organisms are sampled at each point in time; at present there are few population models developed which can adequately account for the variance between individuals (66).

Despite these limitations, this model can still be used to at least give a first approximation of the relative importance of water and different sediment phases in the bioaccumulation of trace metals under controlled laboratory conditions.

Metal Uptake in Aquatic Organisms

Most of the classical studies in the literature assume that metal uptake by an organism occurs largely by the water route (46-49). In these studies the organisms studied were either pelagic or filter-feeding, and possessed gill systems or other epithelia which have large

surface areas adapted for the absorption of dissolved constituents in water. There is no doubt that metal uptake from solution is important for these types of organisms (45). However, there is evidence that some marine organisms, especially intertidal invertebrates, may absorb trace metals chiefly from food (50,51). There is some speculation that this is likely to occur in marine organisms closely related to their terrestrial counterparts, which must accumulate metals derived from their food source. Whether or not an organism absorbs metals predominately from food via the gut rather than from water may then depend largely on the evolutionary history of the organism; those organisms far removed from terrestrial existence, which possess elaborate gill systems or other epithelia adapted for the absorption of dissolved constituents, will likely absorb metals from the aqueous phase (e.g., fishes, filter-feeding mollusks); on the other hand, organisms which live in the sediments, do not possess elaborate gill systems (and may be closely related to terrestrial organisms), and ingest large quantities of sediment relative to water intake, may be expected to accumulate metals predominantly from the solid phase (e.g., some crustaceans and polychaetes).

From Equations 13-15 it is clear that organisms which transport large quantities of water through their gill systems relative to food intake through the gut (e.g., filter-feeders) will be more apt to accumulate metals from the aqueous medium. By contrast, sediment dwelling organisms which have no need to transport large volumes of water through their gill systems for feeding or physiological purposes, may be expected to accumulate trace metals from sediments; for organisms such as these, body weight will be an important factor in trace metal accumulation since smaller organisms require more food per unit body

weight (67) which results in a higher mass flux rate per unit body weight.

A comparison of metal exposure by a typical filter-feeder and deposit feeder can be made as follows. A 20 g oyster (an organism well known for its ability to concentrate metals) can filter approximately 500 1/day of water for feeding and respiration (68). If an aqueous concentration of metal of 0.5 ug/1 is assumed, the oyster would transport 250 ug of metal into its system during this period. By contrast a 50 mg polychaete may pass 1.5 g/day of sediment through its gut and only 88 ml/day of water (68). If a sediment concentration of 200 ug/g for a given metal is assumed, the worm would transport 300 ug of metal into its system per day from the sediment. Thus a 50 mg worm can easily be exposed to the same mass of metal as a 20 g oyster, although in one instance the exposure is from food while in the other it is from water. In addition, the worms' weight is only 1/400 that of the oyster's, so its absorption efficiency could be much lower than the oyster's to maintain equivalent tissue concentrations.

In summary, it appears that the benthic organisms most likely to absorb metals from sediments will be those that ingest large quantities of sediment relative to water intake through the gills and thus must accumulate trace metals predominantly from the solid phase.

Organism Selection

The selection of an organism for laboratory studies is often arbitrary. In most instances organisms are selected because of their experimental convenience or commercial importance. Because of the difficulty in acclimatizing different species to various experimental

environments, it is often difficult to utilize many different species in a study. For these reasons the selection of an organism which was meaningful to the experimental objectives was given high priority.

The evidence obtained so far indicates that certain species of polychaete annelids more closely meet the requirements of the conceptual model to determine the significance of bioavailability of sediment-bound metals. Polychaetes are well known for their ability to overturn sediments and release nutrients into the water column (50). Some intertidal species, because they are continuously subjected to exposure to the atmosphere during low tides, are closely related to terrestrial annelids; this suggests that they are more likely to absorb trace metals from food rather than water.

One species, Abarenicola pacifica (69), was selected as the organism for experimental studies in this laboratory investigation. Abarenicola pacifica is an intertidal polychaete which is known to pass large quantities of sediment through its gut, and easily adapts to experimental conditions (70-73). It is closely related to the terrestrial earthworm, which is significant since earthworms have been shown to accumulate phenomenally high concentrations of heavy metals by soil ingestion (74). It is a non-selective deposit feeder and will indiscriminately ingest sediment particles; this is very important for the purposes of this study since it is necessary to have an organism which will ingest all of the various sedimentary phases for comparative purposes. Most importantly, it is a member of the cosmopolitan family Arenicolidae, which are ecologically significant organisms for many of the world's estuaries.

A. pacifica occupies a U-shaped burrow consisting of a sand-filled head-shaft and an open tail-shaft; the worm usually occupies the horizontal portion of the U-tube. A. pacifica feeds by taking in sediment at the base of the head-shaft and excreting feces at the opening of the tail-shaft. Most of the sediment entering the head-shaft is derived from the surface layer of sediment. A. pacifica has been classified as a non-selective deposit feeder since most studies indicate that it will more or less indiscriminately ingest sediment particles contained in the head-shaft (70-73).

Experimental

Reagents and Glassware

All laboratory glassware used (including the aquarium apparatus) was washed with 50 percent nitric acid and rinsed twice with double-distilled water. Polyethylene bottles were used for the storage of all liquid solutions.

Acid-washed ignited sand (J.T. Baker) that served as support material in the artificial sediments was used without modification. Adsorption or partitioning of trace metals onto the sand phase was found to be negligible.

Seawater (salinity = 32 o/oo) was collected from Oregon coastal waters, filtered sequentially through a sand filter and 0.2 μm membrane filter (Ultipor), and stored at 4°C in polyethylene bottles.

Preparation of Artificial Sediments

Bentonite clay, amorphous iron oxide ($Fe(OH)_3$), and humic acid were prepared according to the procedure outlined in Chapter 2. Each

solid phase was then dosed with either Cu or Cd in seawater to give

solid phase concentrations likely to be encountered in the natural en-

vironment; these concentrations were estimated by using the isotherm

data from Chapter 2 as shown in Figures 23 and 24. The dosed solid phase

was separated from the seawater medium by centrifugation, and then was

mixed with the acid-washed ignited sand. The final metal and solid

phase concentrations used are listed in Table 3.

Before each experiment the requisite metal-phase-sand mixture

($\simeq$ 2000 g) was equilibrated in a polyethylene aquarium with 20 l of

seawater for at least 24 hours. Sediment and solute metal concentrations

were then monitored throughout the course of the experiment.

A requisite volume of stock metal solution was added directly to the

aquarium in the experiments monitoring uptake from seawater to give a

total soluble metal concentration of 50 µg/l for both Cu and Cd. Ad-

ditional metal additions or pH adjustments were not required for any

of the experiments measuring uptake from solution.

Bioavailability Experiments

Specimens of Abarenicola pacifica were collected from the inter-

tidal zone of Yaquina Bay, Oregon. All animals were collected from the

same locale to minimize heterogeneity. The polychaetes were acclimated

without feeding in the filtered seawater at 12°C for 24 hours prior to

each experiment. Since metal accumulation can vary depending on the

size of the organism (53), only worms weighing between 50 and 100 mg

(dry weight at 105°C) were used.

Twenty worms were placed in individual 50 ml beakers containing the

equilibrated metal-phase-sand mixture; the beakers were immersed within
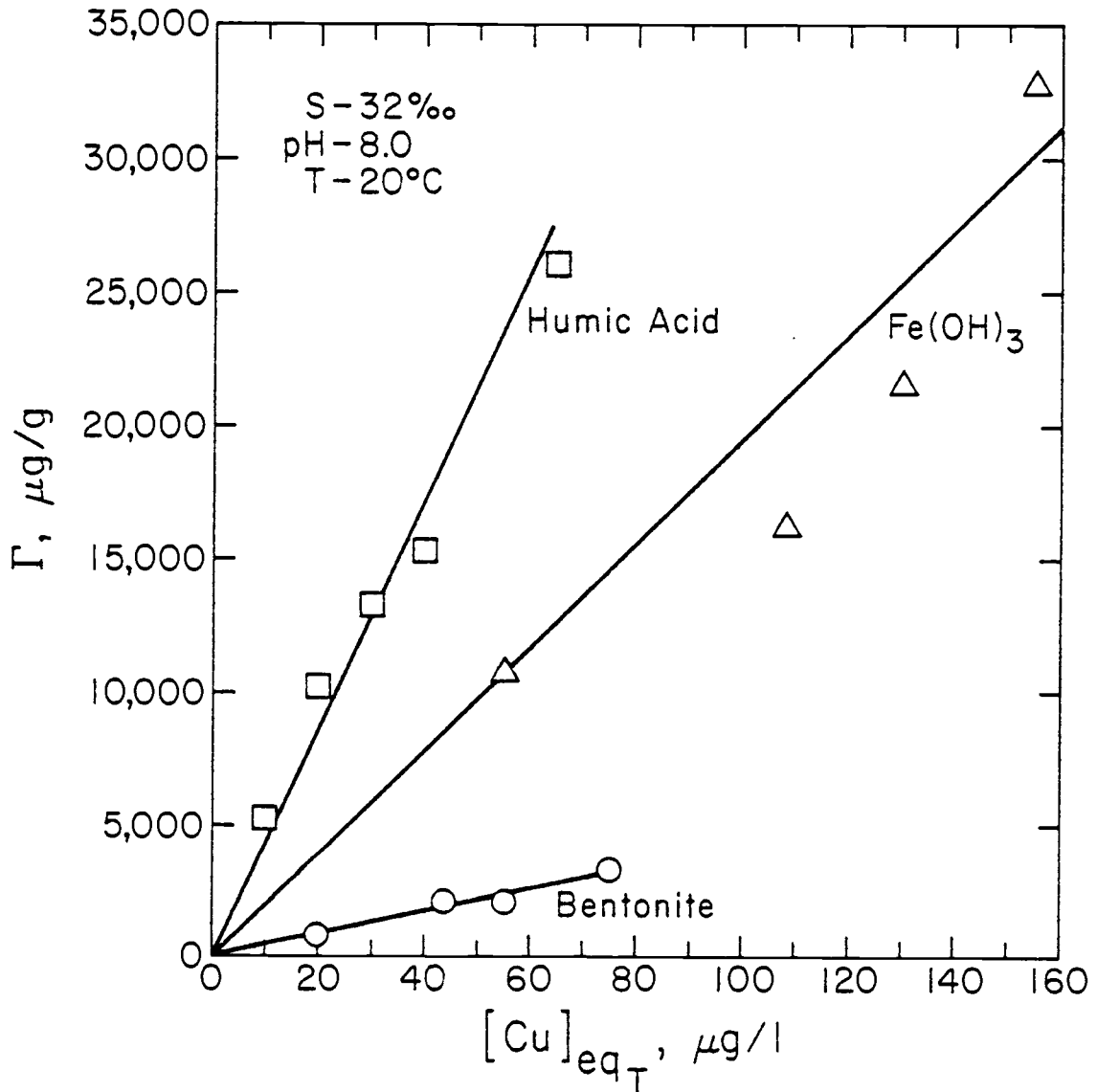
Figure 23. Linear Adsorption Isotherms for Cu on Bentonite,
Fe(OH)$_3$, and Humic Acid in Seawater
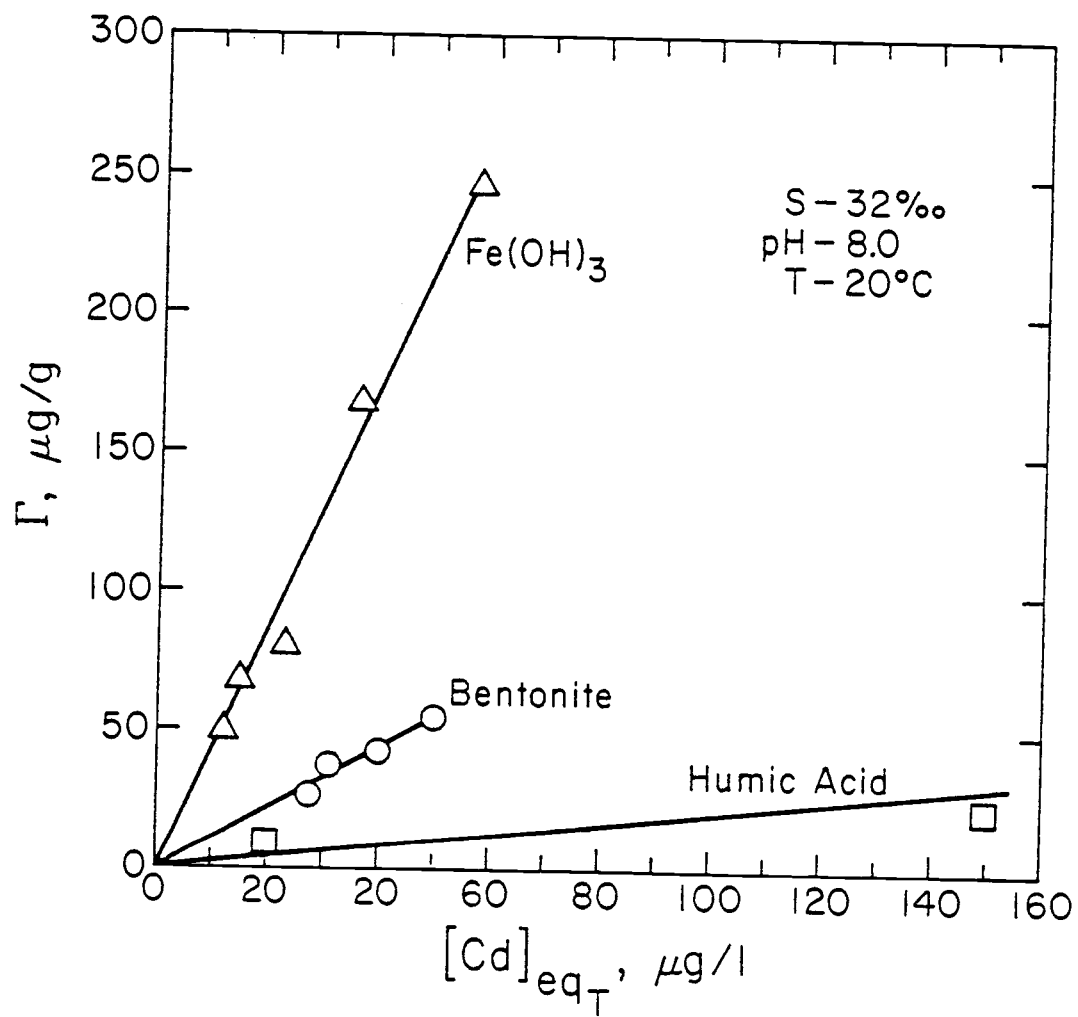
Figure 24. Linear Adsorption Isotherms for Cd on Bentonite, $Fe(OH)_3$, and Humic Acid in Seawater

Table 3. Concentrations of Metals and Solid Phases Used in the
Bioavailability Study.

Solid Phase	Metal Concentration on Pure Solid Phase, $C_p(i)$, ppm.		Approximate Equilibrium Solution Metal Concentration from Figs. 23 and 24, $\mu g/l$		Fraction of Solid Phase in Total Sediment, α_i		Metal Concentration in Total Sediment $C_s(i)$, ppm	
	Cu	Cd	Cu	Cd	Cu	Cd	Cu	Cd
Bentonite	100	8	<5	<5	0.2	0.5	20	3.8
Fe(OH)$_3$	1200	22	5	<5	0.057	0.039	68	3.4
Humic Acid	2000	0.8	<5	<5	0.02	1.0	40	0.8

the 20 1 aquarium, which was aerated continuously. The worms were al-
lowed to burrow and feed in the sediment ad libitum. An additional
ten worms utilized as controls were placed within the aquarium in beakers
containing only the acid-washed sand. All experiments were run in batch
fashion for a 14 day period at 12°C. Weight loss and water quality
changes were negligible over the experimental time period. In the ex-
periments monitoring uptake from water twenty worms were placed in the
spiked seawater in beakers containing only the acid-washed sand. In
both uptake studies from sediment or water, the reservoir of metal in
the medium phase was large enough that it acted as an infinite reservoir
(i.e., organism uptake did not change C_s or C_w).

Three worms were removed at each sampling period and placed in a
clean aquarium containing only seawater for a 24 hour period to purge
their gut contents before analysis. Flegal and Martin (75) have noted
that ingested sediment particles can contribute significantly to the
measured body burden of trace metals if precautionary measures are not
taken. However, since A. pacifica defecates frequently over a 24 hour
period (71), no visible signs of ingested sediment were found in
dissected worms after the purging period.

Analysis

After purging sacrificed worms were dried at 100°C for 24 hours.
Each sample then was digested twice with 10 ml of redistilled concen-
trated HNO_3 by slowly heating on a hot plate to dryness. After the
second digestion the sample was brought to volume with 1 N HNO_3 and
analyzed by flame atomic absorption spectrophotometry.

Sediment samples were digested and analyzed by the same method

(10 ml of concentrated HNO_3 were used for each 1 g of sediment sample). Solution metal concentrations were measured by the methods discussed in Chapter 2; detection limits were 5 ug/l for Cu and 1 ug/l for Cd.

Depuration Experiments

To independently estimate values of k_e, worms that had been exposed to a solute concentration of metal were placed in a clean seawater aquarium and sampled for a period of 12 days. Rate constants were then calculated by linear regression using the logarithmic form of Equation 29.

Statistical Analysis

The rate constants from each experiment were calculated using either a nonlinear or simple linear regression (as discussed in the next section). Because the inherent variability between individual organisms was usually high, an analysis of variance showing lack of fit (76) was calculated for all data that were fit by simple linear regression.

Results and Discussion

The results of all bioavailability studies are shown in Figures 25-32. In each figure the data points represent the mean value for three organisms and the vertical bars one standard deviation; in cases where the bars are missing the standard deviation is smaller than the size of the symbol.

In all experiments monitoring uptake from sediments, the control worms did not accumulate metals. Since neither the measured solution concentrations (5 ug/l for Cu and <1 ug/l for Cd) nor sediment concen-
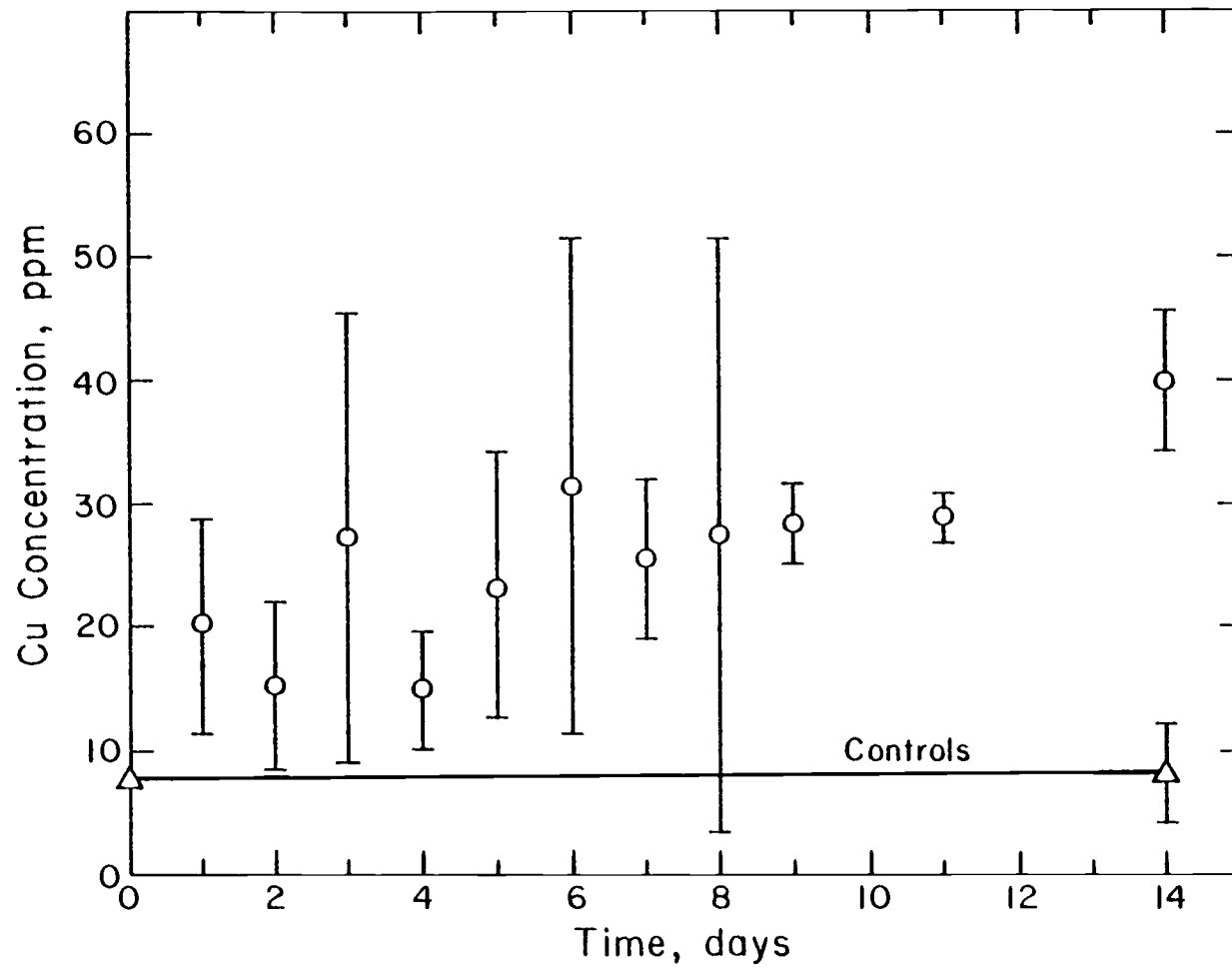
Figure 25.   Uptake of Cu from Bentonite, C_s - 20 ppm

Figure 26. Uptake of Cu from $Fe(OH)_3$, C_s - 68 ppm

Figure 27. Uptake of Cu from Humic Acid, C_s - 40 ppm
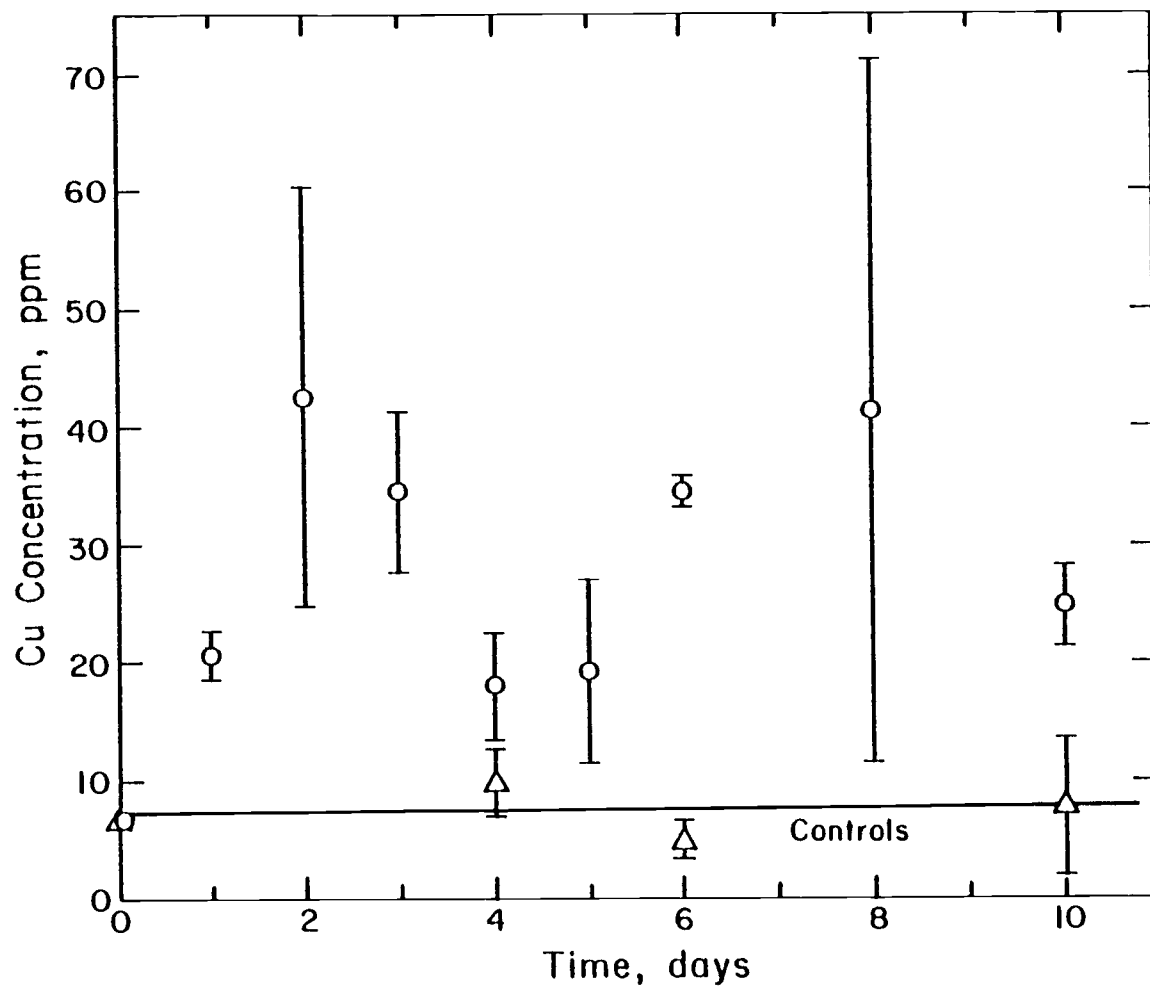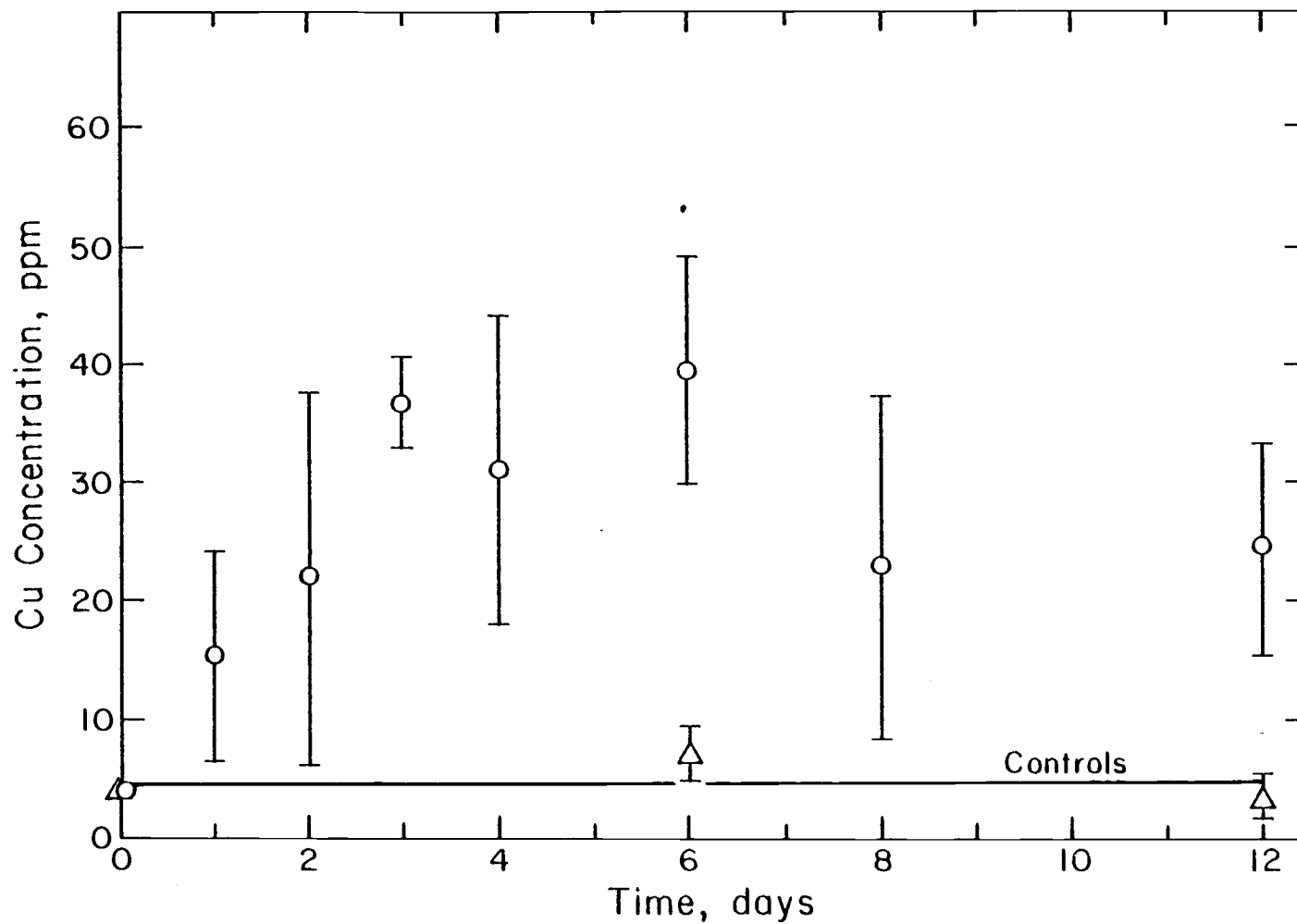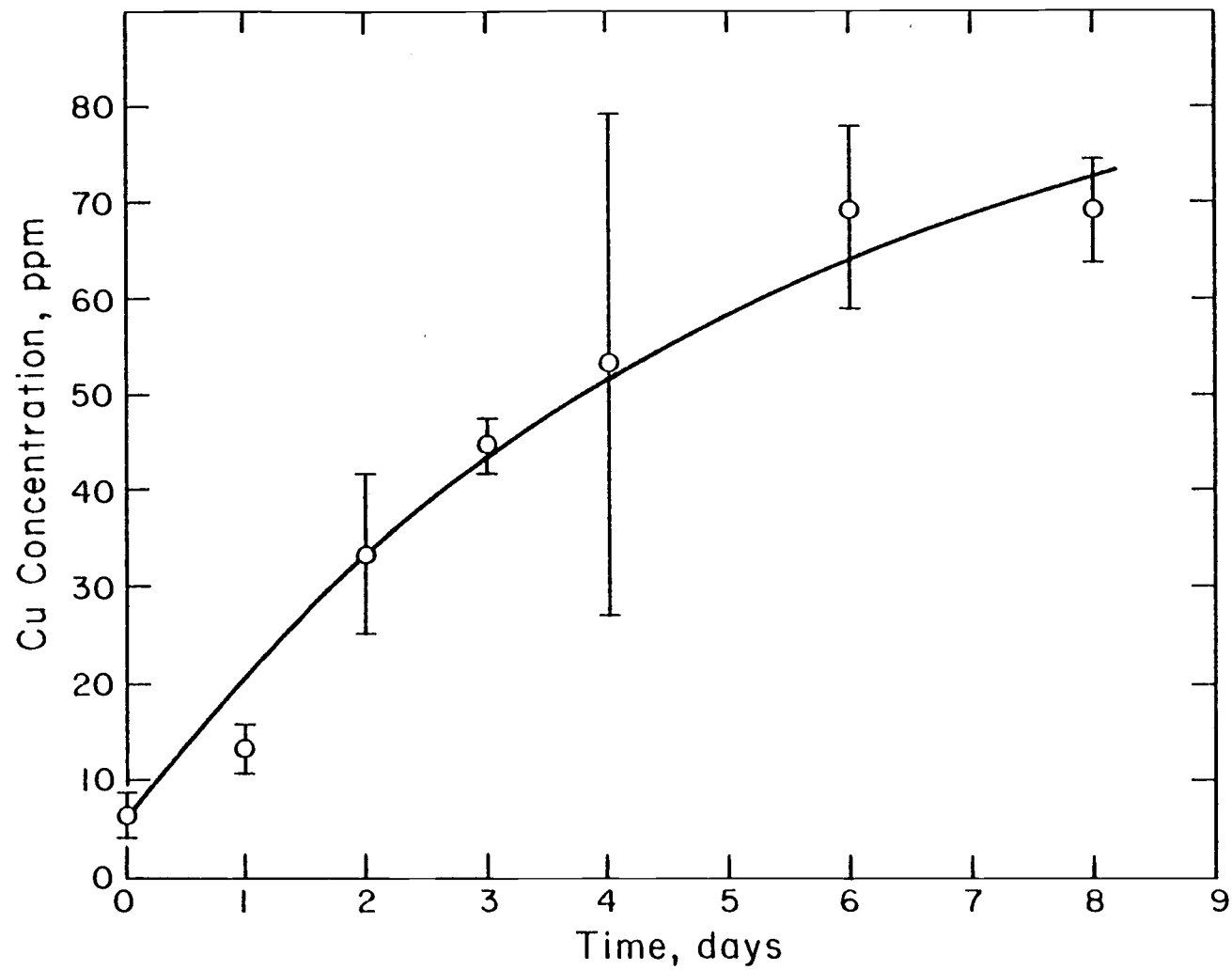
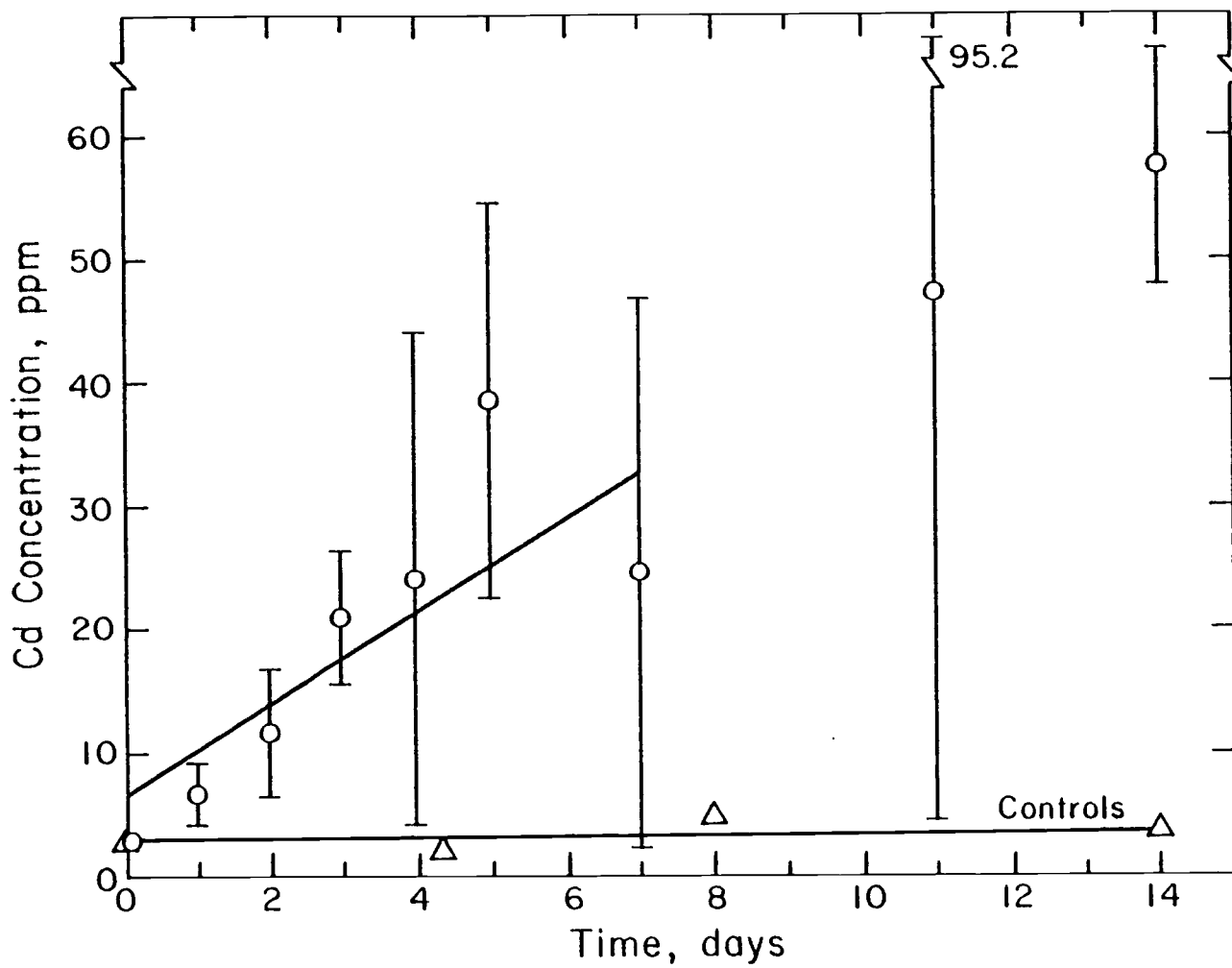Figure 23. Uptake of Cu from Seawater, $[Cu]_T = 50$ µg/l

Figure 29.   Uptake of Cd from Bentonite, C_s - 3.8 ppm
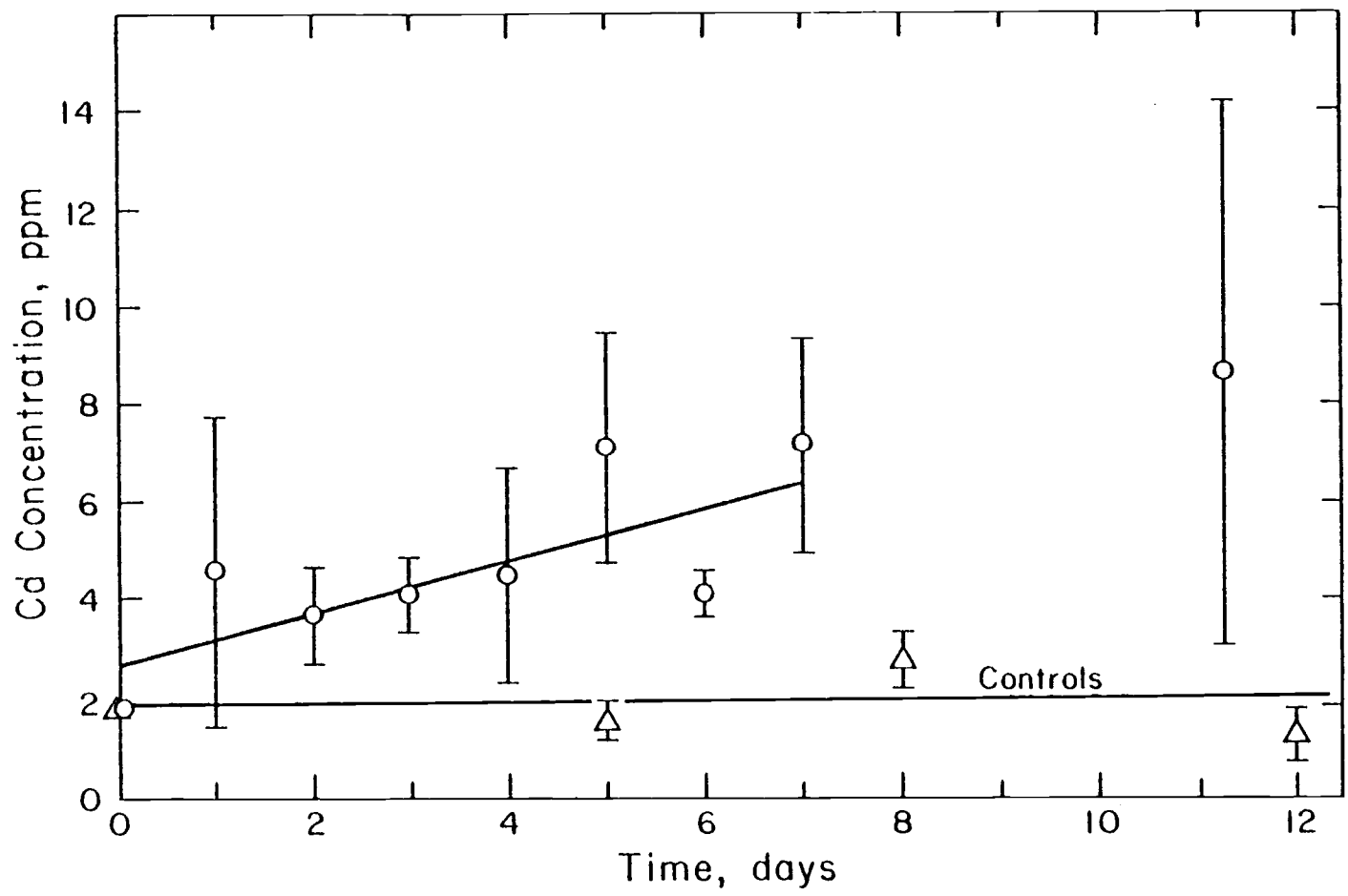
Figure 30. Uptake of Cd from $Fe(OH)_3$, C_S - 3.4 ppm
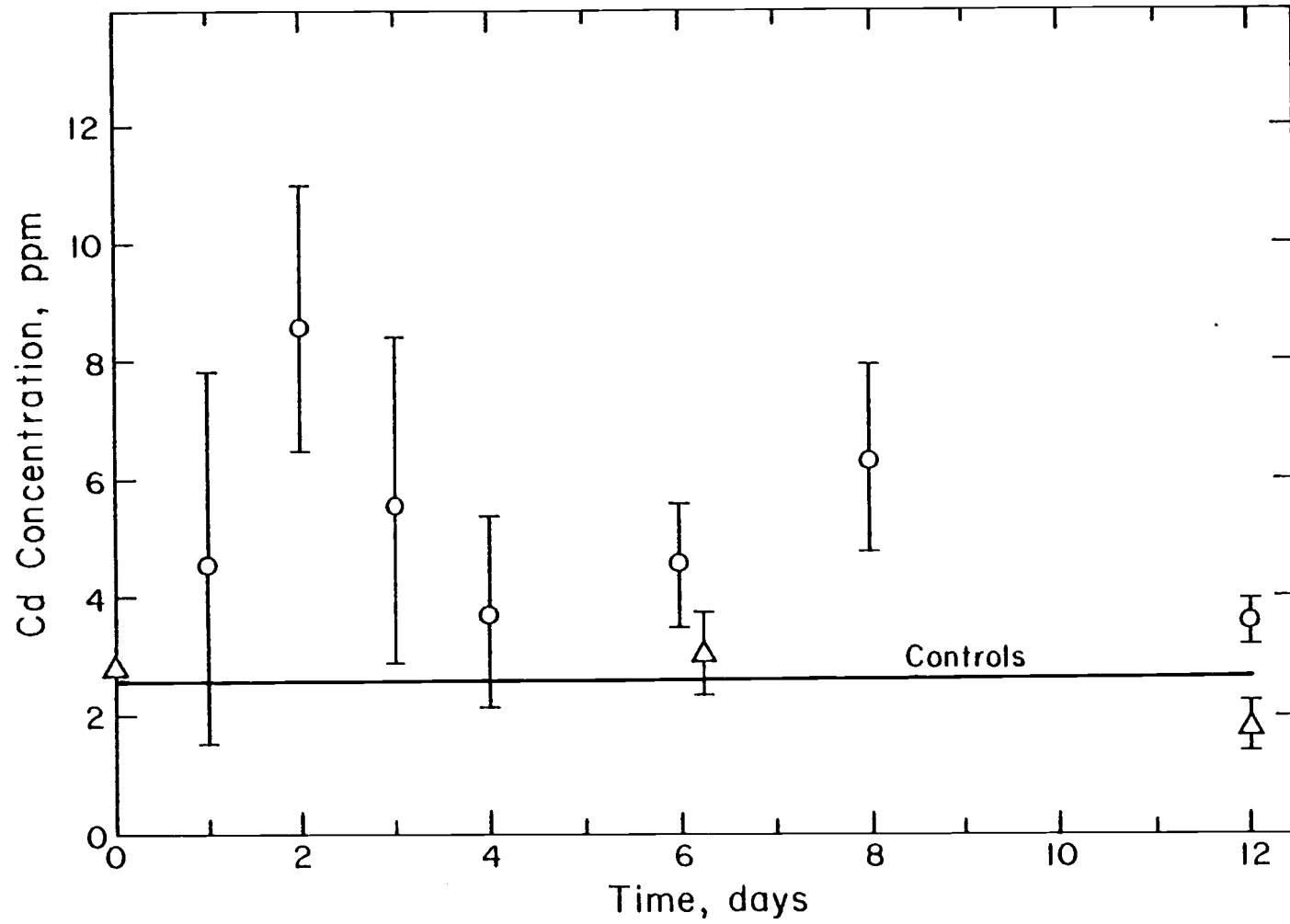
Figure 31. Uptake of Cd from Humic Acid, C_s - 0.8 ppm
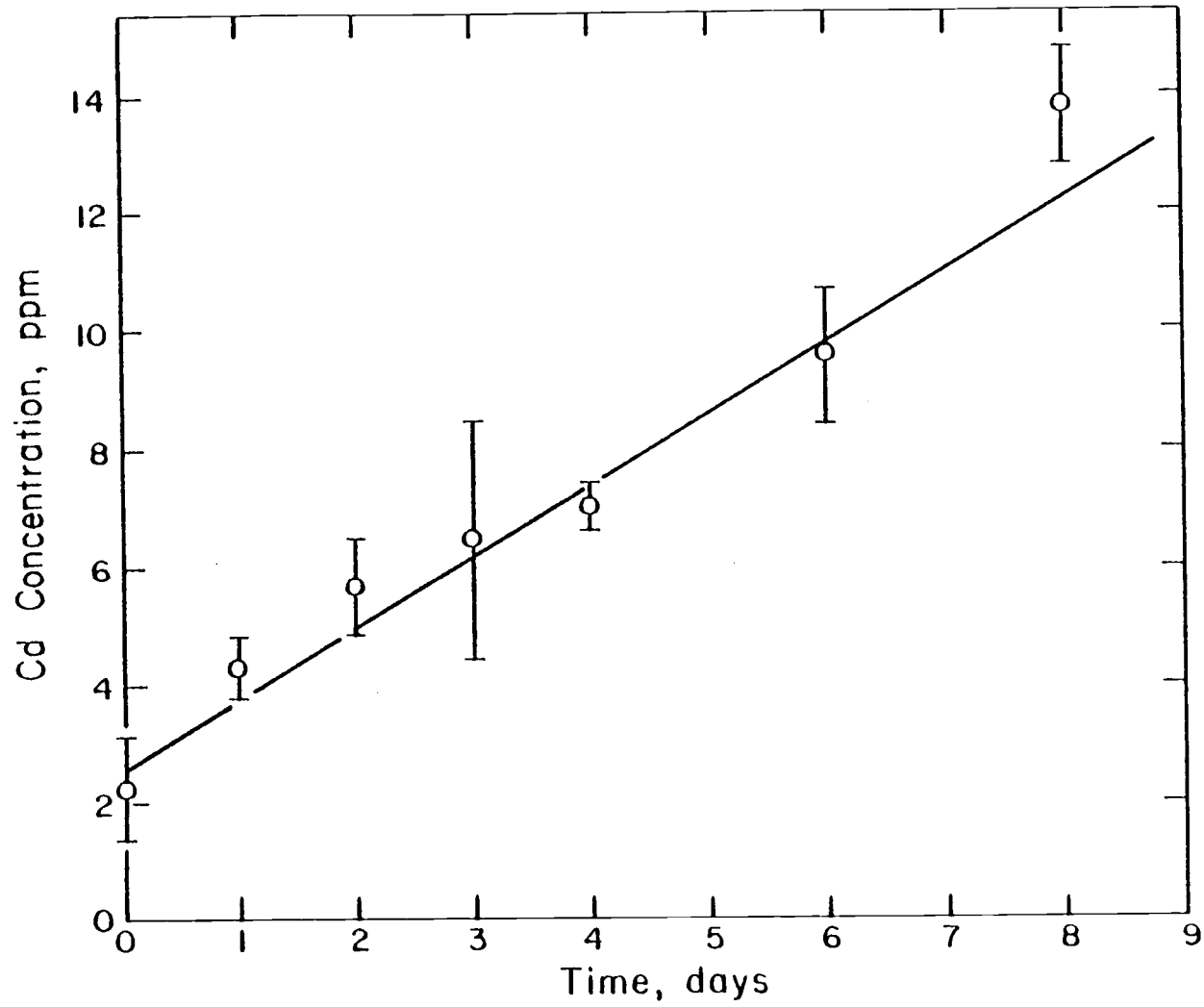
Figure 32.   Uptake of Cd from Seawater, $[Cd]_T = 50 \mu g/l$

trations of metals changed significantly in these experiments, it is probable that the control worms were exposed to solution concentrations typical of the natural environment; hence their tissue concentrations would not be expected to change significantly.

In most cases the data could not be adequately fit by nonlinear regression techniques because a steady-state was not approached. To obtain accurate parameter estimations with nonlinear regression computer programs it is necessary to use accurate initial guesses of k_s and k_e or the program will either not converge, or will converge to a false minimum (62,66). Although values of k_e can be estimated independently from depuration studies, accurate initial guesses of k_s (or k_w) and convergance can only be made if the experimental data have approached a steady-state at the end of the experiment. Only in the case of Cu uptake from seawater was this condition satisfied to the point where reasonable parameter estimates could be obtained from the nonlinear program.

Although bioaccumulation studies for protracted time periods (28-150 days) in an attempt to reach steady-state conditions have been reported in the literature (61,65), there are several drawbacks in long term studies which limit their use. First, there is a general tendency for the variability about the mean to increase with time; this variability is an inherent property of a population of animals (61). In order to statistically alleviate this variability it is necessary to sample a large number of animals at each sampling period.

Secondly, for long term studies it becomes necessary to utilize flow-through systems in which the water medium is constantly changed. In such systems it is difficult to maintain equilibrium between sediments

and water, and values of C_s and C_w may fluctuate widely.

Lastly, the longer an organism is kept under laboratory conditions, the greater the likelihood that physiological changes will occur that can influence the estimated values of the rate constants. These physiological changes are independent of the inherent organism variability discussed above.

In an effort to overcome the difficulties of nonlinear parameter estimation and long-term bioavailability studies, a method was developed which assumes zero-order kinetics for an initial uptake period determined by an independent estimation of the depuration rate constant, k_e; a simple linear regression analysis can then be used to fit the zero-order model and estimate values of k_s or k_w. The use of a zero-order model does not, however, indicate that the first-order model is inadequate, since there is initially a finite time period for which Equations 24-27 can be approximated by zero-order kinetics, as discussed below.

The exponential term in Equations 25 or 27 can be expanded into a Taylor Series,

$$e^{-k_e t} = 1 - k_e t + \frac{(k_e t)^2}{2} - \frac{(k_e t)^3}{6} + \ldots \tag{30}$$

If Equation 30 is substituted into Equation 27, the resulting relationship is

$$C = [\frac{k_s^* C_s}{k_e} - C_0][k_e t - \frac{(k_e t)^2}{2} + \frac{(k_e t)^3}{6} + \ldots] + C_0 \tag{31}$$

If the quantity

$$k_e t \leq 0.5 \qquad\qquad (32)$$

the higher order terms become negligible as compared to $k_e t$, and Equation 31 can then be approximated as

$$C = [\frac{k_s^* \, C_s}{k_e} - C_o] \, (k_e t) + C_o \qquad\qquad (33)$$

$$C = (k_s^* \, C_s - C_o k_e) t + C_o \qquad\qquad (34)$$

in which case k_s^* can be determined from the slope of a straight line on a C versus t plot.

From a plot of $e^{-k_e t}$ and $1 - k_e t$ versus $k_e t$, it can be found that the assumption that the higher order terms in Equations 30 or 31 are negligible produces a 16 percent error at $k_e t = 0.5$, a 10 percent error at $k_e t = 0.4$, and a 5 percent error at $k_e t = 0.3$.

Values of k_e for Cu and Cd were estimated by linear regression from the depuration studies shown in Figures 33 and 34. These values, along with the time period for which $k_e t = 0.5$, are shown in Table 4. From these results the assumptions of Equation 34 should be valid up to a period of 3 days for Cu and 7 days for Cd.

Equation 34 was used to calculate k_s^* values for both metals for bentonite, Cu uptake from humic acid, Cd uptake from $Fe(OH)_3$, and Cd uptake from seawater (substituting $k_w^* \, C_w$ for $k_s^* \, C_s$). Equation 25 was used to model uptake of Cu from seawater; this was the only case where the nonlinear program gave adequate results. Although uptake of Cu from $Fe(OH)_3$ and Cd from humic acid was significant, neither Equation 27 nor 34 could be used because of the randomness of the data.

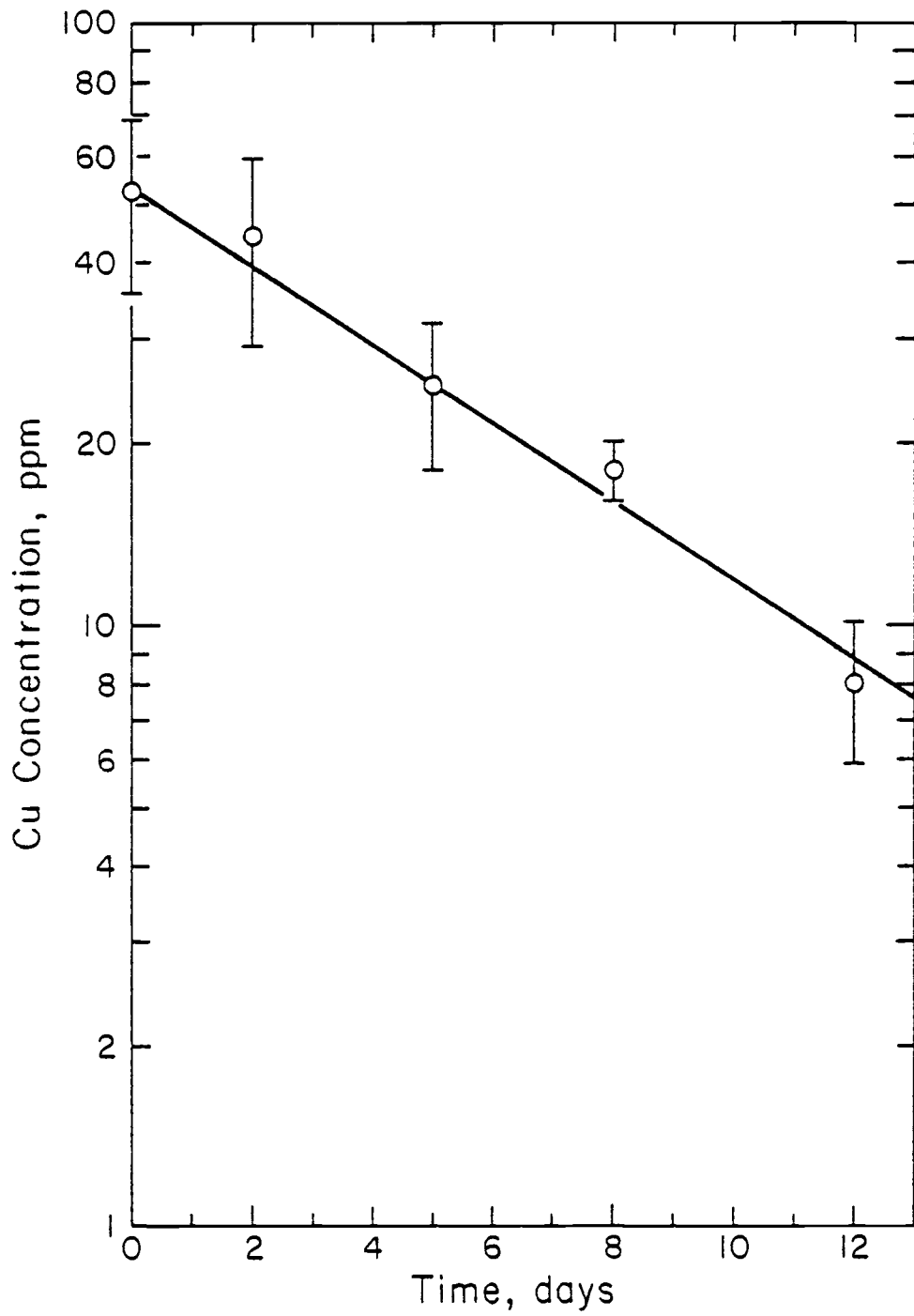Figure 33. Cu Depuration in Seawater
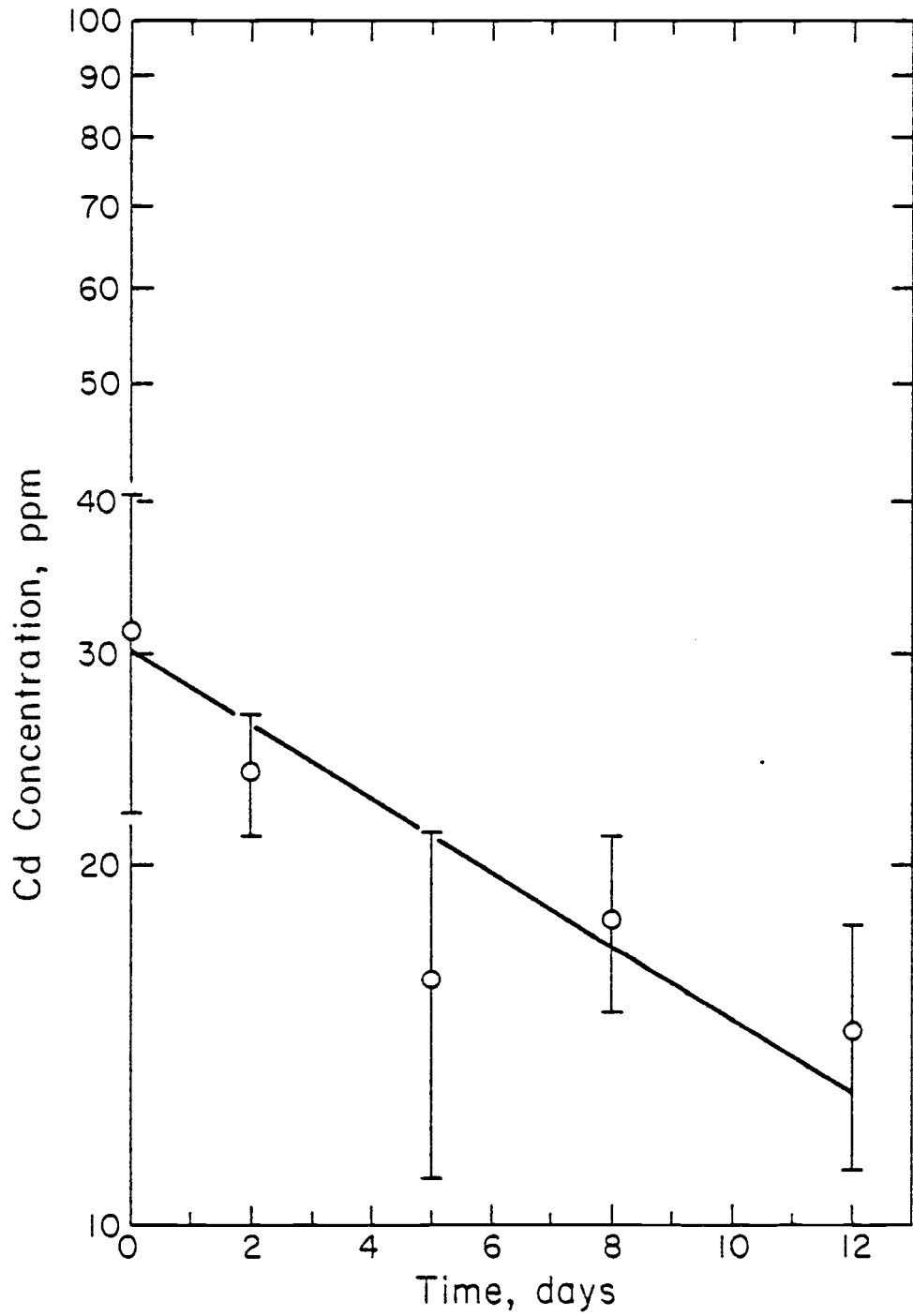
Figure 34. Cd Depuration in Seawater

Table 4. Estimated Values of Depuration Rate Constant, k_e

Metal	k_e, days^{-1}	Biological Half-life, days	Time Period for $k_e t = 0.5$, days	R^2	Lack of Fit
Cu	0.15	4.6	3.3	0.86	Not Significant
Cd	0.07	10	7	0.58	Not Significant

The calculated values for the uptake rate constants are shown in Table 5. For all cases where it was applied, the zero-order model fit the data without a significant lack of fit ($\alpha = 0.01$). Thus the low values of R^2 in some instances were caused by organism variability rather than an inadequacy of the model. Because of the wide variability these data should only be interpreted as giving an order of magnitude estimate of the rate constant.

Although the estimated values of k_w^* for both metals were several orders of magnitude higher than the values of k_s^*, the product of $k_w^* C_w$ was not much greater than $k_s^* C_s$ for Cu on humic acid, and was even lower than $k_s^* C_s$ for Cd on bentonite. Because the solution concentrations of Cu and Cd used (50 μg/l) were much higher than those typically encountered in the marine environment, these results suggest that uptake of metals from sediment phases can be the more significant mode of uptake for Abarenicola pacifica.

Values of $k_s^* C_s$ and $k_w^* C_w$ for different sediment concentrations and for typical seawater concentrations ([Cu] = 5μg/l; [Cd] = 1μg/l) for Cu and Cd are plotted in Figures 35 and 36. These results show that uptake of sediment-bound Cu or Cd can easily be more important than uptake from water under conditions similar to those encountered in the experimental studies.

It is not known why the data for Cu uptake from $Fe(OH)_3$ and Cd uptake from humic acid were so random, but there are several possibilities that need to be taken into consideration for future studies. Age and sex differences between organisms could be one cause of variation. Although toxicity was not considered in this study, it is possible that a toxicity effect contributed to a wider variation in some experiments.

Table 5. Calculated Values of the Uptake Rate Constant, k_i^*

Copper

Geochemical Phase	$k_i^* C_i$ $\mu g/g$-days	C_i,ppm	k_i^* days^{-1}	R^2	Lack of Fit ($\alpha = 0.01$)
Bentonite	3.8	20	0.19	0.35	Not significant
Humic Acid	10.8	40	0.27	0.68	Not significant
Seawater*	17.4	0.05	349	0.96	-

*Calculated by nonlinear regression.

Cadmium

Geochemical Phase	$k_i^* C_i$ $\mu g/g$-days	C_i,ppm	k_i^* days^{-1}	R^2	Lack of Fit
Bentonite	3.8	3.8	1.0	0.51	Not significant
$Fe(OH)_3$	0.7	3.4	0.2	0.35	Not significant
Seawater	1.3	0.05	26.8	0.92	Not significant
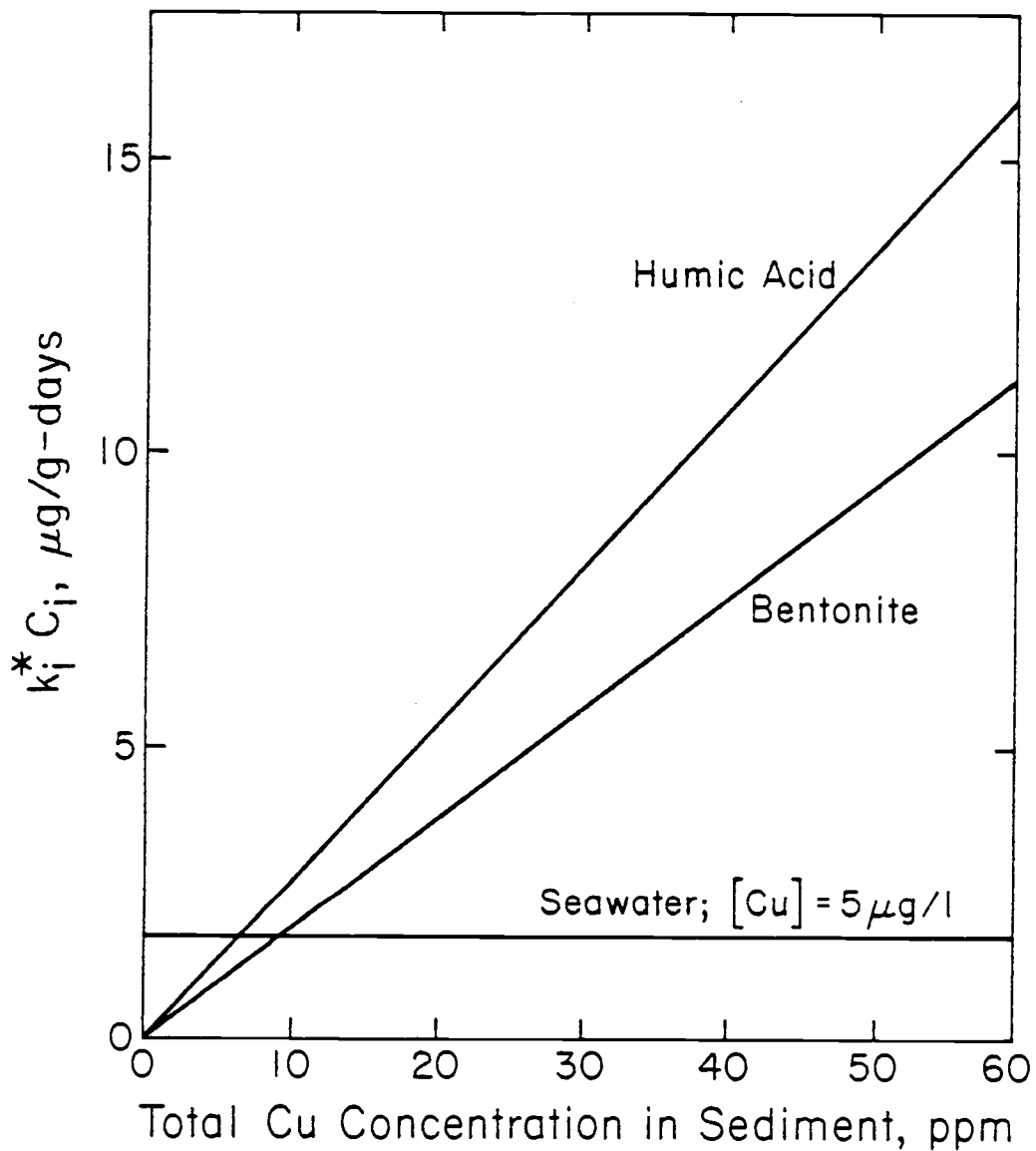
Figure 35. Bioavailability of Cu Associated with Bentonite,
Humic Acid, and Seawater to Abarenicola pacifica
T - 12°C; S - 32 o/oo
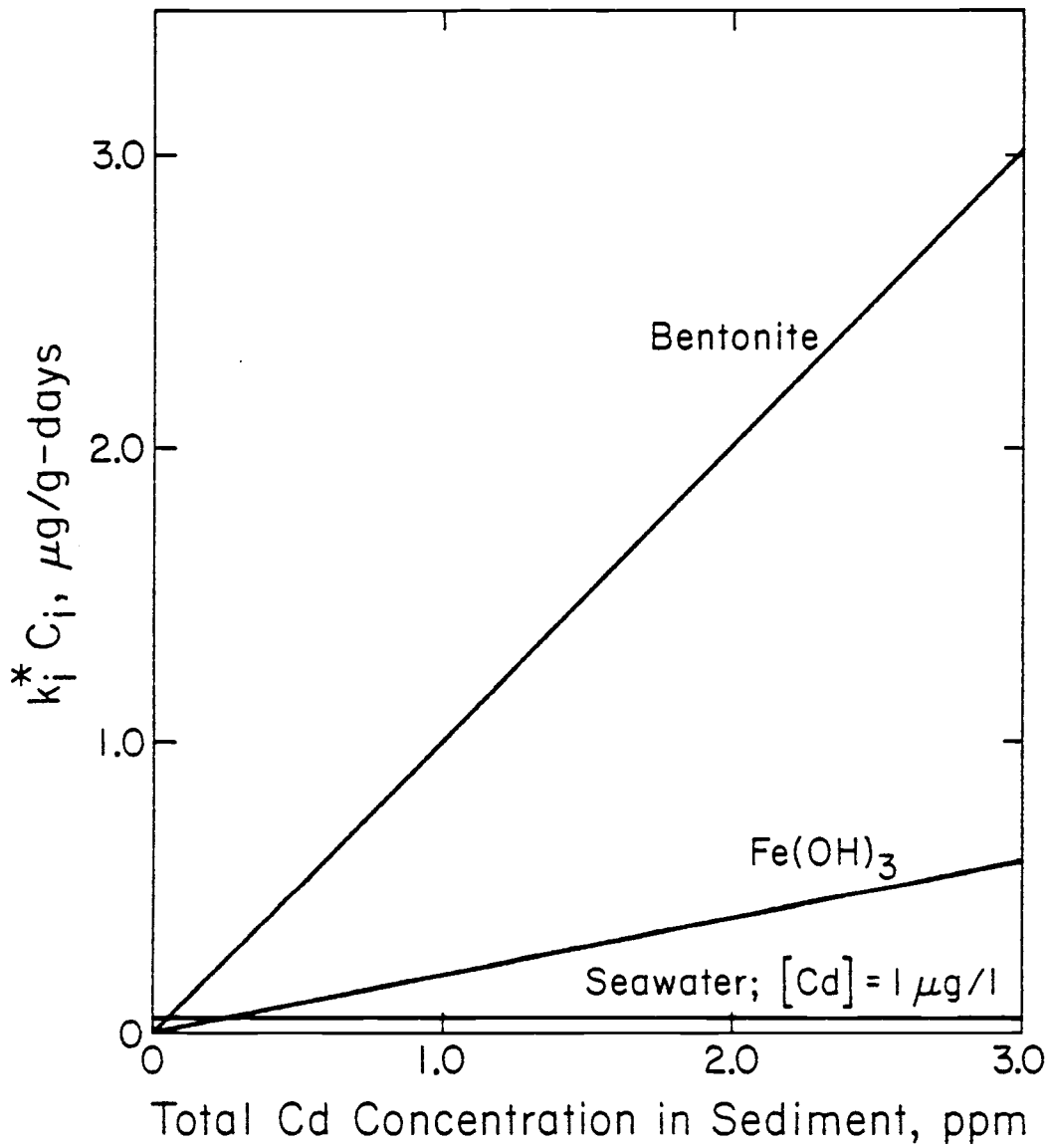
Figure 36. Bioavailability of Cd Associated with Bentonite,
Fe(OH)$_3$, and Seawater to _Abarenicola pacifica_
T - 12°C; S - 32 o/oo

Also a sample size of these organisms, although logistically the largest size that could be used in this study, is probably much too small a number to use to accurately estimate a population mean and standard deviation at a point in time. Further studies employing larger numbers of organisms are needed both to determine the cause of the variation, and to give more accurate estimates of the uptake rate constants.

Conclusions

A simple kinetic model was developed which can be used to estimate the relative bioavailability of trace metals from both different sediment phases and seawater under short term laboratory conditions. This model was used to determine the bioavailability of Cu and Cd from several sediment phases (bentonite clay, humic acid, $Fe(OH)_3$) and seawater to the deposit-feeding polychaete worm, Abarenicola pacifica. The results suggest that, under natural conditions similar to those used in this study, the bioavailability of sediment-bound Cu and Cd to A. pacifica can be much more significant than that of seawater.

CHAPTER 4

CONCLUSIONS

Based on the results of this study, the following conclusions are drawn:

1. Adsorption isotherms for trace metals on different geochemical phases in seawater are linear within the range of typical environmental concentrations of the metals.

2. Conditional equilibrium adsorption constants (K_{AD}) for trace metals can be determined from simple laboratory adsorption experiments utilizing the pure geochemical phase.

3. The partitioning of metals between different geochemical phases in marine sediments can be predicted from a model that was developed which uses experimentally derived K_{AD} values.

4. The partitioning model predicts that the clay fraction may be a major sink for Cu and Cd in marine sediments, based on laboratory results for the adsorption of Cu and Cd on bentonite clay, $Fe(OH)_3$, MnO_2, and humic acid in seawater.

5. The bioavailability of sediment-bound trace metals to deposit feeding organisms depends upon the geochemical phase with which the metal is associated, the concentration of the metal in the phase, and the species of organism.

6. The bioavailability of trace metals from both different sediment phases and seawater under short term laboratory conditions can be quantitatively assessed by a kinetic model that was developed.

7. The bioavailability of Cu and Cd from several geochemical
    phases (bentonite, Fe(OH)$_3$, humic acid) to the deposit-feeding
    polychaete worm, Abarenicola pacifica, can be much more sig-
    nificant than that of seawater at concentrations likely to be
    found in the natural environment.

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