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METAL SPECIATION TECHNIQUES AND THEIR APPLICATION
TO METAL ION INTERACTIONS IN NATURAL WATERS

ROBERT D. GUY, B. Sc.

A Thesis

Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

Carlton University

May 1976

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The undersigned hereby recommends to the Faculty of
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for the degree of Doctor of Philosophy.

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Abstract

Metal ions in natural waters are present in various physicochemical forms; for example, as free hydrated ions, as inorganic complexes with carbonate and hydroxide anions, as metal-organic complexes with fulvic and humic acids, as hydroxy and oxo polymers, and ions adsorbed onto colloidal species. Model systems were employed to represent the aquatic environment, to aid in the evaluation of metal speciation techniques, and to study the various metal interactions in the environment that control the distribution of metal ions between the aqueous and solid (sediment) phases. The model components were bentonite, manganese dioxide, and solid humic acid to represent sediment constituents, and Cu^{+2} , Cd^{+2} , Pb^{+2} , Zn^{+2} , humic acid (HA), tannic acid (TA) and NaHCO_3 to represent the soluble components of the aquatic environment.

Metal species in natural waters are distributed along a size continuum ranging from free ions to colloidal species. A size separation using either dialysis or ultrafiltration (UF), in combination with atomic absorption spectroscopy (AAS) can be used to determine the metal species present in natural waters. UF/AAS can divide the metal species into four size groups, the smallest size (<1.9 nm) being the free ions and simple inorganic complexes. The principal problem with UF/AAS is the adsorption of the metal species onto the membrane surface and porous backing; the net effect of the surface adsorption is to shift the distribution of species to larger size

- fractions. Separations by dialysis of the species required 24 hours to attain equilibrium; the equilibrium distribution does not necessarily represent the distribution between free ion and large species because of the effect of the Donnan membrane equilibrium. The addition of an inert electrolyte overcomes this effect. Separations by dialysis combined with a pH titration and/or a metal ion titration provides a characterization of the water sample in terms of the distribution of metal species as a function of pH or the total metal ion concentration.

The electrochemical speciation technique of most interest was anodic stripping voltammetry (ASV). ASV differentiates between metal species by differences in the kinetics of electrochemical reactions at the electrode; for example, a nonreducible organic complex that dissociates slowly to the free ion does not generate a plating current but free ions and labile complexes do. A comparison of the results of UF/AAS and ASV indicates that the slow electrochemical reaction is probably a heterogeneous diffusion of the metal ion out of the large organic molecule. Adsorption of natural organics, such as gelatin, tannic acid, and cysteine onto the mercury drop produced effects similar to the slow electrochemical step and make interpretation of the stripping voltammograms difficult.

Interactions of metal ions and organic acids in solution were investigated using separations by dialysis and ultrafiltration. The metal-humic acid species are stable at pH values greater than 3.5, whereas the metal-tannic acid complexes are stable at pH greater than 5. Scatchard plots were used to determine the stability constants of the complexes. The stability constants decrease in the order $\text{Pb}^{+2} > \text{Cu}^{+2} > \text{Cd}^{+2} \sim \text{Zn}^{+2}$ and

EDTA >> HA > TA. The humic acids contain two different binding sites; for example, with copper there are 2 mmols/g of sites with $\log K=6.2$ and 5.5 mmols/g of sites with $\log K=5.1$.

The interaction of metal ions with sediment components indicates that the adsorption capacity decreases in the order:

and the metal ions were adsorbed in the order $\text{Pb}^{+2} > \text{Cu}^{+2} > \text{Cd}^{+2} > \text{Zn}^{+2}$.

The distribution of soluble metal and metal adsorbed onto solids depended on the pH of the solution, the ionic strength, and the surface area of the particulates. Metal ions adsorbed onto the solids are released into the solution by ion exchange reactions. The effect of soluble organics on the distribution of metal is to shift the ion exchange equilibrium:

The concentration of soluble metal ion depends on the magnitudes of K_1 and K_2 . Polyhydric phenols, such as pyrogallol, tannic acids, and gallic acid can reduce the hydrous oxides of manganese and iron. A strong pH-dependence was observed and explained in terms of acid hydrolysis of the organic acids to oxalic acid and subsequent reduction of the hydrous oxides by the oxalic acid.

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INTRODUCTION

A simple scheme to characterize a water sample is to divide it into two phases--a solution phase and a solid phase--and then determine the metal concentration in each of the phases. In analysis of natural waters, a filtration through a membrane filter of 0.45 micron pore size is used to separate the two phases. Soluble metal is defined as the metal in the filtrate, and particulate is defined as the metal retained by the filter. Kubota et al. (1) have applied this definition to the analysis of stream waters for the determination of cadmium, copper, zinc and cobalt. Table 1 presents some of their results. An analysis of the results indicates that copper, cobalt and zinc are concentrated in the particulate phase, whereas, cadmium is found mainly in the solution phase. In a similar study, Turekian et al. (2) found that 79%, 8%, and 21% of the cobalt, silver, and selenium, respectively, was in the particulate fraction. The application of a simple operational definition to the characterization of natural waters shows that the distribution of metal ions between soluble and particulate phases depends on the metal ion of interest. The following question must be asked: how good is this definition and does it accurately reflect the metal distribution between solution and solid phases?

Table 1

Concentrations of Metal Particulates in Stream Waters*

Stream	Fraction of Metal in Particulates (%)			
	Cd	Cu	Co	Zn
Canoga	27	68	62	45
Taughanock	28	82	64	86
Buttermilk	8	75	77	91
Six Mile	46	83	77	76
Fall Creek	72	80	83	80

* Taken from reference 1

A close examination of additional analytical results indicates that the operational definition has certain problems associated with it. The first problem is clearly illustrated in Table 2. The data indicate that a significant fraction of the metal in natural waters is present as species larger than 0.1 microns but smaller than 0.45 microns; therefore, the simple filtration scheme does not permit a sufficient resolution to differentiate between small particulates and a soluble species in an unambiguous manner.

The second problem with the operational definition is shown in Table 3. In Table 3, the extractable fraction is the sum of the natural metal species soluble in chloroform and metal species that can interact with diethyldithiocarbamate to produce a species soluble in chloroform. A significant fraction of the metals was found to be nondialyzable through a 4.8 nm pore size membrane.

Zinc, for example, can now be divided into the following size groups:

46% < 4.8nm

4.8nm < 43% < 10nm

10nm < 2.9% < 450nm

450nm < 8.5%

Which fraction of the zinc can be classified as the soluble fraction, and how does the soluble fraction relate to the zinc that was extractable? It is evident that the operational definition for soluble and particulate metal species is inadequate. A definition based on the physicochemical properties of the different metal species would be more accurate.

The physicochemical properties of the metal species

Table 2

Distribution of Metal Ions as a Function of Pore Size*

Metal	Particulate Metal Concentration (%)	
	0.45 μ	0.10 μ
Aluminum	75	81.5
Iron	68.5	93.5
Manganese	15	20

* Taken from reference 3, p. 60

Table 3

Analysis of Sea Water*

Fraction	Concentration (μ g/ml)		
	Copper	Zinc	Manganese
Total	1.3	3.5	0.31
Extractable	0.90	2.6	0.26
Nondialyzable	0.10	1.5	0.02
Particulate ($>0.45\mu$)	0.25	0.3	0.03
Particulate (10nm-0.45 μ)	0.15	0.1	0.01

* Taken from reference 3, p. 64

present in natural waters may be deduced from an investigation of the control processes that determine the metal distribution between the sediment and aqueous phases. In the literature, the distribution of metal ion is generally discussed from one of two viewpoints:

1. The composition of the sediment controls the concentration of the soluble metal ion.
2. The chemical properties of soluble species determines the concentration of metal ions in the solution.

A review of the literature (encompassing both of the above viewpoints) was undertaken to determine:

1. A list of the possible metal species present in the aquatic environment.
2. A list of the current theories explaining how the metal species interact to control the metal ion distribution.
3. A list of areas where further research is deemed necessary.

The following summary of the literature is divided into three sections: 1. an overview, 2. sediment species, and 3. solution species.

I An Overview

Piro et al. (4) have studied the exchange of zinc in seawater between ionic, particulate, and complexed species using a combination of anodic stripping voltammetry (ASV) and a pH titration to differentiate between the three physicochemical forms. Anodic

stripping voltammetry is a two-step procedure (5): a concentration step in which the metals are plated from the solution into a mercury drop or film, and an oxidation step in which the metals are stripped out of the amalgam by the application of a linearly varying potential. In the absence of all interferences, the anodic current is proportional to the metal concentration in solution. In the analysis scheme of Piro et al. (4), there are three assumptions:

1. The only electroactive form of zinc is the free ionic species.
2. During the plating step, the conversion of zinc from the electroinactive forms (particulate and/or complexed species) to the free ionic zinc is negligible.
3. The equilibrium between the three forms is rapidly approached after the pH is adjusted. Piro classified the metal species on the basis of the following criteria: at pH 8, the stripping current corresponded to the free zinc ion; at pH 6, the stripping current corresponded to both the free ion and particulate zinc species; and at pH 2, the stripping current corresponded to the free zinc ion, the particulate zinc species, and the zinc complexes.

For the water sample studied, Piro found that 40%, 42%, and 18% of the zinc was in the complexed, particulate, and ionic species, respectively. Piro attributed the particulate zinc to both zinc hydroxide colloids and zinc adsorbed onto foreign colloids. This overview of the zinc distribution in a water sample introduces several questions:

1. What is the nature of the foreign colloids?

2. Does the adjustment of pH to 6 release all the particulate species or are there colloids that do not decompose until a lower pH is attained?

3. What are the zinc complexes present in natural water? To answer these questions, it is assumed that the sediment species may serve as a good model for the particulates present in the surface waters.

II Sediment Species

Various groups (6-16) have investigated the sorption of metal ions onto sediments and particulates suspended in rivers. Nelson et al. (6) fractionated Columbia River sediments to determine the chemical form in which radioactive elements were present in the sediments. The fractionation scheme and some typical results are given in Tables 4 and 5, respectively. The results indicate that, for zinc and manganese, major fractions of the sorbed metals are associated with organic and reducible species.

The organic fraction of sediments has been investigated by several workers (7-9). Rashid (7) studied humic acids of marine origin to determine their role in the binding of heavy metals to sediments. Rashid mixed humic acid solutions with increasing concentrations of metal ions and took the amount of metal ion necessary to induce coagulation as the metal-holding capacity of the humic acids. Typical results are given in Table 6. The data in Table 6 indicate that the capacity varies for different humic acids and that less iron than copper is required to coagulate humic acid. The metal-holding capacity determined by Rashid should not be

Table 4

Fractionation Scheme for Sediments*

Extractant	Metal Species Released
1 N $\text{NH}_4\text{CH}_3\text{COO}$	Exchangeable
Acetic acid (pH 3)	acid-soluble
Bromoethanol	organic
Sodium dithionite	reducible

* Taken from reference 6.

Table 5*

Distribution of Manganese and Zinc in Sediment

Extractant	Metal Released (%)	
	Zinc	Manganese
1 N $\text{NH}_4\text{CH}_3\text{COO}$	1.6	10.5
Acetic Acid (pH 3)	19	23
Bromoethanol	65	33
Sodium dithionite	9	22

* Taken from reference 6.

Table 6

Metal-holding Capacity of Humic Acids*

Humic Acid	Capacity (mmoles/g)	
	Fe ⁺³	Cu ⁺²
1	0.76	1.50
2	0.87	1.82
3	1.15	2.84

* Taken from reference 7

equated with the number of binding sites present on the humic acid molecule because the difference between iron and copper reflects the Schultze-Hardy rule; that is, the amount of metal ion necessary to induce coagulation of a colloid depends on the charge of the counter ion. In a later study (8), Rashid et al. found that marine humic acid can sorb onto clay minerals. One can then envision the sorption of metal ions onto humic acids that are fixed onto suspended clay colloids.

A study by Szilagyi (9) indicated that humic solids can adsorb ferric ion and reduce some of the ferric iron to ferrous iron. The reduction capacity of the humic acid was found to be 0.03 meq/gram. The results of the studies by Rashid (7,8) and Szilagyi (9) indicate that the organic fraction of the sediments consists of humic acids adsorbed onto the clay particulates, and that the metal-organic interaction is a complicated one because both complexation and redox reactions may be operative.

Nelson et al. (6) attributed the reducible fraction of the sediments to the hydrous oxides of iron and manganese. Jenne (10) has proposed that the hydrous oxides of iron and manganese furnish the principal control mechanism for metal fixation in soils and fresh water sediments. Hydrous metal oxides are known to sorb metal ions (11) and because of their ability to coat clay colloids, their large surface area-to-weight ratio allows the oxides to exhibit a chemical activity far out of proportion to their concentration. Turekian and Scott (12) have analyzed the suspended matter in several American rivers and found that manganese was present at very high levels ranging from 300 to 15,000 ppm. If the manganese

is present as the oxide, then it may be responsible for the fixation of other heavy metals in the suspended matter.

Organic acids and hydrous oxides account for two of the modes of metal fixation in sediments. Nelson's study (6) also indicated that exchangeable and acid-soluble species are present. A study by Sanchez and Lee (13) on the adsorption of copper onto calcareous sediments indicated that the sediment-binding capacity depended on the alkalinity of the sediment. The study indicated that when copper ion was equilibrated with the sediments magnesium and calcium were released. This observation led Sanchez and Lee to propose that copper is bound to the sediment by replacing the magnesium and calcium in the sediment carbonates resulting in the formation of a basic copper carbonate. The copper carbonate would be soluble in acetic acid.

The ion exchange behaviour of the sediments can be attributed to the clay fraction of the sediment. Osterberg et al. (14) compared the desorption of zinc from a Dowex 50 cation exchange resin and the desorption from Columbia River sediment. The results for the desorption of zinc into seawater are shown in Figure 1. The curves in Figure 1 indicate that only 1.5% of the zinc on the sediment was exchangeable, whereas all the zinc on the resin was exchangeable. Similar studies by Murray and Murray (15), and Evans and Cutshall (16) showed that, when sediments were mixed with sea water, 40% of the zinc was exchanged; however, if the pH of the water was lowered to 6, 70% of the zinc was removed from the sediment. If one assumes that the sedimentary materials are good models for the particulate species

Figure 1: The exchange of zinc between sediment, resins, and seawater*

- Columbia River sediment
- ▲ Dowex 50 ion exchange resin

* Taken from reference 14

present in surface waters then the pH studies cited here, when compared with the assumptions of Piro et al. (4), indicate that not all the zinc will be removed from the particulates if the pH of the suspension is lowered to 6. The speciation scheme proposed by Piro et al. (4) does not provide an adequate differentiation between particulate and complexed species.

The studies on metal distribution in sediments indicate the following:

1. Metal ions are associated with organic acids and hydrous oxides of manganese and iron.
 2. A fraction of the metal ion is present on clay colloids.
 3. Basic metal carbonates may play some role in the fixation of metal ions to calcareous sediments.
 4. pH plays an important role in the metal ion distribution.
- The effect of pH is stronger than the effect of changing the ionic strength.

III Soluble Species

The aqueous phase of the aquatic environment has been investigated to determine both the capacity of the water sample to retain metal ions in solution and to determine the size distribution of the natural metal species. Chau (17,18) has studied the interactions between copper ion and complexing species in lake waters. Chau (17) titrated a lake water with copper ions and used anodic stripping voltammetry to determine the free copper ion concentration. The added copper ion is distributed between the

different species:

where L_i is any species that interacts with copper ion. Like Piro et al. (4), Chau assumed that the only electroactive species was the free ion and, therefore, a plot of measured copper concentration as a function of total copper concentration would yield the chelating or binding capacity of the sample. The measured binding capacity for several lake waters varied from 0.1 to 2.5×10^{-6} M. The average concentration of copper in natural waters is 15 $\mu\text{g/l}$ or 2.36×10^{-7} M (19). Therefore, the ratio of complexing sites to copper ion may vary from 0.4 to 10.6. It is possible that significant amounts of copper in natural waters would be associated with a binding agent. In a subsequent study (18), Chau analyzed several lake waters for exchangeable and electroinactive species of copper, lead, cadmium and zinc. The exchangeable metal was taken as the free metal ion and the metal ions released upon addition of the 0.1 M sodium acetate electrolyte. The inactive metal was determined after the sample was oxidized with acid persulphate. In all the waters analyzed it was found that lead and copper were bound in inactive forms whereas zinc and cadmium were distributed between the two forms. The work of Chau (17,18), in agreement with the studies of Piro et al. (4), indicates that some of the metal ions present in solution are bound in species that are electroinactive.

An insight into the nature of the inactive metal species can be obtained from the molecular size distribution of metals in natural waters. Schindler et al. (20) investigated the organic-inorganic interactions present in a water sample that had been equilibrated with a lake sediment. The species in the water sample were separated into different molecular size fractions using ultrafiltration membranes. Iron, manganese and zinc were concentrated in species with a molecular size* greater than 50,000, and no metal was found in the fraction of size less than 500. An analysis of the organic carbon content of each size fraction indicated that the metal ions were associated with organic molecules.

Similar fractionation studies (21-23) of humic acids indicate that between 20% and 40% of the humic acids are present in fractions of molecular size greater than 200,000. The results of a fractionation of iron in the presence of humic acid are given in Table 7. The data in Table 7 indicate that the iron is associated with the organic carbon. A study by Bender et al. (22) in which Sephadex gels were used to fractionate copper in sewage effluents indicated that the copper was distributed in two fractions--a fraction greater than 50,000 in molecular size and a fraction 500-1000 in size. Bender et al. (22) found that on lowering the pH of the solution to 2 the copper present in the large size fraction was shifted to the smaller size fraction. The above fractionation studies indicate that at least one of the possible metal species in natural waters is the metal ion associated with large organic acids.

* see footnote on page 16

Table 7

Fractionation of Iron-Humic acid Species^{*}

Molecular size	Iron content (%)	Carbon content (%)
< 1000	20	12
< 10,000	5	12
< 20,000	9	14
> 20,000	52	54

^{*} taken from reference 21.

Footnote from page 15:

The molecular sizes reported on this page are given as molecular weights. Ultrafiltration and gel permeation separations, however, are by size and not weight (cf. pages 59 and 70) and the weights are only nominal.

Benes (24) has investigated the behaviour of metal ions in solution using dialysis membranes. In a study of the state of manganese in dilute solutions, Benes (24) found that the dialyzable manganese decreased from 100% to 0% as the pH increased from 8 to 10. Benes (24) did not attribute the decrease in the dialyzable manganese to the hydrolysis of Mn(II):

but to the oxidation of Mn(II) to Mn(III); the trivalent ion then hydrolyzes to form a colloid which is nondialyzable. The manganese colloid is very similar to the hydrous oxides present in sediments and should be able to bind other heavy metal ions. Benes and Steinnes (25) applied the dialysis technique to the analysis of natural waters. A 4.8 nm pore size membrane was used to determine the fraction of metals that was present in large species. Some typical results are given in Table 8.

Spiro et al. (26) have investigated the hydrolytic polymerization of Fe(III). In the study (26), an Fe(III) solution with two equivalents of base was dialyzed through a cellulose acetate membrane; only 40% of the iron was found to be dialyzable. Spiro et al. (26) also found that the weight average molecular weight of the polymer was 1.4×10^5 and that the particle size was greater than 7 nm in diameter. This indicates, in agreement with the work of Benes and Steinnes (25), that the manganese and iron hydroxy polymers are small enough to pass through a 0.45 micron membrane filter but are not dialyzable.

Table 8

Dialyzable Metal Ions in Natural Waters^{*}

Metal	Fraction Dialyzable (%)
Sodium	100
Calcium	94
Zinc	54
Aluminum	3.5
Manganese	66
Chromium	48.8
Iron	19.4

^{*} taken from reference 25.

The anodic stripping voltammetry studies of Piro et al. (4) and Chau (18) indicate that metal ions in solution are present as free ions and electroinactive species, whereas the fractionation studies (20-26) indicate that the metal ions are distributed between large organic molecules and free metal ions. The possibility that the electroinactive forms of the metal ions are the large species is a strong one. The important metal species in solution can be summarized as:

1. Metal ions complexed with large organic acids such as humic and fulvic acids.
2. Metal ions associated with hydrous oxide colloids suspended in the surface waters.
3. Metal ions present as the free aquo ion, as simple inorganic complexes, for example, with carbonate ion, and as hydroxy species.

DEFINITION OF RESEARCH PROBLEM

The separate studies of the two natural water compartments (sediment and aqueous phases) provide a picture of metal ion distribution consisting of interactions of free metal ions with both organic acids in solution and with several components in the sediment. The actual metal ion distribution will depend on the relative strengths of two interactions. This simple picture of the aquatic environment leads to several important questions:

1. Which of the particulates--humic colloids, hydrous oxides,

or clays--plays the most important role in the fixation of the ions to the sediment?

2. What are the chemical properties of the particulates that are responsible for the sorption of metal ions?

3. In the aqueous phase, what controls the distribution of metal ions between aquo ions, inorganic complexes, and organic complexes?

4. How are the metal ions that are initially adsorbed onto the sediment released to the aqueous phase? This aspect of the metal ion distribution between solution and sediment is an important one. The soluble organic acids may complex the soluble metal ions; the decrease in the concentration of free metal ion will shift the ion exchange equilibrium (equation I-3) to the right:

Organic acids may also react with the sediment matrix. The reaction between organic acids and sediment matrix is a possible mechanism for metal release from the hydrous oxides of manganese and iron. As noted earlier, Szilagyi (9) found that humic acid can reduce ferric to ferrous iron. Studies by Hem (27) and Theis and Singer (28) indicate that tannic acids may keep both manganese and iron in a reduced state under conditions where the oxidation is rapid (for example, tannic acid can keep Fe(II) stable for a period of 7 days under conditions where, in the absence of tannic acid, the iron is oxidized in a period of minutes). The release of metal ions from sediment should be investigated to determine:

1. The relative importance of metal-humic acid complexes as compared to chloro complexes.

2. The importance of the reduction of hydrous oxides as a mechanism of metal ion release from sediments.

To answer these questions it is necessary to develop procedures for determining the metal species present in solution. Two techniques--anodic stripping voltammetry and ultrafiltration or dialysis--have been proposed as useful for metal speciation; however, the two procedures have not been compared under the same experimental conditions (i.e., the same concentration ranges and on the same water samples). A critical comparison of the two analytical techniques should yield information on several questions:

1. The true nature of the electroactive species, that is, whether it is a simple metal ion (aquo-complex) or a metal organic complex, etc.

2. In describing the anodic stripping voltammetry technique, the term "non-labile" has been applied to the electroinactive species (18,29); what does this term imply and how does this relate to the theory of reduction of metal species at the mercury electrode?

3. Piro et al. (4) made several assumptions (given on page 6) in applying anodic stripping voltammetry to the analysis of natural waters. There may be other factors involved in the technique which may invalidate the above assumptions; if so, what are they?

4. What are the assumptions made in applying the ultrafiltration or dialysis--graphite-furnace atomic absorption spectroscopy techniques to metal speciation in natural waters? With this technique, which

species are separated and how do they relate to the results of anodic stripping voltammetry experiments?

Another important aspect of the problem of identification of soluble species is to define what is meant by the complexing capacity of the water sample. If one equilibrates a natural water sample with a sediment containing heavy metal ions, is the amount of metal released into the aqueous phase equal to the chelating capacity? Or, is it equal to the solubilizing capacity (where the solubilizing capacity is defined as the amount of metal released via complex formation and by ion exchange)? For example, Jackson (30) found that the metal ion-organic acid complex precipitates if the ratio of metal ion to number of binding sites is greater than 1 (similar to the precipitation of humic acid species observed by Rashid (7)). It is evident, therefore, that complexing capacity need not always involve solubilization - it may sometimes also involve precipitation of metal species. Which capacity is the more relevant to heavy metal toxicity with respect to fish, algae, etc?

The metal interactions that are possible in the aquatic environment are summarized in Figure 2. The complexity of the interactions indicate that real sediments and natural waters cannot be used for the studies because all possible interactions will be present at the same time. To simplify the problem, model systems should be developed in which one or two interactions (for example, metal-organic interactions in solution or metal-soluble organic acid-clay interactions) can be isolated. The soluble model components chosen were as follows:

1. Four heavy metal ions: copper, lead, cadmium and zinc;
2. The organic acids: ethylenediaminetetraacetic acid (EDTA), tannic acid, humic acid, and the inorganic anions, bicarbonate and carbonate.

The compounds suitable for the solid (sediment) phase were chosen from a list of model compounds employed for soil studies. Reimer and Toth (31) studied the sorption of copper onto clay minerals, humic acid and sediments. They found that the increasing order for the capacity of the sorbent was:

kaolinite < illite < montmorillonite < humic acid.

The results of a more comprehensive study by Gardiner (32) on the interaction of cadmium with mud solids and model compounds are summarized in Table 9. Gardiner also found that effluent from percolating filters (in a sewage treatment plant) maintained a higher solution concentration of cadmium, that is, the concentration factors were lower in the presence of effluent. Gardiner concluded that sorption of cadmium was a major control mechanism, humic acid being the major component responsible for sorption onto the sediment.

Kharkar et al. (2) extended adsorption studies to include the hydrous oxides. In the sorption of selenium, the increasing order of the adsorption capacity was:

peat < kaolinite < montmorillonite < MnO_2 < $\text{Fe}(\text{OH})_3$.

The most extensive study of a model system was done by McClaren and Crawford (33,34), who studied the adsorption of copper onto clay, hydrous oxides and humic acid. The increasing order of adsorption

Table 9

Concentration Factors of Cadmium onto Model Compounds*

Adsorbent	C_S/C_A^a
Silica	1000
Kaolin	380
Humic acid	18,000
Plant Material	1000
Sediment	6-40,000

* taken from reference 32

$$^a \text{ CONCENTRATION FACTOR} = C_S/C_A = \frac{\text{Cadmium CONC. in sediment}}{\text{Cadmium CONC. in solution}}$$

capacity was:

clay minerals < iron oxides < organic matter < manganese oxides.

Of the copper adsorbed onto the clays, humic acids, and hydrous oxides; 80%, 60%, and 75%, respectively, was found to be exchangeable with ^{64}Cu . This indicates that humic acid has a greater ability to "fix" metal ions onto soils and sediments.

From the above studies, it seemed desirable to employ bentonite (as a model clay), humic acid, hematite, and manganese dioxide to model the sediment components. The model components were investigated to determine the relative capacities of the solids to absorb metal ions, to determine the effect of pH on the adsorption capacity, and to determine whether the method of preparation of hydrous oxide affected the adsorption characteristics.

Organization of the Thesis

The thesis is divided into three sections. The first section (Chapter 1) consists of a description and characterization of the three particulates (clay, manganese oxide, and humic acid) employed in the studies of metal ion sorption onto solids. The second section (Chapters 2,3) describes the methods developed to identify the metal ion species in solution. Chapter 2 covers the methods based on atomic absorption spectroscopy and Chapter 3 discusses the electrochemical techniques. The third section discusses the three metal ion interactions of interest: the metal ion-organic acid interactions in solution (Chapter 4), the metal ion-solid adsorbent

interactions (Chapter 5), and the interactions between soluble organic acids and ions adsorbed onto the solids (Chapter 6). Each chapter consists of a short introduction describing the purposes of the chapter and its relationship to the preceding chapters, a description of the experimental procedures, and a discussion of the results.

Chapter 1

Characterization of Solid Adsorbents

In the introduction it was decided that three main groups of solids should be investigated, that is, the model studies should include a clay, an organic acid, and a hydrous oxide. One of the main problems with clays and humic substances is that they are complex compounds. One approach to the problem is to collect a large quantity of sediment or soil, treat the soil with NaOH to extract the organic acids, acidify the extract and collect the humic acids. This approach is time-consuming and gives a poor yield; for example, one study (35) reported extraction of 1.3 grams of humic acid from 2.5 kg of soil. Since it was expected that several hundred grams of humic acid would be necessary for the experiments, this approach was not attempted (the same comments can be made for clays). The alternative approach is to obtain commercially available clay and humic acids, and then characterize them according to standard procedures. The purpose of this chapter is to describe the three solids employed in this study.

Clay: The clay was a purified bentonite obtained from Anachemia. Bentonite (36) is generally not a pure clay, that is, the dominant clay-mineral component of bentonite is smectite with other minerals, particularly, illite and kaolinite, present in amounts up to 50% of the total clay mineral content. Smectite is composed

of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. In the stacking of the silica-alumina-silica units, the oxygen layers of each unit are adjacent to oxygen layers of the neighbouring units with the consequence that there is a very weak bond between the units and an excellent cleavage plane between them. Isomorphous substitution of aluminum for silicon and of divalent ions for aluminum results in a net negative charge that is balanced by calcium counter ions. The basic structural unit of illite is a layer composed of two silica tetrahedral sheets with a central alumina octahedral sheet. The unit is the same as for smectite except that some of the silicons are always replaced by aluminum and the resultant charge is balanced by potassium ions. Kaolinite is composed of a single tetrahedral sheet and a single alumina octahedral sheet. There is little substitution within the lattice and therefore the kaolinite has a low cation exchange capacity.

The clay was to be employed in the ion exchange experiments, that is:

and therefore, it was necessary that:

1. All the counter ions on the clay be the same.
2. The cation exchange capacity of the sample clay be known.

Bentonite usually contains calcium as the counter ion; however, in the proposed studies a potassium acetate buffer was employed to adjust the solution pH. To simplify studies, the clay was converted to the potassium form as follows (37).

Ten grams of bentonite were equilibrated with one litre of 1.0 M KNO_3 for 24 hours and the clay suspension allowed to settle. The supernatant liquid was decanted off, and the procedure repeated three times with new potassium nitrate solutions. After the third equilibration, the clay sample was washed with several litres of distilled water (until no potassium was observed in the washings), washed with 95% ethanol, and dried at 180 C. The dried clay was ground and sieved through a 80 mesh sieve.

The cation exchange capacity was determined using the ammonium acetate method (38). Clay samples, 100 mg in mass, were equilibrated with 1.0 M $\text{NH}_4\text{CH}_3\text{CO}_2$ (100 ml, solution pH 5.2) for 24 hours. The suspensions were filtered through a 0.45 micron pore size membrane filter, and the potassium released measured by flame emission spectroscopy. The ion exchange capacity of the clay was found to be 59 meq/100 g clay.

The surface area of the clay was determined by the BET method using nitrogen as the adsorbing gas after degassing the sample at 200 C. The surface area was found to be $10.2 \text{ m}^2/\text{g}$. The surface area and cation exchange capacities were in reasonable agreement with the literature values (36, p. 189).

Hydrous manganese oxides: Two different oxides were prepared as follows:

1. Permanganate oxidation of Mn(II). Oxidation of Mn(II) by permanganate under neutral conditions follows the reaction stoichiometry:

The oxide was prepared as follows: 200 ml of 0.10 M KMnO_4 (standardized by the Fisher-Bright method (39)) was mixed with the calculated amount of 0.10 M KOH necessary to neutralize the acid produced. To the well-stirred permanganate solution was added, drop-by-drop, 250 ml of 0.10 M Mn(II) (as MnSO_4). The Mn(II) solution was added slowly to permit the complete oxidation of Mn(II) to Mn(IV) and to prevent the adsorption of Mn(II) onto the hydrous oxide. The preparation was done in such a manner that after the addition of manganous ion excess permanganate was present. The oxide was washed with 0.1 M KNO_3 solution, distilled water, and then filtered. The solid was dried at 180 C.

2. Air oxidation of Mn(II). A solution of 0.10 M MnSO_4 was added dropwise to a 1.0 M KOH solution. Air was bubbled through the suspension for 48 hours. The suspension was washed with 0.1 M KNO_3 , distilled water, and dried at 180 C for 24 hours.

The two oxides prepared by the above procedures should be MnO_2 and Mn_2O_3 , respectively. To check the composition of the oxides both total manganese content and Mn(IV) and Mn(III) content were determined:

1. Total manganese: 20 mg of the oxide was dissolved with concentrated HCl and the resulting solutions diluted to 200 ml with ultrapure water. The solutions (approximately 20 $\mu\text{g/ml}$ in manganese) were analyzed by flame atomic absorption spectroscopy.

2. Oxidation state: The oxides of manganese can react with oxalic acid (40) as follows:

Known weights of the two oxides were added to 100 ml of 0.1 M acid oxalate (5 ml of concentrated H_2SO_4 of specific gravity 1.84 was added to the oxalate solution) and heated to 60 C. After all the oxide was dissolved, the excess oxalic acid was determined by titration with KMnO_4 .

The results of the analysis are given in Table 10. The difference between the calculated and theoretical composition in Table 10 results from the adsorption of potassium counter ions. It is evident that the two oxides prepared by the two different procedures should serve to represent two possible manganese oxides.

The surface areas of the two oxides determined by the BET method were found to be $147 \text{ m}^2/\text{g}$ and $22 \text{ m}^2/\text{g}$ for the MnO_2 and Mn_2O_3 , respectively.

Humic acid: The humic acid was obtained from Aldrich Chemical Co. The humic acid was leached with 0.1 M HNO_3 for 24 hours to remove heavy metal ions. The leached acid was washed with ultrapure water and dried at 180 C. The elemental composition of the crude and leached acids and several soil humic acids are given in Table 11.

A comparison of the compositions of the crude and leached acids with the literature values indicates that the crude acid

Table 10

Analysis of Manganese Oxides

Mode of Preparation	Total Mn (mmoles/g)	Mn(IV)/Mn(III) (mmoles/g)*	% [@]
KMnO ₄ oxidation	9.29 ± 0.08	9.38 ± 0.05	82
Air oxidation	11.29 ± 0.08	11.4 ± 0.2	89

* Mn(IV) and Mn(III) content of the MnO₂ and Mn₂O₃, respectively

$$^{\circ} \frac{\text{Measured Mn content}}{\text{Theoretical Mn content}} \times 100\%$$

Table 11

Elemental Composition of Humic Substances

	Sample [*]	C %	N %	H %
1	Crude HA	55.56	1.04	5.05
2	Acid-leached HA	46.96	0.93	5.76
3	Soil HA	56.4	4.1	5.5
4	Soil HA	56.4	1.6	5.8
5	Soil HA	53.8	3.2	5.8
6	Soil FA	47.6	0.9	4.1
7	Soil FA	42.5	2.8	5.9
8	Water FA	46.2	2.6	5.9

* 3-8 were taken from reference 41, p.30.

HA=humic acid FA=fulvic acid

compares favorably with soil humic acid, whereas the purified acid is comparable to the soil fulvic acids. The infrared spectra of the two acids are presented in Figures 3 and 4, and the literature spectra are presented in Figure 5. A comparison of the four spectra indicates that the acid-leached sample resembles soil fulvic acid. The acid-leached sample was employed in all of the experiments.

The humic acids were characterized by measuring the total acidity of the acid and the number of carboxyl groups present per unit weight of sample.

1. Total acidity: the procedure recommended by Schnitzer and Khan (41) was used. A solution of 0.01 N $\text{Ba}(\text{OH})_2$ was equilibrated with the humic acid:

The excess $\text{Ba}(\text{OH})_2$ remaining after the reaction was backtitrated with 0.100 N HCl.

2. Carboxyl groups: the procedure recommended by Schnitzer and Khan (41) was followed:

The acetic acid released was titrated with 0.100 N NaOH.

3. A discontinuous titration of the two samples was performed as follows: to a known weight (approx. 41 mg) of humic acid were added increasing volumes of 0.010 N NaOH. The suspensions were allowed to equilibrate for 14 days (the samples were shaken for 5 minutes each day), and the pH was measured on the fourteenth day.

Figure 3: IR spectrum of crude humic acid

0.41 mg of humic acid in 200 mg of KBr pressed at 12 tons

Figure 4: IR spectrum of acid-leached humic acid

FIG. 4-4 Infrared spectra of (A) HA, and (B) FA (42).

Figure 5: Taken from reference 41, page 71

The titration curves are given in Figures-6 and 7. The volume necessary to reach pH 7 was used to calculate the total carboxyl concentration (41). The results are given in Table 12.

A comparison of the two samples--crude and acid-leached--indicates that the acid leaching increases the free carboxyl acid content of the sample but the phenolic OH concentration remains constant. The increase in the carboxyl content of the acid can be attributed to (41):

The surface area of the humic acid (both samples) was determined by BET method and found to be $1.7 \text{ m}^2/\text{g}$.

Figure 6: Discontinuous titration of acid-leached humic acid (41.00 mg humic acid used)

Figure 7: Discontinuous titration of crude humic acid (41.00 mg of humic acid used)

Table 12

Acid Contents of Humic Acids

Sample	Total Acidity (meq/g)	Carboxyl (meq/g)		Phenolic OH [*] (meq/g)
		Acetate	Titration	
Crude HA	4.18	1.70	1.34	2.48
Acid-leached	5.85	3.48	3.28	2.38

* Phenolic OH = Total acidity - Carboxyl content

Chapter 2

Metal Speciation Using Atomic Absorption Spectroscopy

Atomic absorption spectroscopy can be used to determine only total metal concentrations. To apply atomic absorption spectroscopy to the speciation of metal ions, one must first separate the species into different fractions and then determine the metal content in each fraction by atomic absorption spectroscopy. The minimum criteria for a successful speciation procedure are:

1. The methods should yield sufficient information to characterize the water sample.
2. The procedure should be simple and require a minimum chemical treatment of the sample. For example, the addition of chelating agents in extraction procedures can introduce higher concentrations of metal contaminants than those present in the sample to be analyzed and often requires extensive purification of reagents and measurement of reagent blanks.
3. The analytical technique chosen for determining the metal content must be sensitive enough to work at the low metal concentrations in natural waters; for example, the mean values of copper, lead, manganese and iron concentrations in surface waters are (19) 15 $\mu\text{g/l}$, 23 $\mu\text{g/l}$, 58 $\mu\text{g/l}$ and 52 $\mu\text{g/l}$, respectively.
4. The analytical techniques must be free from interferences or the interferences must be well defined and amenable to correction.

5. The final results should be readily interpretable in terms of the possible metal species, that is, species such as free ions, metal-organic complexes, and colloids.

Burrell (42) has proposed the idealized speciation scheme given in Figure 8. There are two problems in Burrell's scheme; the first is that extraction procedures may contaminate the sample, and the second is the problem associated with the use of gel filtration to investigate higher molecular weight species. The free metal ions and metal-organic complexes in natural waters are in equilibrium:

and during the gel filtration, the free metal ions are retained in the gel and the large complexes pass through the gel. The result of this separation of free ions and complexes will be to shift equilibrium 2-1 to the right (43). The chromatogram that would result would be a peak for the metal complex, a peak for the free ion, and a shallow valley in between for the free ions produced by the shift in the complexation equilibrium. A second problem associated with gel filtration is the possibility of metal and/or humic species interacting with the gel (44,45); for example, Posner (45) found that significant fractions of iron were sorbed onto Sephadex G-25 during the filtration of partially neutralized ferric ion solutions. The reversible sorption of ions onto the gel would produce long tails in the chromatograms. The use of gel filtration in Burrell's scheme provides a separation of species by size but the shifts in

Figure 8: Metal speciation scheme proposed by D. C. Burrell (42)

equilibria and adsorption problems would result in species concentrations that would be in error.

To overcome the problems associated with Burrell's scheme, a simplified procedure is given in Figure 9. There are two advantages to this scheme; first, no reagents are added to the sample, and therefore, metal contamination will be at a minimum. Secondly, separation by dialysis can be performed under conditions where essentially no shift in the complexation equilibria occurs. For example, if the solution to be dialyzed has a volume of 200 ml and the dialysis bag contains 10 ml, then the equilibrium would be shifted by only 5%. This is true for separation by ultrafiltration where only a small fraction of the solution need be filtered. A comparison of the dialysis and ultrafiltration results would also provide an internal check on the analysis.

The total concentrations of metal ions in natural waters are very low. It is necessary to use analytical techniques of extremely high sensitivity, such as atomic absorption spectroscopy with a resistively-heated atomization cell (e.g., the commercially available Heated Graphite Atomizer 2100, the Carbon Rod Atomizer 63, and the tantalum strip atomizer). The use of a graphite furnace atomizer involves three steps--a drying step to remove the solvent, a charring step to break down and remove wholly or partially the matrix, and an atomization step in which the free atoms are produced and the amount of light absorption is measured. L'vov (46) has indicated that several factors may alter the analytical results obtained by using the graphite furnace atomizer:

Figure 9: A simplified speciation scheme

1. Metal species may be lost during the charring step (especially, volatile lead and cadmium species).
2. Differences in vapour pressures between the sample and standards will result in either high or low metal concentrations.
3. The possibility of light scattering or molecular absorption by the matrix during the atomization step will result in high concentration values and/or poor precision.

The purpose of this chapter is to summarize the investigations into the applicability of atomic absorption spectroscopy with a Heated Graphite Atomizer for quantitative determination of copper, lead, manganese and iron in natural waters. The application of the proposed speciation scheme (Figure 9) to the analysis of natural waters was also tested.

Experimental

Apparatus: A Varian Techtron atomic absorption spectrophotometer, model AA-5, equipped with an air-acetylene premix burner (Techtron model AB51) was used for all flame atomic absorption measurements. A Perkin-Elmer atomic absorption spectrophotometer, model 503, equipped with a Heated Graphite Atomizer, model 2000, and a Deuterium Background Corrector was used for all graphite-furnace atomic absorption measurements.

Dialysis tubing (Spectrum Medical Industries) was treated with a 0.1% (w/v) aqueous solution of sodium sulphide at 80 C for one minute, washed with water at 60 C for two minutes, and acidified

with 3% (v/v) sulphuric acid to remove sulphur contaminants introduced during the manufacture (47).

Ultrafiltration experiments were performed using an Amicon ultrafiltration assembly, model 202, and Amicon filters, UM2, PM 10, PM 30, XM 50 and XM100A. The diameter of the filters was 62 mm.

All pH measurements were performed using a Fisher Accumet pH meter, model 210, with a glass pH electrode (model 13-639-3), and a saturated calomel electrode, model 13-639-52. The pH meter was calibrated daily using standard buffer solutions (Fisher Scientific). The meter was calibrated at pH 2, 4, 6, and 8.

Reagents: Ultrapure water of resistivity 18.3 megohm-cm was obtained from a Milli-Q2 system (Millipore Co.). A humic acid solution was prepared by dissolving 100 mg of acid-leached humic acid in 1000 ml of 1.0×10^{-3} M NaOH. The solution was filtered through a 0.45 micron pore size membrane filter and the heavy metal content analyzed by graphite furnace atomic absorption spectroscopy. The results are given in Table 13. Standard (stock) solutions of copper, lead, manganese and iron were prepared by dissolving copper metal (99.9% pure), $\text{Pb}(\text{NO}_3)_2$ (99.8% pure), iron wire (99.9% pure) and manganese metal (99.9% pure) in nitric acid. The standard (stock) solutions (1000 $\mu\text{g/ml}$) were diluted to prepare a series of standard solutions of lower concentrations immediately before use (to prevent losses through adsorption of the ions onto glass walls, the pH of the solutions was adjusted to 2). Solutions of KNO_3 , NaHCO_3 and CaCO_3 were prepared from reagent grade chemicals. The stock solutions were

Table 13

Concentration of Metals in Stock Solution of Humic Acid

Metal	Concentration (ng/ml)
Copper	3 ± 1
Lead	5 ± 1
Manganese	2 ± 1
Iron	10 ± 1
Cadmium	-
Zinc	5 ± 1

analyzed by flame atomic absorption spectroscopy for heavy metal content (lead, cadmium, iron, copper, zinc, and manganese) and appropriate corrections made for metal concentrations in solutions prepared from them.

The ion exchange resins were Rexyn 101 (a strong acid exchanger with $-SO_3H$ as the active group), Rexyn 102 (a weak acid exchanger with $-N(C_2H_3O_2)_2$ as the active group), and Dowex AG-1 (an anion exchange resin with chloride and sulphate as the exchangeable ions). Rexyn 101 and 102 were treated with dilute nitric acid to remove metallic impurities, then saturated with potassium ions by equilibration with 1M KOH. The anion exchanger was converted into the hydroxide form by equilibration with 1M KOH.

Procedure: The effect of matrix on the peak absorbance was studied using six synthetic matrices--ultrapure water, 1.0×10^{-3} M KNO_3 , 1.0×10^{-3} M $NaHCO_3$, 40 $\mu g/ml$ $CaCO_3$, 10 $\mu g/ml$ humic acid, and 1 $\mu g/ml$ Mn^{+2} at pH 9. Each matrix was spiked to 50 ng/ml of one of copper, lead or iron and the peak absorbance of the sample (5 μl of solution was added to the furnace) was measured using the instrument settings given in Table 14. In all experiments the Deuterium Background Corrector was used to correct for the light scattering and molecular absorption.

Dialysis experiments were performed using 250 ml of test solution and a dialysis bag containing either 10 ml (for the Spectrapor 3 membrane) or 20 ml (for the Spectrapor-1 and 2 membranes) of ultrapure water. Several experiments were designed to

Table 14

Instrument Settings for Graphite Furnace Atomic Absorption Spectroscopy

Element	Drying Temp., C	Ashing Temp., C	Atomization Temp., C	Sensitivity* (1.0×10^{-12} g)
Copper	110	400	2700	24
Iron	110	600	2700	6
Manganese	110	600	2700	2
Lead	110	400	2700	18

* Defined as the weight of element that gives an absorbance of 0.0044

test the conditions necessary for reliable analytical results: these included a study of the amount of sample dialyzed as a function of time; the effect of the charge on the species on the results of dialysis, and the effect of ionic strength of the test solution on the dialysis. Model systems of 5 µg/ml copper with 40 times excess of one of EDTA, ethylenediamine, tartaric acid, humic acid, and tannic acid were equilibrated with ultrapure water, and the copper concentration in the test and dialysis bag solutions was determined at 24-hour intervals by flame atomic absorption spectroscopy.

To compare the different analytical techniques with one another, it was decided to apply these techniques to the study of a model system--copper and lead in humic and tannic acid solutions at different pH values. Solutions of either 10 µg/ml humic acid or 20 µg/ml tannic acid with 50 ng/ml lead or copper ion were adjusted to different pH values between 1 and 9 with nitric acid or sodium hydroxide. The solutions were then equilibrated for 24 hours with ultrapure water in a Spectrapor 3 dialysis bag, and the metal concentrations determined using graphite furnace atomic absorption spectroscopy.

The ultrafiltration procedure was tested to determine whether there was a significant loss of the analyte due to sorption onto the membrane filter. Solutions containing 50 ng/ml of the four metal ions and one of 1.0×10^{-3} M NaHCO_3 or 1.0×10^{-5} M EDTA were analyzed as follows: 200 ml of the test solution was placed in the ultrafiltration cell, and 20 millilitres of filtrate was collected--the test solution and the filtrate were analyzed using graphite furnace atomic

absorption spectroscopy. The distribution as a function of molecular size of 50 ng/ml each of iron, copper and lead and 25 ng/ml of manganese in a solution of 10 µg/ml humic acid was determined by ultrafiltration. The distribution as a function of pH of a 50 ng/ml solution of lead and copper in a 10 µg/ml humic acid matrix was studied by filtering through the PM10 filter. The metal concentration in the filtrate was determined by graphite furnace atomic absorption spectroscopy.

Ion exchange was studied using 150 ml of test solution equilibrated with 0.5 gram of ion exchange resin. Solutions containing 1.0×10^{-5} M copper ion, and 40-fold excess of one of EDTA, ethylenediamine, tartaric acid, humic acid and tannic acid were equilibrated with the resin. The metal concentration in solution as function of time was determined by flame atomic absorption spectroscopy. The distribution of 50 ng/ml copper in the presence of 100-fold excess of complexing agent was determined by graphite furnace atomic absorption spectroscopy.

Results and Discussion

The most widely used mode of measuring atomic absorption signals from a graphite furnace is that of the peak height (46,48,49). L'vov (46) has studied a mathematical model of atom production using two parameters τ_1 , the time necessary for complete atomization, and τ_2 the residence time of the free atoms in the cell (the residence time is defined as the time taken for the peak absorbance

to decay to $1/e$ of its value). A condition for the peak height mode to be valid is that $\tau_1/\tau_2 \ll 1$. If the ratio of τ_1/τ_2 is changed from 0.1 to 0.2, then the peak absorbance is changed by 5%. It is important to determine whether a change in sample matrix changes the ratio τ_1/τ_2 , and hence the peak absorbance. τ_1 is very susceptible to changes in the rate of atomization (48). With an approximately constant value of τ_2 in a series of samples containing a particular analyte, the value of τ_1 determines the τ_1/τ_2 ratio and hence the peak absorbance.

The bulk composition of river and lake waters is reasonably constant (50), and a typical composition is shown in Table 15. If a metal ion is present at a concentration of 20 ng/ml, then after the drying stage, the ratio of the dissolved solid to the copper in the dried sample is:

$$\frac{\text{dissolved solid}}{\text{copper}} = \frac{300 \text{ } \mu\text{g/ml}}{0.020 \text{ } \mu\text{g/ml}} = 15,000 : 1$$

Therefore, at the end of the drying step, one part of copper is present in 15,000 parts of matrix and will probably be encapsulated into the matrix (51,52). In such a case, the volatility of the matrix will affect the volatility of the encapsulated copper (51,52); and the peak absorbance will be depressed or enhanced (compared to the peak absorbance given by the same mass of copper alone) depending on whether the matrix is more or less volatile than copper alone, respectively. This matrix effect is extremely important when

Table 15

Bulk Composition of River Waters (50)

Component	Concentration ($\mu\text{g/ml}$)
Ca^{+2}	40
Mg^{+2}	8
HCO_3^-	100
Organic	10
Dissolved solids	300

one considers that in an analysis, the metal concentration is usually determined from a standard curve prepared with a pure, soluble, inorganic salt of the analyte. Table 16 shows the concentrations found when the model matrices were analyzed for copper. The recoveries for lead, manganese and iron were also very close to 100%; therefore, it can be concluded that the matrix will probably not interfere in the analysis of the four metal ions. This last statement is in agreement with the work of Briese and Giesy, (53), who found that naturally occurring organics in river waters did not interfere in the determination of lead and cadmium. Karyakin et al. (54) also found that the macrocomponents of natural waters do not interfere with the "evaporation" of metals from a graphite electrode. The sensitivity of the graphite furnace technique combined with the relatively interference-free nature of natural waters indicates that the determination of metal ion concentrations is relatively simple and rapid. Therefore, an analytical scheme for speciation using graphite furnace atomic absorption spectroscopy (to determine the concentrations of the separated metal species) is feasible.

Dialysis as a separation technique is based on the relative rates of diffusion of substances through membranes (55). To obtain a separation, therefore, it is necessary that one substance should be able to pass through the membrane while the second substance be unable to pass through the membrane. The cellulose membranes with the under-mentioned molecular weight cutoffs were available:

Spectrapor 1	6000-8000
Spectrapor 2	12000-14000
Spectrapor 3	3500

Table 16

Copper Concentrations in Model Matrices

Matrix	Copper Conc. Taken (ng/ml)	Copper Conc. Found (ng/ml)
Standard	50	50 ± 1
1.0×10^{-3} M NaHCO_3	50	49 ± 2
1.0×10^{-3} M KNO_3	50	50 ± 1
40 $\mu\text{g/ml}$ CaCO_3	50	49 ± 1
10 $\mu\text{g/ml}$ humic acid	50	50 ± 1
1 $\mu\text{g/ml}$ Mn^{+2}	50	50 ± 2
Rideau River water	50	51 ± 3

The above cutoffs are such that a species with a weight much greater than the cutoff will not pass through the membrane; however, the cutoffs are valid only for neutral species. In Figures 10-12 are presented the amount of the different copper-containing species that are dialyzed as a function of time and molecular weight cutoff of the membrane. Examination of the three figures indicates that the negatively charged copper-EDTA complex is dialyzed more slowly than the positively charged Cu(en)_3^{+2} and neutral copper-tartrate complexes. The dialysis membranes used in this study have a net negative charge (55). The separations depend not only on size but on the charge of the species--the effective pore size for a negatively charged species is smaller than the geometric pore size because of repulsion between like charges; hence, a negatively charged species takes longer to diffuse through the membrane. In natural waters many of the species are anions (56), therefore, it is necessary to provide a sufficiently long time for the dialysis experiment to attain equilibrium.

The dialysis experiment involved the separation of the test solution from an ultrapure water sample using a membrane. When the membrane is impermeable to one of a number of ionic species, ionic diffusion through the membrane sets up a difference in ionic distribution on the two sides of the membrane and a potential difference arises. The potential difference is given by (57):

$$2-1 \quad \Delta \psi = \frac{RT}{zF} \ln \frac{a_i^{II}}{a_i^I}$$

where z is the charge of ion i , and a_i^I and a_i^{II} are the activities

Figure 10: Dialysis of copper as a function of species (using a Spectrapor 3 membrane)

Figure 11: Dialysis of CuEDTA^{-2} as a function of membrane pore size

Figure 12: Dialysis of copper as a function of species (using Spectrapor 1 membrane)

○ Copper only ΔCuEDTA^{-2} ● Copper-humic acid □ Copper-tannic acid

of the ion on sides 1 and 2 of the membrane. The condition for equilibrium is (57):

$$2-2 \quad (a_+)_1 (a_-)_1 = (a_+)_2 (a_-)_2$$

where a_+ and a_- are the activities of the cation and anion, respectively, and 1 and 2 represent the two sides of the membrane. One can consider the case of a metallo-organic complex CuR , and an inorganic species CuCO_3 on one side of the membrane, and ultrapure water on the other. If the membrane is impermeable to both CuR and the free anion R^{2-} then the distribution at equilibrium is:

The initial concentration of CuR is C_0 , and if C_0 , C_{Cu} and C_{CO_3} are small, then activity coefficients may be considered roughly equal to one (57). The condition for membrane equilibrium is:

$$2-3 \quad C_{\text{Cu}}^{\text{I}} C_{\text{CO}_3}^{\text{I}} = C_{\text{Cu}}^{\text{II}} C_{\text{CO}_3}^{\text{II}} = (C_{\text{Cu}}^{\text{II}})^2$$

and the condition for electroneutrality is:

$$2-4 \quad C_{\text{CO}_3}^{\text{I}} = C_{\text{Cu}}^{\text{I}} - C_{\text{R}}^{\text{I}}$$

Combining the two equations one obtains:

$$2-5 \quad (C_{\text{Cu}}^{\text{II}})^2 = (C_{\text{Cu}}^{\text{I}})^2 - (C_{\text{Cu}}^{\text{I}})(C_{\text{R}}^{\text{I}})$$

$$2-6 \quad \frac{C_{Cu}^{II}}{C_{Cu}^I} = \sqrt{\frac{C_{Cu}^I - C_R^I}{C_{Cu}^I}} = \lambda$$

where λ is called the Donnan ratio. If the free copper ion and CuR complex are in the equilibrium:

where K , the equilibrium constant, is 1.00×10^{-7} , and the initial CuR concentration is 1.00×10^{-7} M, then the ratio λ can be calculated for different $CuCO_3$ concentrations and are given below:

$CuCO_3$	λ
1.00×10^{-6}	0.99
5.00×10^{-7}	0.98
1.00×10^{-7}	0.84

The values calculated for λ indicate that the Donnan membrane equilibrium causes a difference in metal concentrations on the two sides of the membrane. If, in the dialysis separation, it is assumed that the metal concentration inside the dialysis bag is equal to the free metal ion concentration in the water sample then the analytical results for the water sample would be wrong.

The Donnan effect arises simply because there is a lack of diffusible anions (as in the example cited above)—if an inert electrolyte (such as KNO_3) is added, the effect is nullified because

of the "swamping" out by the nitrate ions (55). The addition of a strong electrolyte, however, may introduce several problems; for example, the equilibrium constant K is dependent on the ionic strength (41) and some species (such as clay colloids) may undergo ion exchange reactions:

The addition of potassium will shift the equilibrium to the right and increase the free metal ion concentration. The effect of potassium ion concentration on the dialysis of copper in the presence of humic acid is shown in Table 17. To nullify the Donnan effect and to minimize the effect of ionic strength changes, all subsequent dialysis experiments were performed after the solution was made $1.0 \times 10^{-2} \text{ M}$ in KNO_3 .

Table 18 presents results of the dialysis of $5 \text{ } \mu\text{g/ml}$ copper in the presence of EDTA, $20 \text{ } \mu\text{g/ml}$ tannic acid and $10 \text{ } \mu\text{g/ml}$ humic acid as a function of dialysis membrane. The results indicate that the copper species in the presence of the two naturally occurring organics is large, i.e., greater than the 14000 molecular weight cutoff. In subsequent experiments the Spectrapor 3 membrane was used to separate the metal-organic species from the free ion. The distribution of copper and lead in the organic acid solutions as a function of pH is given in Figures 13 and 14. In both cases studied, the dialysis as a function of pH curves were sigmoidal in shape. This is expected for a system consisting of a metal ion in equilibrium with a weak acid complexing agent.

Table 17

Dialysis of Copper as a Function of Ionic Strength*

K ⁺ Concentration (M)	Copper Dialyzed (%)
1.0×10^{-1}	11
1.0×10^{-2}	11
1.0×10^{-3}	5
1.0×10^{-4}	4

* The concentrations of humic acid and copper were 10 µg/ml and 5 µg/ml, respectively.

Table 18

Dialysis as a Function of Membrane*

Species	Dialysis (%)		
	Spectrapor 1	Spectrapor 2	Spectrapor 3
Cu EDTA ⁻²	100	100	100
Cu-Humic acid	16	16	16
Cu-Tannic acid	8	8	8

* After equilibration for 80 hours.

Figure 13: Dialysis of copper as a function of pH

A. Humic acid

B. Tannic acid

▲ Copper ion only

Figure 14: Dialysis of lead as a function of pH

The dialysis results for small metal species (such as free copper ion, CuEDTA^{-2} , etc.) and for copper and lead in the presence of humic and tannic acids strongly indicate that dialysis using the Spectrapor 3 membrane separates species into two fractions:

1. One fraction contains free metal ions and small complexes.
2. The other fraction contains large species such as humic acid complexes.

The dialysis technique was applied to the analysis of a natural water sample; the results are presented in Table 19.

Ultrafiltration is a process for separating dissolved or particulate substances from a fluid, using a selectively permeable membrane to retain the desired constituents. The solvent and membrane-permeable substances are driven through the membrane by pressure. The Amicon filters are a thin membrane on a highly porous substructure. Table 20 lists the characteristics of the different Amicon ultrafilters employed in this study. The molecular weight cutoff listed in Table 20 is for protein molecules and serves only as a rough guide--like dialysis, the separation by ultrafiltration depends on the size, shape and charge of the species.

Amicon ultrafilters are thin membranes on a porous backing. An electron micrograph (59) of the filter indicates that the porous backing is a series of long channels that present a large surface area to the solution. A problem that may arise is that the large surface area of the backing may cause sorption of the separated species onto the backing. If sorption of the separated species occurs, then the concentration of metal in the filtrate would be lower than

Table 19

Analysis of a Rideau River Water Sample

Metal	Total Conc. (ng/ml)	Dialyzable metal (%)
Copper	34 ± 2	73
Iron	90 ± 5	61
Lead	60 ± 1	84
Manganese	34 ± 1	61

Table 20

Characteristics of Amicon Ultrafilters (58)

Filter	Pore Diameter (nm)	MW Cutoff	Pressure Employed (atm.)
XM100A	5.2	100,000	2
XM50	3.2	50,000	2
PM30	2.5	30,000	2
PM10	1.8	10,000	2
UM2	1.2	1,000	4

the true species concentration. Table 21 presents results for the ultrafiltration of copper, manganese, iron and lead in the presence of NaHCO_3 and EDTA. The results indicate that sorption with the UM2 filter is extensive but not with the PM10 filter. This sorption may have been onto the porous backing, and since the UM2 filter is negatively charged (25), sorption of the cations onto the surface of the membrane is also possible. Sorption of the analyte species onto the UM2 filter militates against its use for metal speciation; therefore, only filters XM100A to PM10 were used in subsequent experiments.

Solutions of copper, manganese, lead and iron in humic acid were analyzed to determine the distribution of the metals as a function of the size of the species. The results are shown in Table 22. The distribution of copper and lead in humic acid solutions as a function of pH are shown in Figure 15.

The results in Table 22 and Figure 15 indicate that ultrafiltration provides a separation of the metal species into several size fractions with the filtrate of the PM10 filter containing small complexes and free metal ions. The ultrafiltration results for iron and manganese in Rideau River water are shown in Table 23.

The separation of metal species using cation and anion exchange resins was evaluated using 5 $\mu\text{g/ml}$ copper in several solutions containing excess chelating agents. The sorption curves as a function of time are given in Figures 16-18. The sorption curves as a function of time indicate that equilibrium is reached in about 600 seconds; the resins do not sorb all the species present; and the copper-EDTA species is sorbed by the anion resin but not by the cation exchange resin.

Table 21

Results of Analysis of Solutions after Ultrafiltration

Element	Total	Concentration in the Filtrate (NaHCO ₃ , ng/ml)				
		XM100A	XM50	PM30	PM10	UM2
Copper	50	50	50	50	50	19
Lead	50	50	50	50	50	14
Manganese	25	25	25	25	25	0
Iron	50	50	50	50	50	15

Element	Total	Concentration in the Filtrate (EDTA, ng/ml)				
		XM100A	XM50	PM30	PM10	UM2
Copper	50	50	50	50	50	42
Lead	50	50	50	50	50	36
Manganese	25	25	25	25	25	12
Iron	50	50	50	50	50	28

Table 22

Results of Ultrafiltration of Humic Acid Solutions

Metal Retained by Filter (%)

Filter	Iron	Manganese	Copper	Lead
XM 100 A	43	24	32	64
XM 50	88	54	100	100
PM 30	88	70	100	100
PM 10	88	84	100	100
Spectrapor 3	88	84	100	100

Figure 15: Metal distribution in humic acid as a function of pH

Table 23

Results of Ultrafiltration of Rideau River Water Samples

Metal Retained by Filter (%)

Filter	April 25/75		May 1/75	
	Fe	Mn	Fe	Mn
XN100A	41	16	73	25
XM 50	47	16	73	25
PM 30	56	16	73	25
PM 10	61	16	73	30

Figure 16: Sorption of copper onto Rexyn 101

Figure 17: Sorption of CuEDTA^{2-} as a function of time

● Rexyn 101 ▲ Dowex AG-1

Figure 18: Sorption of copper onto Relyn 101 as a function of time

2

OF/DE

3

An assumption implicit in using ion exchange resins for the identification of metal species is that the resin exchanges only species of the correct charge and does not affect the concentration of other species. Unfortunately, in the case of cation exchange resins two equilibria are involved:

1. The ion exchange equilibrium:

2. The metal and metal-organic complex equilibrium:

The distribution coefficient, λ_0 , for the ion exchange in the absence of a complexone is defined as:

$$2-11 \quad \lambda_0 = \frac{\text{amount of metal on resin}}{\text{amount of metal in solution}}$$

and, λ , in the presence of a complexone as:

$$2-12 \quad \lambda = \frac{\text{metal on resin}}{\text{amount of metal in solution}}$$

where the metal in solution is both the free ion, Me^{+2} , and the metal-organic complex, Me-Org .

Schnitzer and Khan (41) have combined the expressions for λ , λ_0 and K to obtain:

$$2-13 \quad \log (\lambda_0 / \lambda - 1) = \log K + \log [\text{Org}]$$

Equation 2-13 is valid under the following conditions:

1. The solution contains only one complex, Me-Org .
2. The complex, Me-Org , is neither adsorbed nor exchanged.

If $\log K$ is 7 and $\log [\text{org}] = 6$, then λ_0/λ is 11. This indicates that a comparison of the distribution coefficient obtained for a pure metal solution and a natural water sample may yield some information about the charge of the species. Table 24 shows the distribution coefficients for several species in the presence of the two resins. Inspection of the data in Table 24 indicates that for metal speciation, separation by ion exchange is not promising; for example, the competition between the two equilibria (cation exchange and complex formation) makes interpretation of the distribution coefficients difficult and the possibility of ligand sorption onto anion exchange resins (with consequent sorption of metal ions onto the resin) make the results too unreliable.

Summary

The speciation scheme outlined in Figure 9 is feasible for both dialysis and ultrafiltration but the use of ion exchange resins was not justified by experiment. The principal problems with the scheme were:

1. The long times necessary for the separations by dialysis to attain equilibrium.
2. The separations by dialysis were complicated by the effect of Donnan membrane equilibrium.
3. The sorption of metal species onto the ultrafiltration membranes may shift the metal distribution to higher size fractions. Atomic absorption spectroscopy in combination with dialysis or ultrafiltration can readily distinguish between small complexes

Table 24

Distribution Coefficients*

Species	Dowex AG-1.	Rexyn 101
Cu^{+2}	0	2.38
Cu(en)_3^{+2}	0	1.65
Cu-tartrate	0	1.56
Cu-EDTA^{-2}	1.17	0.22
Cu-tannic acid	0.78	1.50
Cu-humic acid	0.92	0.72

* distribution coefficient =
$$\frac{\mu\text{g metal on resin}}{\mu\text{g metal in solution}}$$

and large metal-organic species. The separations, however, do not distinguish between free ions and small complexes. In Chapter 3, electrochemical methods for the speciation of metal ions are compared with the atomic absorption methods.

Chapter 3

Electrochemical Techniques of Metal Speciation

The speciation techniques described in the last chapter are based on the separation of the species by size and subsequent measurement of the concentration of species by atomic absorption spectroscopy. The problem with this approach is that the smallest pore size permits free ions and small complexes to pass through the membrane, and therefore, differentiation between aquated metal ions and metal carbonates is not possible. A more direct speciation could be obtained if a technique selective for the free metal ions is used, such as the electrochemical techniques: anodic stripping voltammetry (4, 17,18,22, 29,60) and ion selective electrodes (61,62).

Anodic stripping voltammetry (ASV) is a two-step procedure; a plating step, in which metal ions in solution are reduced and concentrated in a mercury drop or film, and a stripping step, in which the electrode potential is linearly varied and the metals are oxidized and stripped from the amalgam. These two steps provide the means to differentiate between metal species; for example, in the plating step the plating potential can be set such that certain metal ions are not reduced (e. g., in sodium acetate buffer, a plating potential of -0.800 v versus SCE reduces Cu^{+2} , Pb^{+2} , and Cd^{+2} but not Zn^{+2}), and in the stripping step the peak potentials depend on the metal species produced in solution (e. g., Cu^{+2} is stripped at different

potentials in KNO_3 and KNO_3/EDTA solutions). In this study, the ability of ASV to differentiate between metal species is illustrated by cyclic voltammetry. The cyclic voltammogram simulates the ASV experiment because the cathodic and anodic scans of the cyclic voltammogram correspond to the plating and stripping steps in ASV, respectively (63,64).

The terms "labile" and "nonlabile" have been commonly applied to metal species in natural waters when ASV has been used to perform the analysis. The definition of labile used by inorganic chemists is (65):

"the ability of a particular complex ion to engage in reactions which result in replacing one or more ligands in its coordination sphere by others is called its lability. Those complexes for which reactions of this type are very rapid are called labile ... and as a more explicit definition of the terms labile and inert we may adopt an operational definition which says that complexes whose reactions may be studied by static methods are inert and the faster ones labile". Static methods can measure reactions with a half life, $t_{1/2}$, greater than one minute. The use of the term "labile" in natural water analysis will be reconciled with the inorganic chemists' definition by considering the four formal steps in an electrochemical reaction.

Organic constituents in natural waters include humic, fulvic, and amino acids, peptides and similar natural products. Since these can act as surfactants, the possibility of adsorption of the organics onto the mercury drop was investigated. The consequences of adsorption on the use of ASV for metal speciation will be discussed.

Ion selective electrodes (ISE) measure the ion activity in solution. If the activity is equated to the free metal ion concentration, then the ISE can be used to distinguish between free metal ions and complexed species. The applicability of ISE to metal speciation is discussed in terms of sensitivity and the possible interferences that may arise in natural waters.

The final section of this chapter is devoted to a direct comparison of the three speciation techniques--size separation combined with atomic absorption spectroscopy, ASV and ISE. The techniques were applied to the determination of the metal ion distribution as a function of pH in model solutions of humic acids.

EXPERIMENTAL

Apparatus: Anodic stripping voltammograms were obtained by using a Princeton Applied Research Polarographic Analyzer, model 174A, (PAR 174A) equipped with a Metrohm, microfeed hanging mercury drop electrode, model E405. The voltammograms were recorded by using a Honeywell Elektronik 194 strip chart recorder.

The PAR 174A does not contain the electronic circuits necessary for cyclic voltammetry, and therefore, a new circuit was fabricated and installed to automatically initiate the reverse scan (the electronic circuit diagram by P. C. Bertels is available upon request). The modification consists of a relay and a timing circuit. A 10-turn potentiometer is used to set a scan time of 0-20 sec, and after the preset time, the relay initiates the reverse scan.

Current-time curves were obtained using the PAR 174A, equipped with a PAR Mercury Drop Timer, model 172A. The current-time curves and cyclic voltammograms were recorded on a Techtronix Storage Oscilloscope, model 549, and photographed using a Polaroid camera.

Ion selective electrode measurements were obtained using an Orion model 801A digital voltmeter and Orion model 94-29 (copper) and model 94-82 (lead) ion selective electrodes. The reference electrodes were an Orion model 90-01 single junction electrode and an Orion model 90-02-00 double junction electrode.

Reagents: The complexing agents (humic acid, tannic acid, etc.) were the same as those used in Chapter 2. The sodium acetate buffer was purified by electrolyzing it over a pool of mercury at -1.40 v versus SCE for 48 hours. The electrolyte was stored in a clean polyethylene bottle.

Procedure: Cyclic voltammograms were recorded for 4×10^{-5} M solutions of lead and copper in 0.040 M sodium acetate buffer at pH 5.8. The scan rate was 50 mv/sec and the scan interval was 650 mv. Aliquots of 0.100 M EDTA, 1000 $\mu\text{g/ml}$ tannic acid, and 100 $\mu\text{g/ml}$ humic acid were added to determine the effect of complexing agents on the cathodic and anodic peak potentials.

Current-time curves were recorded for solutions of 7.81×10^{-4} M Cu^{+2} , 1.0×10^{-2} M EDTA, and 0.040 M sodium acetate (pH 5.8) at a potential of -0.600 v versus SCE using a natural drop time (as opposed to a forced drop) of 3.8 sec. Aliquots of tannic acid, humic acid, camphor, cysteine, and gelatin were added to study

the effects of surfactants. In addition to CuEDTA^{-2} , the species Cutartrate ($4.81 \times 10^{-4} \text{ M Cu}^{+2}$, and $1.0 \times 10^{-2} \text{ M tartrate}$ at pH 5.8), and Cu(en)_3^{+2} ($4.81 \times 10^{-4} \text{ M Cu}^{+2}$ and $1.0 \times 10^{-2} \text{ M ethylenediammine}$) were also studied in the presence of surfactants.

Differential pulse anodic stripping voltammograms (DPASV) were recorded using 50 ml of 0.040 M sodium acetate buffer. The plating step was carried out at a potential of -0.800 v versus SCE for 60 seconds with stirring, followed by a 30 second settling period, and, in the stripping step, the sweep rate was 5.0 mv/sec with an imposed pulse of 10 mv every 0.5 second. Calibration curves for 0-100 ng/ml lead and copper were recorded and the effect of chelating agents investigated by addition of humic and tannic acid. The distribution of species as a function of pH was determined by adjusting the pH of solutions (containing 50 ng/ml of Cu^{+2} and Pb^{+2} , 0.01 M KNO_3 , $1.0 \times 10^{-3} \text{ M NaHCO}_3$, and 20 $\mu\text{g/ml}$ of tannic or humic acid) from pH 8 to 1 by addition of nitric acid, and then recording the DPASV as noted above.

Studies with ion selective electrodes were performed using solutions containing 0.10 M KNO_3 to set the ionic strength. Aliquots of 0.10 M lead and copper were added to prepare calibration curves. The ability of the ISE to determine metal species in natural waters was investigated using $1.0 \times 10^{-6} \text{ M Cu}^{+2}$ in 0.10 M KNO_3 and measuring the electrode response after the addition of aliquots of complexing agents.

RESULTS AND DISCUSSION

An electrode process consists of a number of consecutive steps (66,67):

1. Transport of the reactant from the bulk of the solution to the reaction zone.
2. A chemical reaction in which an electroactive species is generated.
3. Electron transfer.
4. A chemical change in the electroactive species due to the electron transfer.
5. Transport of the products of electron transfer from the reaction zone.

In the analysis of natural waters, the term "nonlabile" is employed when the metal species shows no stripping current, and so, the term does not necessarily mean that the species is inert but means that one of the five steps in the electrochemical reaction is slow. During the plating step of an anodic stripping voltammetry experiment, the solution is stirred; therefore, the transport of species is controlled mostly by convection. The plating potential is chosen such that the reduction current of the free metal ion is controlled by the transport of the species from the bulk of the solution to the electrode surface. Two possibilities exist for the nonlability of the metal species.

The first possibility is that the reaction preceding the electron transfer step controls the kinetics of reduction. Steps 2

and 3 of the electrode process can be written as:

$$3-3 \quad K = \frac{[\text{Me}^{+2}][\text{R}^{-2}]}{[\text{Me-R}]} = \frac{k_f}{k_b}$$

where Me-R and Me^{+2} are the electroinactive and electroactive species, respectively. If $K \ll 1$, the equilibrium is shifted towards Me-R, and the plating current is small because of the low concentration of Me^{+2} in solution. In this case the current is controlled by the rate of dissociation of the complex. An approximate solution to this problem (68) can be obtained by assuming the existence of a thin reaction layer at the electrode surface. In the reaction layer the electrode process and the associated chemical reaction proceed under steady state conditions. The decrease in concentration of the reacting components within the reaction layer is counterbalanced by transport from the bulk of the solution. If one assumes that the electroactive species (once formed) is reduced rapidly compared to dissociation of the complex and if first order reaction kinetics (for reaction 3-1) is assumed then:

$$3-4 \quad \ln \frac{[\text{Me-R}]_I}{[\text{Me-R}]_I - [\text{Me-R}]_t} = k_f t$$

where $[\text{Me-R}]_I$ is the initial concentration of the complex and $[\text{Me-R}]_t$ is the concentration of the complex at time t . The half-life of

a first-order reaction, $t_{1/2} = \frac{\ln 2}{k_f}$, can be used to estimate

the k_f necessary for a species to be termed nonlabile. Table 25 presents calculated values of $t_{1/2}$ and the amount of complex dissociated after 100 seconds for various k_f values. Table 25 indicates that, if the nonlabile complex is one for which no dissociation of the complex occurs, then a first order rate constant of the order of $1.0 \times 10^{-5} \text{ sec}^{-1}$ would be necessary. In the case of a large k_f , the plating current will be controlled by mass transport. Langford and Gamble(69) have reported a value for k_f of $7.0 \times 10^{-3} \text{ sec}^{-1}$ for an Fe^{+3} - fulvic acid complex. This indicates that the nonlability of the naturally-occurring species may arise from some other factor than simple dissociation of the complex, such as, diffusion of the electroactive species out of small particulates or large molecules (that is, the slow step in the electrochemical reaction is a heterogeneous reaction instead of a homogeneous reaction).

The second possibility is that the reactions subsequent to electron transfer control the plating currents. Steps 3 and 4 can now be written as follows:

Table 25

Effect of k_f on Electrochemical Reaction

k_f (sec^{-1})	$t_{1/2}$ (sec)	Complex Decomposed after 100 sec (%)
10	0.069	100
1	0.69	100
0.5	1.38	100
0.1	6.93	100
1.0×10^{-3}	693	9.5
1.0×10^{-5}	693 000	0

the experiment, no conversion of Me-R to Me^{+2} occurs, and the species is termed nonlabile.

2. The species, Me-R, is reducible and (i) if the species dissociates rapidly then it is termed labile; (ii) if a competing reaction reoxidizes the metal ion, a diminished concentration of the metal in the amalgam would result and the species would be termed "nonlabile".

It should be emphasized that the above classification is purely operational and depends on the time scale of the experiment; after a sufficiently long plating time some of the nonlabile component will be converted into the electroactive form and would be measured as a labile component. The time scale of the experiment becomes especially important in cyclic voltammetry; Nicholson and Shain (64) have treated the system of equations 3-1 and 3-2 for voltammetry at a stationary electrode. Qualitatively, the effect of a preceding chemical reaction depends on several factors, and distinct limiting cases can be recognized. First, if

$\frac{k_f + k_b}{a}$ (where a is proportional to the scan rate) is small, then the experiment is over before Me-R can be converted to Me^{+2} , and the cathodic peak occurs at the normal reduction potential but is reduced in magnitude (and dependent on the equilibrium concentration

of Me^{+2}). If $\frac{k_f + k_b}{a}$ is large, then the peak potential depends on the magnitude of K --the smaller K , the more cathodic the peak potential.

If a labile species is present, then during the stripping step, anodic peaks will be observed. Figure 19 shows the cyclic voltammograms for lead in sodium acetate buffer alone and in the presence of excess EDTA. The voltammogram for $\text{Pb}^{+2}/\text{EDTA}$ shows that the reduction potential is shifted to a more cathodic potential and decreased in magnitude. The anodic scan indicates that the stripping peaks occur at the same potential for both solutions.

Figure 20 shows the cyclic voltammogram for lead in sodium acetate buffer and for lead in the presence of humic acid; in this voltammogram the lead stripping peak in the presence of humic acid is cathodic to the peak in sodium acetate solution. Bradford (70) has interpreted this behaviour by considering the magnitudes of k_b and k_o in equations 3-1 and 3-2. If $k_o > k_b$, then the stripping potential is the same as the potential in the noncomplexing media (cf. Figure 19), whereas if $k_b > k_o$, then the stripping potential is cathodic to the normal stripping potential.

The above considerations indicate that the anodic stripping voltammetry can distinguish between three types of species; nonlabile species, labile species whose stripping potential is the same as the free metal ion potential, and labile species whose stripping potential is cathodic to the free metal ion potential.

In natural waters, the species Me-R and Me^{+2} are in a pH-dependent equilibrium; for example, Figure 21 shows the cyclic voltammogram for lead in Meach Lake water at pH 6.4 and 2.0. At the higher pH, the lead is present in a species that has a stripping

↑ +i

A

↑ +i

B

Figure 19: Cyclic voltammograms for lead in different media

A. 4×10^{-5} M lead in 0.040 M sodium acetate

B. 4×10^{-5} M lead in 4×10^{-5} M EDTA

Both scans were from -0.300 v to -0.950 v versus SCE

Scan rate 50 mv/sec and current scale was $0.1 \mu\text{A/cm}$

Figure 20: Cyclic voltammogram for lead in sodium acetate buffer and in humic acid

A. 4×10^{-5} M lead in 0.040 M sodium acetate

B. 4×10^{-5} M lead in 0.040 M sodium acetate and 50 $\mu\text{g/ml}$ humic acid

Both scans were from -0.300 v to -0.950 v versus SCE

Scan rate 50 mv/sec and current scale was $0.1 \mu\text{A/cm}$

↑
+L

A

↑
+L

B

Figure 21: Cyclic voltammograms for lead in 0.040 M sodium acetate/Meach Lake water

A. pH 6.4

B. pH 2.0

Both scans were from -0.300v to -0.950 v versus SCE

Scan rate 50 mv/sec and current scale 0.1 μ A/cm

potential cathodic to the normal lead potential, whereas at pH 2, the stripping potential is the same as the normal lead potential. It is possible, therefore, to determine the total labile and nonlabile metal concentrations in natural waters by adjusting the pH to a value in which all the metal is present as free metal ion.

Figures 22 and 23 present the DPASV for lead and copper in $\text{KNO}_3/\text{NaHCO}_3$ and $\text{KNO}_3/\text{NaHCO}_3/\text{humic acid}$, respectively. In the sodium bicarbonate media at pH 8.2, no lead stripping peak was observed, and the copper stripping peak was shifted to a more cathodic potential. Zirino and Yamamoto (71) have calculated the distribution of copper and lead in bicarbonate media as a function of pH and found that, in the pH region 7-8, the lead was present as PbCO_3 and the copper was present as Cu(OH)_2 . Ernst et al. (72) employed differential pulse polarography to study the distribution (as a function of pH) of lead and copper in bicarbonate media. They found that Cu^{+2} , CuCO_3 and Cu(OH)_2 are the predominant copper species in solution, whereas, for lead, the predominant species was PbCO_3 . Ernst et al. (72) also noted that the peak current decreased with time and this was attributed to the slow growth of the metal hydroxide and carbonate precipitates. The DPASV for copper and lead in humic acid (Figure 23) shows that both the copper and lead species are behaving as nonlabile species. Figure 24 presents the peak current (at the stripping potential of the ion in noncomplexing media) for lead and copper in bicarbonate and humic acid media at different pH values. The curves strongly indicate that in humic acid media

Figure 22: DPASV for Pb^{+2} and Cu^{+2} in 1.0×10^{-3} M NaHCO_3 and 1.0×10^{-3} M KIO_3

A. pH 8.2 B. pH 3.3

Figure 23: DPASV for Pb^{+2} and Cu^{+2} in 1.0×10^{-3} M KNO_3 , 1.0×10^{-3} M NaHCO_3 , and

50 g/ml humic acid A. pH 8.0 B. pH 2.2

Figure 24: DPASV peak currents as a function of pH

A. Copper

B. Lead

the copper ion is present as a humic acid complex, whereas, for lead, the humic acid and bicarbonate curves overlap and no conclusion could be formed as to which species is present. It is evident that a plot of peak current as a function of pH may serve as a means of characterizing the species present.

Figure 25 presents the DPASV for Rideau River water at pH 8 and 2. At pH 2, a stripping current equivalent to 20 ng/ml Cu^{+2} was observed, whereas, at pH 8, the stripping current was equivalent to less than 1 ng/ml. One problem in determining the concentration of species is that the labile components at the pH of natural water do not necessarily undergo electrode reaction at the same rate; for example, consider a water sample that contains three labile components with different k_f . The plating and stripping currents depend on the magnitudes of the rate constants, and if a calibration curve is used to determine the concentration of species, significant error would result because of the differences in rate constants. This problem cannot be solved by using a standard addition technique because there is no guarantee that the added metal ion would distribute equally between the three components. In DPASV, therefore, the best one can do is compare the stripping currents at the reduction potential of free metal ion at the different pH values, and record a relative concentration of free metal ions (relative to the total concentration determined at low pH).

There are two principal assumptions in the application of ASV to the analysis of natural waters:

1. In the stripping voltammograms each stripping peak corresponds

Figure 25: DPASV of Rideau River water

to a different chemical species in solution;

2. the nonlabile nature of a species is a result of its chemical behaviour alone and that a second species does not induce the effect.

Figure 26 shows the cyclic voltammograms of copper in tannic acid. Curve A is the cyclic voltammogram recorded immediately after the formation of the hanging mercury drop whereas curve B was taken after a 60 sec equilibration period. In curve B, two poorly resolved anodic peaks are present; Wopschall and Shain (73) attribute this behaviour to the sorption of a species onto the electrode. Three cases can be recognized (73) as follows:

1. reactant adsorbed onto the drop:

2. product adsorbed onto the drop:

3. a nonreactive species is adsorbed onto the drop:

In cases 1 and 2, two peaks are observed in the cyclic voltammogram--one corresponding to the reduction (or oxidation) of the adsorbed species and one to the reduction (or oxidation) of the species in solution. It is evident, therefore, that adsorption of species onto the electrode invalidates assumption 1.

↑
+i

A

↑
+i

B

Figure 26: Cyclic voltammograms for copper in a tannic acid solution, Cu^{+2} , 4×10^{-5} M and 20 $\mu\text{g/ml}$ tannic acid in 0.040 M sodium acetate.

A. no equilibration period

B. after a 60 sec equilibration period

Both scans were from ± 0.050 v to -0.600 v versus SCE. The current was $0.04 \mu\text{A/cm}$

Many studies (74-77) have been reported on the effect of adsorption of a second species on electrochemical techniques. Schmid and Reilley (77) have studied the effects of adsorption of surfactants in polarography and noted that the following effects may be observed:

1. shift of half-wave potentials;
2. decrease in limiting currents;
3. splitting of waves;
4. complete elimination of a wave.

Effects 2 and 4 are very similar to the nonlabile behaviour of naturally-occurring species. To investigate the possibility of naturally-occurring organics sorbing onto the drop, the effect of several surfactants on the current (i)-time(t) curves of CuEDTA^{-2} , Cu(en)_3^{+2} and copper tartrate was studied. Figure 27 shows the i-t curves for the EDTA species in the presence of gelatin and tannic acid. Table 26 summarizes the results for the complete set of experiments. Several points can be noted-- natural organics such as humic acid, tannic acid, cysteine and gelatin can make a labile species, such as CuEDTA^{-2} , "nonlabile" through adsorption. The effects are more noticeable for negatively charged species. Schmid and Reilly (77) have interpreted the charge effect by invoking a general mechanism for the reduction of negatively charged species, that is, a negatively charged species must acquire, by a chemical reaction step, a less negative charge before an electron transfer from electrode to species may occur. The adsorbed film on the electrode slows down the chemical reaction step and the greater the surface coverage the greater the decrease in the limiting current.

1. 0.040 M sodium acetate

2. 60 ug/ml tannic acid

0.02% gelatin

Figure 27: i - t curves for CuEDTA^{-2} (7.85×10^{-4} M Cu, 0.010 M EDTA, pH 5.8)

Table 26

Summary of Adsorption Studies

Species	Surfactant	% depression
Cu^{+2} / EDTA	0.02% Camphor	100
	60 $\mu\text{g/ml}$ tannic acid	100
	20 $\mu\text{g/ml}$ tannic acid	53
	0.02% gelatin	100
	1.0×10^{-5} M cysteine	73
	100 $\mu\text{g/ml}$ humic acid	69
Cu(en)_3^{+2}	0.02% gelatin	0
	60 $\mu\text{g/ml}$ tannic acid	20
Cu-tartrate	0.02% gelatin	0
	60 $\mu\text{g/ml}$ tannic acid	0

Many species in natural waters are negatively charged (56), and adsorption may cause serious problems in their analysis. However, it is necessary to examine the evidence for interference due to an adsorption in the analysis of natural water. Figure 28 presents i-t curves at a hanging mercury drop electrode for CuEDTA^{-2} in sodium acetate buffer, and in Rideau River water at the same pH (set with sodium acetate buffer). The current for the Rideau River water is only 75% of the current for the standard solution. This depression can be attributed to either adsorption of a species onto the mercury drop or exchange of copper between the EDTA complex and some species, CuR (which is nonlabile), as follows:

where

$$K = K_1 \cdot K_2$$

$$K_1 = \frac{[\text{EDTA}][\text{Cu}^{+2}]}{[\text{CuEDTA}]} >$$

$$K_2 = \frac{[\text{CuR}]}{[\text{Cu}^{+2}][\text{R}^{-2}]}$$

In this experiment, the relevant values are:

$$\begin{aligned} \text{CuR} &= 2.5 \times 10^{-5} \text{ M} \\ \text{CuEDTA}^{-2} &= 7.5 \times 10^{-5} \text{ M} \\ \text{EDTA} &= 9.25 \times 10^{-4} \text{ M} \\ \text{R}^{-2} &= 1.0 \times 10^{-6} \text{ M (estimated)} \end{aligned}$$

A

B

Figure 28: i - t curves at a hanging mercury drop electrode for a 1.0×10^{-4} M copper and 1.0×10^{-3} M EDTA solution

A. 0.040 M sodium acetate, pH 5.8

B. 0.040 M sodium acetate/Rideau River water, pH 5.8

therefore, $K = 308$ and $K_2 = 1.9 \times 10^{21}$. Ramamoorthy and Kushner (78) have estimated the conditional stability constants for copper complexes in the Rideau River water to be 5000. The above calculation indicates that the decrease in current is probably a result of adsorption of some species onto the mercury drop rather than an ion exchange reaction.

Gadde and Laitinen (79) have studied the effect of corn root exudate on the pulse polarography of lead. A shift of one volt in the half-wave potentials of the polarographic wave of lead was observed. From a comparison of diffusion currents and reactivity with EDTA, Gadde and Laitinen (79) concluded that the wave shift must result from adsorption of organics onto the mercury drop. Brezonik (80) found that gelatin and soluble alkaline phosphatase strongly affected the ASV's of cadmium and copper. Adsorption of organics onto the mercury drop producing nonlabile behaviour negates the second basic assumption in ASV.

The ion selective electrodes employed in this study were mixed $\text{Ag}_2\text{S}/\text{MeS}$ membranes. These electrodes show Nernstian response for the metal ion of interest over a region of metal concentration 10^{-7} M--1.0 M. Table 27 shows some typical electrode responses for 50 ng/ml copper, in 0.10 M KNO_3 , spiked with different complexing agents. It is obvious that the electrode responds to the activity of the copper ion. Figure 29 presents plots of the apparent copper concentration as a function of pH for humic acid and Rideau River solutions. The "apparent" concentration was the concentration taken from a calibration curve prepared in 0.10 M KNO_3 at pH 3.0. It is

Table 27

Copper ISE Response in Different Solutions*

Solution	Electrode Response (mv)
0.10 M KNO_3	90.3
0.10 M KNO_3 /Rideau River	41.5
0.10 M KNO_3 / 10^{-3} M NaHCO_3	0
0.10 M KNO_3 / 10^{-5} EDTA	-43.0
0.10 M KNO_3 /20 $\mu\text{g/ml}$ humic acid	-70.4

* All solutions contain 50 ng/ml copper.

Figure 29: Copper distribution as determined with a copper ISE

A. Humic acid B. Rideau River water

evident from these curves that ion selective electrodes may serve as a suitable monitor for the activity of the metal ion in natural waters.

A direct comparison of the three techniques--ASV, ISE, and size separation/atomic absorption spectroscopy--was accomplished by determining the copper distribution in humic acid as a function of pH. The distribution curves for lead and copper are shown in Figure 30 and good agreement is observed for the three techniques. The agreement between ASV and dialysis/AAS raises the question of whether the nonlabile nature of the species in ASV results from the size of the metal species. A comparison of the distribution by ultrafiltration (Table 22, chapter 2) with the DPASV of the same solution (Figure 23, chapter 3) indicates that copper and lead were present in species > 3.2 nm in size and nonlabile, whereas, at pH 2 the ions were < 1.8 nm in size and labile. The nonlabile behaviour in ASV probably results from a slow chemical step preceding the electron transfer, and the rate constant necessary (10^{-5} sec^{-1}) was much smaller than the rate constants for dissociation of ordinary complexes. If one considers the large species size and the concept of humic acid molecule as a gel-like substance (81), then the diffusion of the ion out of the humic acid may be the "slow reaction". The kinetics of diffusion in gels and small particulates would be the same as the kinetics observed in ion exchange resins (82,83). Helfferich (84) notes that two types of diffusion control are present in resins; particle diffusion control and film diffusion control. For an ion exchanger, the half-life, $t_{1/2}$, is given by:

Figure 30: A comparison of metal distribution in humic acid

$$\text{particle diffusion: } t_{1/2} = \frac{r_0^2}{D} \times 0.030$$

$$\text{film diffusion: } t_{1/2} = 0.23 \cdot \frac{r_0 \delta \bar{C}}{DC}$$

where r_0 is the radius of the particle, D the diffusion coefficient, δ the film thickness, $\bar{C}$ and C are the concentrations of ions in the particulate and solution, respectively. For particle diffusion control, typical half-lives for ion exchange beads of diameter 0.1 cm are of the order of seconds or minutes for a univalent ion and a strong acid ion exchange resin; however, for a divalent ion and a weak acid exchanger, the half-life may be longer by several orders of magnitude. If the exchange is controlled by film diffusion, then the half time is of the order of hours for a layer of thickness (δ) 5×10^{-3} cm and a diffusion coefficient of 10^{-5} cm²/sec. It is evident, therefore, that the kinetics of the diffusion of ions out of particulates may be the controlling step in the electrode reaction.

In Figure 31 is shown the distribution of copper in NaHCO₃ as measured by ASV and by dialysis. The curves show that ASV has one advantage over dialysis in that it can differentiate between free ions and hydroxy and carbonate complexes whereas simple size separations cannot. A comparison of Figures 24b and 14a shows that in the case of lead the dialysis separation permits a differentiation between the lead humic acid species and the lead carbonate species whereas ASV could not. The two figures indicate that the humic acid species

Figure 31: A comparison of copper distribution in NaHCO_3

● DPASV Δ Dialysis/AAS

is controlling the free ion concentration.

SUMMARY

An analysis of the results of chapters 2 and 3 permits several conclusions to be drawn:

1. DPASV is suitable for the speciation of four metal ions--copper, lead, cadmium and zinc-- and the differentiation between species is a result of the kinetics of the different electrode reaction steps. The assumptions of one peak, one species and that the kinetic behaviour arises solely from the species itself are found to be invalid if surfactants are present.
2. Ion selective electrodes measure the equilibrium activity of metal ions. The problems with ion selective electrodes are poor sensitivity (that is, the lower limit of detection is $\sim 10^{-7}$ M, whereas the upper limit of the metal concentrations in unpolluted waters is 10^{-7} M), and the electrodes are subject to interferences from sulphide and iron (sulphide may be present at appreciable concentrations in waters near the sediment-water interface). Adsorption of surfactants onto the membrane (85) may also be a problem in natural waters.
3. UF/AAS separates metal species by size and charge; it is applicable to most metals. The possibility of the species adsorbing onto the membrane or porous backing of the filter seriously limits its usefulness.
4. Dialysis/AAS also separates the species by size and charge

characteristics. The problems with dialysis are the long equilibration times, the possibility that the equilibrium attained is not necessarily representative of the true metal distribution, and adsorption of species onto the dialysis membrane may cause the analytical results to be in error.

5. The speciation techniques do not identify the actual species present (except for the determination of Me^{+2} by ISE) but do provide information on the kinetics of dissociation, species size, and the relative distribution of metal ions as a function of pH.

It is evident from the above that no one technique is perfect and that all results must be treated with caution. A more informative and comprehensive approach is to apply two of the techniques to each sample, and then use the results for an internal check on the validity of conclusions drawn.

The second part of this thesis (chapters 2 and 3) introduced two possible approaches to the study of metal ions in solution; these techniques will now be used to investigate the interactions of metal ions with organic acids and sediment components.

Chapter 4

Interactions of Metal Ions and Organic Acids in Solution

Metal ions in solution may be distributed among various species; for example, aquated ions, inorganic complexes, and complexes of metal ions and organic acids. The problem of analysis of metal ions in natural waters can be attacked from two points of view--the ideal case, where the concentration of every species is determined (including the identification of the species); or the practical case, where the total metal concentration is determined by atomic absorption spectroscopy or neutron activation analysis. The results presented in chapters 2 and 3 indicate that the ideal speciation scheme is not available. The total metal concentrations do not provide the biologically significant fractions of the metal species, which are necessary for the purpose of evaluating the toxicity of natural waters to aquatic biota; for example, Hutchinson and Stokes (86) found no relationship between the total concentrations of copper (as determined by atomic absorption spectroscopy) and the results of algal bioassay. The two extremes of metal analysis are either unavailable or unsatisfactory, and therefore, a compromise scheme of analysis must be found. Since metal species are distributed along a size continuum, differentiation by size, for example, "small" (free ions and inorganic complexes), "medium" (organic complexes), and "large" (organic colloids), in conjunction with the chemical

behaviour of the size groups (such as, changes in the distribution due to variation in the pH and total metal concentrations) may serve as suitable criteria for the characterization of a natural water sample. This compromise scheme of analysis is based on the results shown in chapters 2 and 3, which indicated that the results of separations by dialysis were easier to interpret than those of anodic stripping voltammetry (also, dialysis is applicable to more elements), and the knowledge that the two variables most amenable to change are metal concentrations and pH. To test this hypothesis, separations by dialysis were employed in studies of the interactions of metal ions with the organics, humic acid and tannic acid, as a function of pH, total metal concentration, and competition with the synthetic complexing agent EDTA.

Gamble and Schnitzer (87), and Gamble et al. (88) have reported extensive studies on the interactions of metal ions with humic and fulvic acids. The organic acids, because of their structure and functional groups, are weak acid polyelectrolytes in solution. The following points about the chemistry of the organic acids are important (87):

1. The organic acids have a very irregular polymeric structure, which contain no identifiable monomer units; therefore, one must assume that no two carboxyl groups are inherently chemically identical;
2. The properties of the carboxyl groups will depend on the molecular weight;
3. As neutralization advances to more weakly acidic carboxyl groups, the electrostatic charge accumulating on the polymer molecule

will make the carboxyl groups even more weakly acidic;

4. Salicylic and phthalic acid groups may be undergoing reactions with cations:

A consideration of the above properties indicates that metal-organic acid interactions are a function of both pH and concentrations of metal ions. Two aspects of the metal-organic acid interactions of interest are the competition for binding sites by different metal ions and the competition for metal ions between different complexing agents.

The distribution of metal ions as a function of total metal concentration offers a measure of the complexing capacity of the solution. Several procedures have been proposed to determine the complexing or binding capacity including bioassays (89), anodic stripping voltammetry (90), and ion selective electrodes (78). The relationship between the stability constant of the metal complex and the measured complexing capacity will be discussed.

EXPERIMENTAL

The apparatus and reagents employed were the same as those described in earlier chapters.

Procedure: Complexing or binding capacity was determined using the procedure of Ramamoorthy and Kushner (78). A calibration curve was prepared by adding aliquots of a standard solution containing 1000 $\mu\text{g/ml}$ copper to a 0.010 M KNO_3 solution at pH 3. The chelating capacity of the solution was then determined by titrating the solution with the standard copper solution and determining the concentration of the free copper ion using a copper ion selective electrode. A plot of $\frac{C_A - C_m}{C_A}$ versus C_a (where C_a is the concentration of added copper, and C_m is the measured concentration of copper from the standard curve) shows a definite break at the endpoint corresponding to the binding capacity. The binding capacity of EDTA, tannic acid, humic acid and natural water samples was thus determined.

The distribution of metal ion in solution was studied using separation by dialysis and determining the metal concentrations by flame atomic absorption spectroscopy. Two types of experiments were performed. 1. The competition between complexing agents for metal ions. A dialysis bag, Spectrapor 2, was employed to separate the metal species associated with humic and tannic acids from the simple carbonate and EDTA complexes. The dialysis bag containing 20 ml of ultrapure water was equilibrated with 200 ml of solution containing 0.01 M KNO_3 , 5 $\mu\text{g/ml}$ metal ion, 20 $\mu\text{g/ml}$ organic acid, 1.0×10^{-4} M EDTA, and 1.0×10^{-3} M NaHCO_3 . The systems were equilibrated for 24 hours. The metal concentration inside the dialysis bag was taken as the concentration of metal-EDTA complex. 2. The competition for

complexing sites among the heavy metal ions, Cu^{+2} , Pb^{+2} , Cd^{+2} and Zn^{+2} was studied as follows. Solutions containing 20 $\mu\text{g/ml}$ humic or tannic acid and $1.57 \times 10^{-5} \text{ M}$ each of the metal ions were dialyzed for 24 hours. The concentration of metal ion inside the dialysis bag was taken as the concentration of free metal ions.

Solutions of 20 $\mu\text{g/ml}$ humic and tannic acid were titrated with standard solutions of metal ions, and the titrated solutions were dialyzed for 24 hours. The concentration of metal ion inside the dialysis bag was that of the uncomplexed metal ion (M_f), and the difference between the concentration of the uncomplexed (M_f) and added metal ion (M_a) is the concentration of bound metal ion (M_b). A plot of M_f versus M_a was used to determine the complexing capacity of the solutions based on size separation.

RESULTS AND DISCUSSION

The distribution of a metal ion between different soluble species is governed by a number of equilibria

where M^{n+} is the free metal ion and R^{m-} may be carbonate, sulfide, hydroxide, chloride, humic acid, etc. The determination of a solution's binding capacity by titration with heavy metal ions will depend on the magnitude of K and the sensitivity of the detection technique chosen for the determination of the free metal ion concentration. The ion selective electrode is responsive only to the activity of metal ion, and therefore, a theoretical titration curve may be obtained

(by calculating the concentration of free metal ion for different K and concentration of M^{n+} and R^{m-} . Figures 32 and 33 show the theoretical titration curve for a species MR with a stability constant of 10^7 , and the experimental titration curve for a humic acid solution, respectively. The titration error for $K = 10^7$ is 32%, for $K = 10^3$ is 10%, for $K = 10^9$ is 2%, and for $K = 10^{10}$ is 0%.

In natural waters, metal species have stability constants of the order of 10^8 ; therefore, considerable errors can occur if one assumes that the measured complexing capacity is the total ligand concentration. Table 28 presents the measured binding capacity for several model ligands and natural waters. For weak metal-organic complexes in natural waters, the binding capacity as determined by the above titration will be low, and perhaps a better characterization of the water sample would be the plots of the concentration of free metal ion as a function of the total metal concentration as shown in Figures 34 and 35. There are two reasons for this suggestion--first, the toxic metal species in natural waters is generally thought to be the free metal ion (62), and secondly, such a plot would be useful in evaluating the effect of a sudden addition of metal ions to a watercourse from a foreign source.

The competition between metal ions for the binding sites is based on the relative stability constants of the metal-organic acid complex. Figures 13 and 14 in chapter 2 showed the distribution of metal as a function of pH for lead and copper in the presence of tannic and humic acids. Similar studies were performed for the metal ions, Cd^{+2} and Zn^{+2} , and the results are shown in Table 29. From

THEORETICAL TITRATION CURVE FOR DETERMINATION
OF CHELATING CAPACITY ($K = 10^7$)

Figure 32: Theoretical curve for complexing capacity
 $K_{MR} = 10^7$, $[\text{Organic ligand}] = 1.0 \times 10^{-6} \text{ M}$

Figure 33: Experimental curve for complexing capacity of a 10 $\mu\text{g/ml}$ humic acid solution

Table 28

Binding Capacity of Model Solutions

Solution	Binding Capacity (μM)
20 $\mu\text{g/ml}$ humic acid	50.4 $\pm$ 0.5
3.0 $\times 10^{-5}$ M EDTA	30.0 $\pm$ 0.1
10 $\mu\text{g/ml}$ tannic acid	22.0 $\pm$ 0.5
Rideau River water	49 $\pm$ 2
Meach Lake water	29 $\pm$ 1
Pinks Lake water	23 $\pm$ 1

Figure 34: Free copper ion concentration as a function of total copper concentration for a 20 $\mu\text{g/ml}$ solution of humic acid

Figure 35: Free copper ion concentration as a function of total concentration for Rideau River water

Table 29

pH Characteristics of Metal-Organic Species

Metal Ion	Organic [*]	100% dialysis pH	50% dialysis pH
Copper	TA	5.0	6.0
Copper	HA	3.1	4.6
Lead	TA	5.0	6.0
Lead	HA	2.9	4.4
Cadmium	TA	4.9	6.2
Cadmium	HA	3.4	4.8
Zinc	TA	5.4	5.6
Zinc	HA	4.0	5.5
Manganese	TA	5.4	6.0
Manganese	HA	3.5	6.0

* HA = humic acid TA = tannic acid

Table 29 it can be seen that the humic acid can bind the metal ions at a lower pH than tannic acid. The main reason for this difference is the pK_a values of the two acids; humic acids have a $pK_a < 4$, whereas tannic acid has a reported value of $pK_a \sim 6$ (28). The pH value at which the 50% of the metal ion is complexed depends on the stability constant of the complex; the lower the pH the stronger the complex. Table 29 shows that the stability constants decrease in the order:

The competition for binding sites as a function of pH is shown in Figure 36. In the pH range 6--7, 100% of the copper and lead is complexed (within the experimental uncertainty), and at pH 5 the concentration of free metal ions increases in the order:

$Pb^{+2} < Cu^{+2} < Cd^{+2} < Zn^{+2}$. The dialysis curves in Figure 36 show pronounced minima in the concentration of dialyzable metal between pH 6 and 7, whereas, in Figures 13 and 14 (in chapter 2) no minima were observed. The results in Table 30 show the total metal complexed as a function of pH and indicate that the competition for complexing sites is not responsible for the minima; that is, more sites are used at pH 6 or 6.9 than at pH 7.6; therefore, the sites are available. The reason for the difference between Figures 13, 14, and 36 is that in Figure 36, $NaHCO_3$ was also present; hence, three competing equilibria are present:

Figure 36: Distribution of metal as a function of pH in a humic acid solution

A. Experimental

B. Theoretical

Table 30

Total Metal Complexed by Humic Acid

pH	Metal in Complex (μM)
2.78	0
3.98	10.5 ± 0.1
4.90	24.5 ± 0.1
6.00	40.8 ± 0.1
6.90	45.1 ± 0.1
7.60	31.0 ± 0.1

NOTE. Total concentration of the four metals was 6.28×10^{-5} M.

Comparison of equations 4-4 and 4-5 indicates that Cu^{+2} and CuCO_3 predominate at $\text{pH} < 6$, and $6 < \text{pH} < 9.3$, respectively; therefore, only the competition between the carbonate and the organic ligand need be considered. In the pH range 6--9, the equilibrium is represented by:

from which equation 4-8 may be derived:

$$4-8 \quad \log \frac{[\text{Cu-Org}]}{[\text{Cu CO}_3]} = \log K_4 - \log [\text{CO}_3^{-2}] + \log [\text{Org}^{-2}]$$

Equation 4-8 was evaluated using the constants given in Table 31; the theoretical curve (dialysis--pH) is shown in Figure 36B. Figure 36B indicates that the competition between carbonate and humic acid will indeed increase the concentration of dialyzable metal at a $\text{pH} > 6.5$.

Competition for metal ions between organic ligands and inorganic anions is not uncommon. Langford and Khan (91) noted in the complexation of Fe^{+3} by fulvic acid, that as the pH increased the conditional formation constant tended to decrease because of the hydrolysis of the ferric ion. Gardner (92) has calculated the competition of amino acids and free hydroxycarboxylic acids (such as, glycollic acid, malic acid, and citric acid) with sulphide and

Table 31

Stability Constants for the Theoretical Curve (Figure 36B)

$$10. \alpha_2 = \left(\frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1 \right)^{-1}$$

(cont'd)

Table 31 (cont'd)

Stability Constants for the Theoretical Curve (Figure 36B)

$$11. \quad \alpha_2' = \left(\frac{[H^+]^2}{K_1' K_2'} + \frac{[H^+]}{K_2'} + 1 \right)^{-1}$$

$$12. \quad \log \frac{\text{CuOrg}}{\text{CuCO}_3} = \log K_4 - \log C_T' + \log C_T - \log \alpha_2' + \log \alpha_2$$

polysulphide ligands for metal ions and concluded that the free hydroxy acids would not account for the metal solubility in sulphidic waters, that is, the organics could not compete with the sulphur ligands.

Humic acid can complex metal ions using salicylic and phthalic acid groupings, and it was of interest to determine if the organics could compete with EDTA for the metal ions. Table 32 presents the results of dialysis of copper in different solutions of EDTA, humic acid, and tannic acid. The results indicate that the natural organics cannot compete with EDTA. The stability constants of the metal-humic acid and metal-tannic acid complexes are much less than those of the respective metal-EDTA complexes; it would be of interest to determine the stability constants of metal humates.

To calculate the stability constant of a metal complex, the equilibrium concentrations of the free metal ion, complexed ion, and free ligand are required. Figure 37 presents a plot of the concentration of dialyzable copper versus the concentration of total copper for a 20 µg/ml solution of humic acid at pH 6.9 (adjusted with KOH). If one assumes that the only species that is dialyzable is uncomplexed copper (both Cu^{+2} and CuOH^+), then a titration of the complexing agent would provide the concentration of both bound and unbound copper; the stability constant could then be readily evaluated. Mantoura and Reilley (93) have used a gel filtration procedure to determine the stability constants of natural organic--metal ion complexes. They employed the equation:

$$4-9 \quad \bar{v} / M_f = K_f (n_f - \bar{v}) \quad \text{where } \bar{v} = \frac{\text{bound metal}}{\text{humic acid}}$$

Table 32

Competition of Ligand for Copper Ions

Solution	Dialysis (%)
1.0×10^{-4} M EDTA	100
20 $\mu\text{g/ml}$ HA	0
1.0×10^{-4} M EDTA/20 $\mu\text{g/ml}$ HA	100
10 $\mu\text{g/ml}$ TA	0
1.0×10^{-4} M EDTA/10 $\mu\text{g/ml}$ TA	100

Figure 37: Concentration of dialyzable copper as a function of the total copper concentration (for a 20 $\mu\text{g/ml}$ humic acid solution)

K_i is the stability constant of the complex i , and n_i is the number of binding sites per molecule of the acid with stability constant K_i , M_f is the concentration of free metal ion. Figure 38 presents a plot of $\bar{v} / M_f$ v. $\bar{v}$ for the titration given in Figure 37. The Scatchard plot (94) indicates that two types of binding sites are present. The stability constants* for the heavy metal complexes with humic and tannic acids found are given in Table 33. The stability constants obtained were evaluated for the concentration of humic acid in units of weight per unit volume because of its uncertain composition (an estimate of the molecular weight from dialysis membrane cutoff values or ultrafiltration separations would not be valid because the separations are based on size, shape and charge characteristics and not on molecular weight). The stability constants obtained are conditional constants for the pH and ionic strength employed. Inspection of Table 33 does indicate that the order of stability is: $Pb^{+2} > Cu^{+2} > Cd^{+2} > Zn^{+2}$, which is in agreement with the results of the pH and competition studies. A comparison of the stability constants obtained in this work with other published values is given in Table 34.

The interaction of metal ions with humic acid in solution is at specific binding sites. The Scatchard plot (e.g., Figure 38 and Table 33) indicate that two types of sites are present on the molecule - 2 μ moles/g of sites that strongly bind copper and lead, and 6 μ moles/g of sites that weakly bind the metal ions. Table 12 indicates that the humic acid employed has 2.38 μ moles/g of phenolic

* See I. M. Klotz and D. L. Hunston, *Biochemistry*, 10, 3065 (1971) for the methods employed to determine the constants from Scatchard's plot

Figure 38: Scatchard plot for copper-humic acid

Table 33

Stability Constants For Metal-Organic Complexes

Metal Ion	Ligand	K_i	n_i
Copper	HA	1.6×10^6	2 mmoles/g
		1.2×10^5	5.5 mmoles/g
Cadmium	HA	1.1×10^5	3.0 mmoles/g
Zinc	HA	1.0×10^5	4 mmoles/g
Lead	HA	3.4×10^6	2 mmoles/g
		2.0×10^5	6 mmoles/g
Copper	TA	2.2×10^5	11 mmoles/g
Lead	TA	2.4×10^5	11 mmoles/g
Zinc	TA	1.8×10^4	11 mmoles/g
Cadmium	TA	1.8×10^4	11 mmoles/g

Table 34

Stability Constants of Metal-Organic Acid Complexes

Metal Ion	Organic Acid	log K	Conditions		Method	Reference
			pH	μ^*		
Copper	Humic Acid	6.2 5.1	6.9	0.02	dialysis	this work
	Fulvic acid	8.8	8.6	0.02	gel filtration	(93)
		8.05	8.6	0.02	- "	(93)
	Fulvic acid	4.35	5	0.1	ISE	(95)
	Humic acid	16.8	6.8	0.2	DPP	(72)
	Natural water	3.69	-	-	ISE	(78)
Lead	Humic acid	6.5 5.3	6.9	0.02	dialysis	this work
	Humic acid	14.8	6.8	0.2	DPP	(72)
	Natural water	3.94	-	-	ISE	(78)
Cadmium	Humic acid	5.0	6.9	0.02	dialysis	this work
	Fulvic acid	3.64	5.95	0.1	ISE	(95)
	Natural water	3.67	-	-	ISE	(78)
Zinc	Humic acid	5.0	6.9	0.02	dialysis	this work
	Fulvic acid	5.14	8.6	0.02	gel diltration	(93)

* μ = ionic strength

OH and 3.48 mmole/g of carboxyl groups. If it is assumed that each OH group is adjacent to a carboxyl group, then there are at most 2.38 mmole/g of salicylic acid sites which can bind 2.38 mmole/g of metal ion. It is possible, therefore, that the stronger site corresponds to the salicylic acid sites. It is difficult, however, to explain the 6 mmole/g of weaker sites. At pH 6.8 both lead and copper are present as $PbOH^+$ and $CuOH^+$ species (72), and it is possible that at the higher metal ion concentrations the species are bound as follows:

or, that the hydrolysed metal ions are caught up in the humic acid gel (similar to ion exchange resins). One other possibility is that the method employed for the determination of carboxyl and phenolic groups is in error. For the determination to be accurate, the Ca^{+2} ions or Ba^{+2} ions must be able to penetrate the humic acid particulate in order to saturate all the binding sites; if this does not occur then the determination of acidic sites will yield low results. However, no conclusion on these two possibilities can be drawn.

The two curves shown in Figures 37 and 38 indicate that at higher metal concentrations the weaker complexes of metal-organic acid are formed. Table 35 presents the results of ultrafiltration for humic acid solutions with different copper concentrations.

Table 35 indicates that as the total copper concentration increases,

Table 35

Ultrafiltration of Copper in Humic Acid^{*}

Size	Copper in Fraction (%)				
	0.05 $\mu\text{g/ml}$ [@]	0.5 $\mu\text{g/ml}$ [@]	3 $\mu\text{g/ml}$ ^{***}	5 $\mu\text{g/ml}$ ^{**}	10 $\mu\text{g/ml}$ ^{**}
>5.1 nm	32	74	84	67	56
>3.1 nm	68	11	9	4	5
>2.4 nm	-	-	-	-	-
>1.9 nm	-	-	-	-	-
<1.9 nm	-	10	7	-24	40

* Humic acid concentration 20 $\mu\text{g/ml}$, with 0.01 M KNO_3 , and pH 6.8

@ This work

** reference 96

a greater proportion of the metal is concentrated in the large size fractions (until the species is saturated and the metal is then found in the small or free ion fraction). If one interprets the results of ultrafiltration as indicating that the complexing capacity is concentrated in the large molecules, then one is forced to conclude that the weaker complexes are present in the larger size fractions (cf. Table 33 - the majority of the humic acid binding sites have weaker stability constant). The other possibility is that at larger copper concentrations, the copper may be coagulating the organic acids into larger units (this is particularly evident for tannic acid, where at higher concentrations of copper and lead the tannic acid complexes start to precipitate). Rashid (8) has reported that the sedimentary humic acids have most of their binding capacity in the lower size fractions, and Smith (97) has found that the complexing capacity of dissolved organic matter in seawater is mainly in the smaller size fractions. Smith has also noted that fresh water samples have a more even distribution of complexing capacity over the entire size range.

SUMMARY

The studies of the metal-organic acid interactions show that the humic and tannic acids are able to lower the concentrations of free metal ions; for example, a 10 $\mu\text{g/ml}$ humic acid solution has 2×10^{-5} moles of binding sites with a K_{CuL} of 1.6×10^6 in one litre of solution. A 50 ng/ml solution of copper would have only 3% of the copper ions as small species, and these would probably be complexed

by carbonate (or the weaker binding sites). This decrease in the concentration of free metal ion will have a profound effect on the distribution of metal ions between the solid and the solution. This effect will be examined in Chapter 6, but first, interactions between metal ions and solid adsorbents in the absence of complexing agents will be discussed.

Chapter 5

Interactions of Metal Ions and Particulates

In natural waters, metal ions interact with complexing species such as OH^- , CO_3^{2-} , and organic acids to yield free ions, inorganic complexes, and metal-organic complexes. The studies reported in Chapter 4 involved the interactions between the free metal ions and complexed species; however, in the aquatic environment interactions between soluble and particulate species at the water-sediment interface are possible. The sediment components--clay, hydrous oxides and organic acids--may sorb metal ions by ion exchange and specific sorption. The question that immediately arises is how does the distribution of metal ion in the solution and in the solid depend on the soluble metal species and the different solid combinations that are possible? The answer to this question was sought by separately studying the free metal ion-solid interactions and then evaluating the effect of the addition of organic complexing agents to the solution.

In the simple metal ion-solid interactions, three factors were studied; first, the distribution as a function of the concentration of metal ion, secondly, the distribution as a function of pH of the solution, and thirdly, a comparison of the ability of the different solids to sorb metal ions. At this stage, it is necessary to emphasize that in these studies simple model compounds were employed; in the real environment, the hydrous oxides may not

be the same as the synthetic ones employed in this study, and the different oxide and organic substances in the environment do not occur as bulk solids but as coatings on clay minerals; therefore, the ratio of the surface area to weight is much greater in the real environment.

EXPERIMENTAL

The solids employed have been described in Chapter 1. The studies can be divided into three groups--kinetic studies, studies on sorption as a function of the concentration of metal ions, and the sorption as a function of the pH of the solution. In the kinetic experiments, known weights of the solids were added to 500 ml of 10 $\mu\text{g/ml}$ Cu^{+2} solution (pH 5.0) and the concentration of copper ion in solution was monitored for 24 hours by flame atomic absorption spectroscopy. The kinetic experiments indicated that the soluble metal concentration reached a constant value after 90 minutes, and it was then decided an equilibration period of 24 hours would be sufficient for the sorption experiments.

The sorption of copper, cadmium, lead and zinc ions onto the model solids was studied by adding known weights of solid to metal ion solutions having initial metal concentrations of 0-25 $\mu\text{g/ml}$ (buffered to pH 5.0 with 2.0×10^{-3} M potassium acetate). After 24 hours, the suspensions were filtered through a 0.45 micron pore size membrane filter (Millipore), and the concentration of soluble metal was determined by flame atomic absorption spectroscopy. The weight of

metal sorbed onto the particulate equalled the difference between the initial and final metal concentrations. It should be noted that parallel (to the sorption runs) experiments using only standard metal and buffer solutions were also done to correct for the sorption onto the glass surfaces.

The effect of pH and ionic strength on the sorption of metal ion onto the different solids was investigated by adding known amounts of model solid to solution of metal ion (6.29×10^{-5} M metal ion and 2.0×10^{-3} M in potassium acetate) and adjusting the pH with dilute nitric acid or adjusting the ionic strength with KNO_3 . The suspensions were analyzed in the same way as in the previous sorption studies.

The relative capacity of the solids to sorb metal ions under identical conditions was studied by equilibrating 100 ml of solution containing 6.29×10^{-5} M metal ion with known weights of solid and measuring the amount of metal ion sorbed after 24 hours.

RESULTS AND DISCUSSION

The first problem was to identify the metal ion species present in a potassium acetate-acetic acid buffer as a function of pH. Two sets of equilibria are of interest:

The distribution of metal ions between free ions, acetate complexes, and hydroxo complexes was calculated using the equilibrium constants in Table 36, and the results are shown in Figures 39 and 39a. The diagrams of species distribution indicate that in no case is the acetate complex greater than 10% of the total concentration, and therefore, the acetate buffer would not be expected to interfere sensibly in the adsorption experiments. To study solutions at pH greater than 5.5 would require a different buffer and no "good" buffer for pH 5.5 or greater exists; for example, citric acid and tris(hydroxymethyl)aminomethane (THAM) buffers would complex the metal ions, and a $\text{CO}_2\text{-NaHCO}_3\text{-Na}_2\text{CO}_3$ buffer would tend to precipitate the metal as carbonates (the solubility of copper at pH 7 in sodium bicarbonate is approximately 6 ng/ml); therefore, sorption studies were performed in the pH range less than 5.5.

The second condition necessary to perform the adsorption studies was the time necessary to attain equilibrium. The three solids (humic acid, clay, and MnO_2) were equilibrated with copper ion, and the concentration of soluble ion as a function of time is presented in Figure 40. It is evident from Figure 40 that a 24-hour equilibration period would be adequate.

The interaction of metal ions with the solid surfaces will be either by physical adsorption or by chemisorption. The surfaces of many substances are inert in the sense that the valency requirement of their atoms is satisfied by bonding with adjacent atoms. With this type of surface, adsorption tends to take place simply through forces of physical attraction (98), such as van der Waals forces,

Table 36~

Equilibrium Constants for the Formation of Metal Complexes

Reaction	Log K
1. $\text{HOAc} \rightleftharpoons \text{OAc}^- + \text{H}^+$	-4.75
2. $\text{Cd}^{+2} + \text{OAc}^- \rightleftharpoons \text{CdOAc}^+$	1.77
3. $\text{CdOAc}^+ + \text{OAc}^- \rightleftharpoons \text{CdOAc}_2$	1.0
4. $\text{Cu}^{+2} + \text{OAc}^- \rightleftharpoons \text{CuOAc}^+$	2.34
5. $\text{CuOAc}^+ + \text{OAc}^- \rightleftharpoons \text{CuOAc}_2$	0.90
6. $\text{Pb}^{+2} + \text{OAc}^- \rightleftharpoons \text{PbOAc}^+$	2.04
7. $\text{PbOAc}^+ + \text{OAc}^- \rightleftharpoons \text{PbOAc}_2$	0.24
8. $\text{Zn}^{+2} + \text{OAc}^- \rightleftharpoons \text{ZnOAc}^+$	1.70
9. $\text{Cd}^{+2} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$	-9.0
10. $\text{Cu}^{+2} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-7.0
11. $\text{Pb}^{+2} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+ + \text{H}^+$	-7.80
12. $\text{Zn}^{+2} + \text{H}_2\text{O} \rightleftharpoons \text{ZnOH}^+ + \text{H}^+$	-9.3

Figure 39: Distribution of lead and copper in an acetate buffer

Figure 39a: Distribution of zinc and cadmium in an acetate buffer

A. Cadmium B. Zinc ● Me^{+2} ■ MeOH^+ ▲ MeAc^+

Figure 40: Sorption of copper onto solids as a function of time

and is called physical adsorption. Many surfaces are, however, unsaturated, and in adsorption such a surface will tend to form chemical bonds with a nearby phase, and this process is called chemisorption (98). The difference between chemical and physical adsorption is that electron transfer takes place between adsorbent and adsorbate in chemisorption, but does not take place in physical adsorption. The clays, humic acids, and hydrous oxides are solid acids (99) and will tend to interact with metal ions in solution by chemisorption. Two adsorption isotherms are common in chemisorption experiments (100):

1. If the heat of adsorption is assumed to be constant (independent of coverage) then a Langmuir isotherm, as expressed by equation 5-3 is observed:

$$5-3 \quad X = \frac{X_m C}{1 + bC}$$

where X is the amount of metal sorbed per unit weight of solid, X_m is the limiting value for adsorption, C is the equilibrium concentration of metal ion in solution, and b is a constant.

2. If the heat of adsorption varies with the coverage, then the isotherm depends on the relationship between ΔH_j (the heat of adsorption) and coverage. For example, if the relation between the heat of adsorption and the site is:

$$5-4 \quad n_j = n_0 e^{-\Delta H_j / \Delta H_m}$$

where n_j is the number of adsorption sites, ΔH_j is the heat of adsorption for site j , n_0 and ΔH_m are constants then the Freundlich isotherm, as expressed by equation 5-5, is observed:

$$5-5 \quad X = kC^{1/n}$$

where X is the amount adsorbed per unit weight of solid, C is the equilibrium concentration of metal ion in solution, k and n are constants with $n > 1$. The sorption isotherms for metal ions onto the different solids were evaluated using equations 5-3, 5-5.

Metal Interactions with Clay Minerals

The general structure of the bentonite employed in these studies was described in Chapter 1. Electrokinetic studies (101) of clay sols indicate that, at all pH values above two or three, the clay particles have a net negative charge which attracts a layer of positive counter ions.

The counter ions, such as Ca^{+2} and K^+ , on the clay can exchange with heavy metals in solution:

The ion exchange reaction can be characterized by a thermodynamic equilibrium constant (84):

$$5-7 \quad K_{eq} = \frac{\left[\frac{(C_{K^+})^2}{C_{\text{Cu}^{+2}}} \right]_{\text{aq}}}{\left[\frac{(C_{K^+})^2}{C_{\text{Cu}^{+2}}} \right]_{\text{CLAY}}}$$

where C_K^+ and C_{Cu+2} stand for the activities of the respective metal ions in the solution and on the clay, as indicated by the subscripts aq. and clay, respectively. A more readily determined constant (84) is the separation factor:

$$5-8 \quad \alpha_B^A = \frac{\bar{x}_a \bar{x}_b}{x_a \bar{x}_b}$$

where, for example $\bar{x}_a = \frac{z_a \bar{m}_a}{z_a \bar{m}_a + z_b \bar{m}_b}$, z_a, z_b are the

ionic charges and $\bar{m}_a, \bar{m}_b$ are the molalities of the ions on the clay. The separation factor is a measure of the preference of the ion exchanger for one of the two counter ions. The separation factor is usually not constant but depends on the total ion concentration of the solution, the temperature, and the equivalent fraction, x_a . The distribution coefficient (84) is given by:

$$5-9 \quad \lambda_i = \frac{\bar{m}_i}{m_i} = \frac{\bar{x}_i \bar{m}}{x_i m}$$

where $\bar{m}, m$ are the total equivalent molalities on the clay and in solution, respectively. The use of the distribution coefficient is particularly advantageous if the species is only a trace component (that is, $m_a \ll m$ and $\bar{m}_a \ll \bar{m}$), and in such cases the sorption curve is close to the origin and is a straight line. The exchange isotherm for cadmium onto potassium bentonite is presented in Figure 41.

Figure 41: Isotherm for exchange of cadmium onto potassium bentonite in the presence of 2.0×10^{-3} M potassium acetate

For $X_{\text{cd}} < 0.03$, a nearly straight line is obtained with a slope of 5.5; that is, the cadmium is concentrated in the clay fraction. Table 37 presents the values for λ and α for the four metal ions studied. It is evident from Table 37 that the order of sorption is:

and the metal ions prefer the clay fraction over the aqueous phase.

The ion exchange isotherm in Figure 41 has been replotted in Figure 42 using the expression:

$$\log X = \log k + 1/n \log C$$

(that is, the logarithmic form of the Freundlich equation), where the units of X are mmole metal/gram clay and of C are mmoles metal/gram water. Table 38 presents values of n and k for the four ions studied.

The number of sorption sites is related to the energy of sorption by equation 5-4, and ΔH_s can be expected to be proportional to the charge of the ion, the surface charge of the clay, and the radius of the metal ion. The radii of the aquated ions are (102):
 Cu^{+2} 0.419 nm; Pb^{+2} 0.401 nm; Cd^{+2} 0.426 nm; Zn^{+2} 0.430 nm;
 and K^{+} 0.331 nm. The charge to radius ratio of the metal ions decreases in the order:

which is the same order as that of preference of the clay for the metal ions.

Table 37

Coefficients for Ion Exchange*

Metal Ion	λ_{He}	$\alpha_{\text{K}}^{\text{He}}$
Cu^{+2}	7.5	8.0
Pb^{+2}	8.1	8.5
Cd^{+2}	6.0	6.3
Zn^{+2}	6.0	6.3

* λ_{He} and $\alpha_{\text{K}}^{\text{He}}$ were determined at $x_{\text{He}} = 0.01$

Table 38

Constants for Freundlich Isotherm

Metal Ion	k	n
Cu^{+2}	136	1.35
Pb^{+2}	148	1.25
Cd^{+2}	63	1.43
Zn^{+2}	21	1.72

Figure 42: Freundlich plots for cadmium and copper onto potassium bentonite

The ion exchange will depend on the ionic strength because the cations in the solution will compete with the heavy metals for exchange sites on the clay. The amount of copper ion sorbed onto the clay as a function of potassium concentration is given in Figure 43. The effect of decreasing the pH will be similar to the effect of increasing the ionic strength--at low pH the protons compete with metal ions for exchange sites. The concentration of metal ion in solution as a function of pH is presented in Figure 44. The pH at which 50% of the metal ion is in solution increases in the same order as for the clay's preference for ions given earlier.

Metal-ion-Humic Acid Interactions

The sorption of metal ions onto solid humic acids involves the same mechanism as the formation of soluble metal-humic acid complexes, that is, the formation of salicylic acid complexes at the particulate's surface. Two conclusions can be drawn from this mechanism; first, the amount of metal sorbed will be proportional to the active complexing sites on the surface of the particulate, and secondly, the maximum amount of metal sorbed per unit weight of humic acid will be less for the solid than for the number of binding sites found in solution.

The "surface" of a humic acid particulate is not as clearly defined as the surface of clay minerals or hydrous oxides. Earlier, humic acids were compared with gel-like substances similar to the beads of an ion exchange resin. One can then consider the surface

Figure 43: Sorption of copper onto potassium bentonite as a function of potassium ion concentration

Figure 44: Sorption of metal ion onto clay as a function of pH.

A lead B copper C cadmium D zinc

of the humic acid particulate to consist of the region where the humic acid molecules are swollen by water molecules (that is, if one travels from solution into the particulate one would first meet bulk water, then a humic acid gel consisting of humic acid and water molecules, and finally, bulk humic acid not swelled by water molecules). It is evident, therefore, that if in solution all the humic acid molecules are swollen by water, and if in the particulate only a small fraction of the molecules are swollen by water, then fewer complexing sites (per unit weight) are available in the particulate.

The isotherms for the sorption of copper, lead, cadmium and zinc onto humic acid obeyed the Langmuir equation. The isotherms for copper and lead are presented in Figure 45, and the X_m value for copper and lead was 0.42 mmoles metal/gram acid, whereas, the X_m value for cadmium and zinc was 0.21 mmoles/gram. The metal ions are adsorbed in the order of their stability constant for formation of metal-humate complexes, that is, lead $\sim$ copper $\geq$ cadmium $\sim$ zinc. The number of binding sites available on the solid surface (0.42 mmoles for copper) and the number of sites in solution (7.5 mmoles for copper) indicates approximately 6% of the binding sites are on the surface of the particulate. Humic acids are known to adsorb onto clay minerals (8), and since the surface area per unit weight of the humic acid would be expected to increase on sorption of the acid onto the clay then the binding capacity of the humic acids in the real environment could be expected to be greater than 0.45 mmoles/gram but less than 7.5 mmoles/gram. A comparison

Figure 45: Langmuir isotherms for copper and lead onto humic acid

A, copper B, lead

of the number of soluble binding sites for copper (7.5 μ moles/g) and cadmium (3.1 μ moles/g) indicates that the X_m values reflect the number of binding sites available with sufficiently high complex stability constants to form a metal complex at the surface of the particulate.

The sorption of the metal ions onto the humic acid as a function of pH showed the same behaviour as the binding of metal ions by soluble humic acid shown in Figure 15 and Table 29.

Metal-Hydrous Oxide Interactions

Two hydrous oxides were studied—iron oxide (hematite) and manganese oxides. Initial studies of adsorption of copper onto the solids as a function of solution pH showed that both hematite and Mn_2O_3 particulates adsorbed copper only above pH 4.5, whereas, MnO_2 sorbed metal at pH values as low as 1.5. For the sorption studies a pH range of 1-5 was desirable; therefore, only MnO_2 was employed to obtain adsorption isotherms, whereas, the three oxides were employed in all comparative studies.

The oxides of manganese and iron can interact with water at the solid-water interface (103-110):

and the adsorbed water molecules are weakly acidic (92):

The charge on the surface of the particulate will be pH-dependent; at high pH, the surface will be negatively charged, and at low pH, positively charged. Metal ions can then interact with the metal oxide in two ways (111): first, by the formation of a counter ion layer, and secondly, by the specific sorption of metal ions onto the surface:

The second mechanism is very important for the sorption of heavy metal ions.

Two conclusions can be drawn from the above observations:- the distribution of metal ions will be pH-dependent, and the zero point of charge (zpc, the point where the net surface charge is 0) will be dependent on the hydrous oxide. Figure 46 presents the amount of copper ion in solution as a function of pH for the three

Figure 46: Sorption of metal ions as a function of pH

A. MnO₂ B. Mn₂O₃ C. Hematite

oxides. The pH for the complete release of copper ions into solution increases in the order $\text{MnO}_2 < \text{Mn}_2\text{O}_3 \sim \text{hematite}$. Healy et al. (106) investigated the relationship between zpc and the crystal structure of the solid and found that for the five manganese oxides studied, the zpc ranged from 1.5 to 7.3. Similarly, Parks and Bruyn (103) have studied the zpc for iron oxides and reported values ranging from 6.5 to 8.6. The divalent metal ions which are chemisorbed onto the particulate surface are not fully desorbed at the zpc (112) because the metal ions can compete with the protons for the surface hydroxyls (cf., in metal chelates, the chelates are often stable at a pH below the pK_a of the free acid).

The mechanism of metal sorption onto the hydrous oxides indicates that the ionic strength, pH, and the surface area of the solid will affect the amount of metal ion sorbed onto the particulate. The sorption experiments involving MnO_2 can be performed in two ways; first, a suspension of MnO_2 could be prepared in situ, the pH could be adjusted, and the metal ions added; or secondly, a preparation of the bulk solid could be dried and used in separate experiments. Figure 47 shows the amount of copper ion sorbed by the two methods as a function of weight of MnO_2 . The curves indicate that the in situ preparation has a capacity about 3 times greater than the dried solid. The drying of the oxide removes some of the waters of hydration (113), and possibly changes the crystal structure of the oxide. This change in crystal structure will change the zpc of the solid. The in situ material will have a larger surface area than the dried solids and therefore should have a larger capacity for metal ions. The

Figure 47: Sorption of copper ions onto MnO₂

- ▲ in situ MnO₂
- air dried MnO₂

(in both experiments 1000 μ g of copper were in solution)

above considerations indicate that the in situ material would be more suitable for sorption experiments. However, because the clay and humic acids were only sieved through a 80 mesh sieve, a comparison of different solids of the same particle size was desirable; therefore, the air-dried MnO_2 was used for all comparison studies. The sorption of copper, cadmium, lead and zinc onto the MnO_2 followed a Langmuir isotherm. Table 39 presents the values of X_m derived from the sorption isotherms. The values of X_m indicate that the order of sorption was Pb^{+2} Cu^{+2} Cd^{+2} Zn^{+2} , which is the same order as for the sorption onto clay and humic acid.

The effect of ionic strength on the sorption of copper onto in situ MnO_2 is presented in Figure 48. A comparison of the value at a potassium ion concentration of 10^{-3} M with that of 10^{-1} M makes it evident that about 16% of the copper ion is adsorbed in the counter ion layer. If one considers the sorption mechanism shown in Figure 49 then the following expression can be derived (104,107):

$$5-11 \quad K = \frac{Me_s}{Me_a} \cdot [H^+] \cdot \frac{[MnO_2^{x-n}]}{[MnO_2^x]}$$

where MnO_2^{x-n} and MnO_2^x are free oxides of two different charges; for example, A and C or A and B, and Me_s and Me_a are the amounts of metal ion on the solid and in the solution, respectively. Taking the logarithm of both sides of the equation 5-11 one obtains:

Table 39

Sorption Values for MnO_2

Metal Ion	x_M^* (in situ)	x_M^* (dried)
Cu^{+2}	1.95	0.88
Pb^{+2}	1.92	0.84
Cd^{+2}	1.70	0.38
Zn^{+2}	0.96	0.35

* mmols metal ion/gram MnO_2

3

OF/DE

3

Figure 48: Sorption of copper ions onto MnO_2 at different potassium ion concentrations

Figure 49: Metal sorption onto hydrous MnO_2

$$5-12 \quad \log \frac{Me_s}{Me_a} = \log K + npH - \log \frac{[MnO_2^{x-n}]}{[MnO_2^x]}$$

and a plot of $\log \frac{Me_s}{Me_a}$ as a function of pH would be linear with a slope of n. Several authors (104,107) have used this approach to evaluate the sorption of cations onto δ - MnO_2 (104) and onto

goethite (107). The ratio of $\frac{[MnO_2^{x-n}]}{[MnO_2^x]}$ is also a

function of pH but if it is assumed that the pH of the solution is sufficiently removed from the zpc then either B or C will predominate, and at low coverage the ratio can be taken as a constant. Therefore, equation 5-12 becomes:

$$5-13 \quad \log \frac{Me_s}{Me_a} = A + npH$$

Figure 50 presents plots of equation 5-13 for lead, copper, and cadmium. The values of A and n were:

Metal ion	n	A
Cu^{+2}	0.4	1.5
Pb^{+2}	1.4	1.2
Cd^{+2}	0.26	1.5

Figure 50: $\log \frac{Me_s}{Me_a}$ as a function of pH

● lead ■ copper ▲ cadmium

The values for n can be interpreted as follows: for copper and cadmium, the pH region for metal ion sorption is such that a mixture of A and B exists at the solid surface and adsorption will release between 0 and 2 protons; whereas, for lead at the lower pH values, more of species A exists at the surface, therefore, more protons will be released on sorption of lead ion.

The investigations of metal sorption onto the individual particulates have indicated that metal ions are concentrated onto the solids from the solution. Table 40 presents the results of an experiment comparing the amount of ions sorbed per unit weight for identical solution conditions of pH and initial metal concentration (100 ml of solution at pH 5 with $6.29 \times 10^{-5} M$ metal ion). The results in Table 40 indicate that the order of sorption of the metal ion is:

and for the different particulates is:

which is the same order as that found by McClaren and Crawford (33).

The studies reported in this chapter indicated that the sorption of metal ion followed the same order for each solid, and the order reflected the charge to radius ratio of each ion. These studies were for simple systems in the absence of complexing agents; in the next chapter the sorption of ions onto the solids is studied in the presence of organic acids.

Table 40

Sorption of Metal Ions onto Particulates

Metal Ion	Sorbent* (mmoles/g)				
	MnO ₂	Mn ₂ O ₃	HA	Clay	Hematite
Cu ⁺²	0.44	0.03	0.43	0.08	0.08
Pb ⁺²	0.54	0.13	0.49	0.12	0.12
Cd ⁺²	0.38	0.01	0.18	0.07	0
Zn ⁺²	0.34	0	0.15	0.07	0

* Weights of solid employed

MnO₂ 12 mgMn₂O₃ 20 mg

hematite 40 mg

clay 40 mg

humic acid 12 mg

Chapter 6

Interactions of Particulates and Organic Acids

The dialysis of metal ions associated with large molecules was complicated by the Donnan membrane equilibrium because the large anion was unable to diffuse through the membrane to maintain electroneutrality; the solid-solution interface also acts as an impermeable membrane. If a clay, humic acid or hydrous oxide particulate with adsorbed metal ions is added to distilled, deionized water, the adsorbed metal ions would remain on the particulate because the fixed negatively charged surfaces cannot pass across the interface to maintain electroneutrality. Metal ions can be released from the particulate in any of the following ways:

1. Ion exchange where a cation from the solution passes through the "membrane", which then releases the adsorbed ion into the solution.

2. Solubilization of the matrix; for example, the organic acids fixed to the sediment may be redissolved resulting in the adsorbed metal ions being taken back into the solution.

3. Ion exchange to release the metal ion followed by complexation with an organic ligand. The metal ions released into solution by ion exchange encounter a bicarbonate matrix at a pH of 6 to 8, and the released metal ions will tend to precipitate as the carbonate or hydroxide unless the concentration of free ion is decreased by

complexation.

The distribution of metal ion between the solution and the particulate depends both on the relative magnitudes of K_1 and K_2 and on the concentration of the organic ligand.

4. The hydrous oxides of manganese and iron are redox-active; for example, the MnO_2 particulate is in equilibrium with Mn^{+2} ion:

$$K = \frac{[\text{Mn}^{+2}]}{[\text{H}^+]^4 [\text{e}^-]^2} = 6.91 \times 10^{40} \quad (50)$$

Rearranging the expression for K by taking the logarithms of both sides:

$$6-4 \quad \log K = \log [\text{Mn}^{+2}] + 4 \text{ pH} + 2 \text{ pe}$$

A relation exists between the manganese concentration in solution and the redox potential of the environment:

$$6-5 \quad \log [\text{Mn}^{+2}] = 40.84 - 4 \text{ pH} - 2 \text{ pe}$$

One of the controlling mechanisms of the redox potential in natural waters is the dissolved O_2 :

* $\text{pe} = -\log \{e\}$ cf. reference 50, pages 304-319

If the pH of the water is 7 and if P_{O_2} is taken as 0.21 atm, then the p_e of the system is 13.42. Substituting this value into equation 6-5, one finds that the soluble manganese concentration is 1.0×10^{-14} M. Organic molecules can undergo redox reactions; for example, the quinone/hydroquinone couple:

$$6-8 \quad p_e = 11.8 + \text{pH} + \frac{1}{2} \log \frac{[\text{quinone}]}{[\text{hydroquinone}]}$$

If the pH of the solution is 7 and the quinone/hydroquinone ratio is 10^7 , then the p_e is 8.3 and the soluble manganese concentration is 1.73×10^{-4} M. It is evident, therefore, that dissolved organics in the aquatic environment can lower the p_e sufficiently to solubilize the hydrous oxides of manganese.

The release of metal ions from particulates was investigated by equilibrating copper-spiked MnO_2 , clay or humic acid with various complexing agents, and measuring the released copper ion. The complexing agents employed were EDTA, humic acid, and tannic acid. The redox mechanism was simulated by using solutions of pyrogallol, gallic or tannic acids at pH values ranging from 8 to 2.

EXPERIMENTAL

Three particulates were employed in the studies: hydrous MnO_2 , bentonite, and humic acid. The particulates were spiked with copper ion by equilibrating two grams of the solid with 1 litre of $1.0 \times 10^{-3} \text{ M Cu}^{+2}$ at pH 5.0. The precipitate was then filtered, washed with ultrapure water, and air-dried. The copper content of the solid was determined by leaching the solid with 100 ml of 6 M HNO_3 , and determining the released copper ion by flame atomic absorption spectroscopy. The copper contents found were: in MnO_2 0.14 mmole/g; in humic acid 0.088 mmole/g; and in clay 0.18 mmole/g.

The experiments can be divided into three sets. The first set of experiments was the investigation of the release of metal ion from the spiked particulates by solubilization and by ion exchange. Humic acid 50 mg, clay 50 mg, or MnO_2 20 mg, were equilibrated for 24 hours with ultrapure water, $1.0 \times 10^{-3} \text{ M NaHCO}_3$, and 20, 40, or 60 $\mu\text{g/ml Ca}^{+2}$ solutions. The suspensions were filtered and the released copper ion concentrations determined by flame atomic absorption spectroscopy. The solutions containing calcium were tested for calcium uptake by determining the calcium concentration before and after equilibration. The solubilized humic acid solution was also fractionated by molecular size using flame atomic absorption and ultrafiltration.

The second set of experiments was the investigation of the effect of organic complexing agents on the distribution of metal ion

between the solution and the particulate. Solutions containing 10 µg/ml humic acid and one of 6.30×10^{-5} M Cu^{+2} or Pb^{+2} were equilibrated for 24 hours with either 50 mg clay, 15 mg MnO_2 or 10 mg of humic acid (at pH 5.0 buffered with 1.0×10^{-3} M potassium acetate) and the metal uptake determined. The distribution of metal ion between the soluble and particulate forms for clay over the pH range 5 to 1 was also investigated.

The release of metal ion from sediments by the complexation mechanism was studied by equilibrating (for 24 hours) increasing concentrations of tannic acid, humic acid, or EDTA with the spiked particulates, and determining the concentration of the soluble metal. In the case of tannic and humic acids, free ions were distinguished from complexed ions by dialysis through a Spectrapor 3 membrane, where the dialyzable metal concentration was taken as that of the free metal ion. In addition to determining the soluble metal concentration, the solutions were also fractionated by size using ultrafiltration. The ultrafiltration experiments were performed on several natural waters equilibrated with copper-spiked bentonite.

The third set of experiments was the investigation of the release of metal ion from the hydrous oxides by the reduction of the oxide by organics. Polyhydric phenols are well known reducing agents; therefore, pyrogallol, gallic acid, and tannic acid were equilibrated for 24 hours with MnO_2 and hematite at pH values ranging from 8 to 2, and the soluble iron and manganese determined by flame atomic adsorption spectroscopy. To investigate the release of adsorbed copper ions from MnO_2 , a solution of 50 ng/ml Cu^{+2} , 10 µg/ml tannic acid, and

0.01 M in KNO_3 was equilibrated for 24 hours with 10 mg MnO_2 . The pH of the solution was adjusted with HNO_3 . Separations by dialysis, followed by graphite furnace atomic absorption spectroscopy was used to determine the species in solution.

RESULTS AND DISCUSSION

The results of the experiments on the release of copper from spiked sediments by ion exchange and solubilization of the organic matrix are presented in Tables 41 and 42. The results indicate that for MnO_2 the calcium adsorbed did not release any copper ion into solution. The amount of calcium adsorbed--0.48 mmol/g--compared with the amount of copper ion present--0.14 mmol/g--and the maximum capacity of the oxide--0.88 mmol/g--indicates that the calcium ion is exchanging at sites other than those occupied by copper ion; for example, the calcium ion is either replacing potassium in the counter ion layer or H^+ ions of the sorbed water molecules.

The competition between Ca^{+2} and Cu^{+2} for humic acid sites will favour the copper ion because of the larger copper-humic acid stability constant. The results in Table 42 indicate that at high calcium concentrations some adsorbed copper ion is released into the solution but that the ratio of calcium ion exchanged to copper ion released is not 1:1. The sorption studies cited in Chapter 5 indicated that the capacity of humic acid for divalent ions was about 0.45 mmol/g; therefore, for the experiments reported in Table 41 and 42 the total number of binding sites available is 23 μmoles , and 6.8 μmoles are

Table 41

Release of Copper Ion From Particulates

Solution	Copper ion released (μg)		
	clay	humic acid	MnO_2
$1.0 \times 10^{-3} \text{ M NaHCO}_3$	50	57	0
distilled water	0	0	0
$20 \mu\text{g/ml Ca}^{+2}$	1	6	0
$40 \mu\text{g/ml Ca}^{+2}$	2.5	15	0
$60 \mu\text{g/ml Ca}^{+2}$	4	28	0
available Cu^{+2}	572	430	112

Table 42

Exchange of Calcium Ion on Particulates

Ca^{+2} CONC. ($\mu\text{g/ml}$)	Ca^{+2} sorbed (μmoles)			Cu^{+2} released (μmoles)		
	clay	HA	MnO_2	clay	HA	MnO_2
20	0.3	16	5	0.02	0.1	0
40	1.6	16	10	0.03	0.2	0
60	2.4	20	11	0.06	0.4	0

occupied by copper ion. After equilibration with calcium ion, the number of sites occupied by calcium was 16 μ moles, and therefore, about 0.3 μ moles of copper should be released, which is in good agreement with results presented in Table 42. It is evident that at high concentrations of calcium ions, copper will be displaced from the organic solids; however, the amount of metal ion released will depend both on the total number of binding sites available on the solid and the number of sites occupied by the heavy metal ion--if a sufficient number of vacant sites are present for adsorption of calcium ion, then no copper ion will be released.

The interaction of calcium ion in solution with the copper ion sorbed onto clay will be by the ion exchange reaction given by equation 6-1 except that calcium is used instead of potassium. The extent of this reaction will be governed by the relative exchange coefficients of the two ions. The amount of copper ion exchanged depends upon the amount of copper ion present on the clay relative to the total ion exchange capacity of the clay. The exchange capacity of the clay was 0.59 meq/g; therefore, the capacity of the samples used in this experiment was 14.7 μ moles metal ion (on 50 mg of clay), and the copper ion was equivalent to 9 μ moles of the capacity. Therefore, if less than 5 μ moles of calcium ion was sorbed, it could be expected to replace the potassium ions instead of the copper ions. The results in Table 42 support this conclusion.

Metal ions released in the presence of the sodium bicarbonate solution indicated that copper ion was released from the clay by ion exchange, whereas, the copper ion was released from humic acid by

solubilization of the humic acid (the solution was brown in colour indicating that humic acid went into solution). The released copper ion from the humic acid was fractionated using ultrafiltration. The results are presented in Table 43. The results in Table 43 conclusively show that the copper in the solution is present in large species. The initial set of experiments served to prove that the metal ion is released from humic acid and clay by means of ion exchange reactions, whereas, the hydrous MnO_2 has such a large capacity that calcium ion was sorbed without displacing copper ions. The effect of natural organic acids on the release of metal ion was investigated next.

The first experiments were designed to determine the effect of soluble humic acid on the sorption of copper ion and lead ion onto the three particulates. Table 44 presents the results obtained for the sorption of copper ion and lead ion onto the particulates with and without humic acid present. The results indicate that the presence of organic acids in the solution prevent the metal ion from sorbing onto the particulate. The effect is most noticeable for the sorption of the ions onto clay, where the amount of lead ion and copper ion adsorbed was lowered by 66% and 41%, respectively. The clay-metal ion-soluble humic acid system was investigated further over the pH range of 5 to 1. Figures 51 and 52 present the results for the lead ion and copper ion, respectively. In the presence of soluble humic acid, the amount of lead ion sorbed per unit weight of clay shows a pronounced maximum at a pH of 3.5 and, if the corresponding results for the sorption of lead ion onto clay in the absence of humic acid is plotted, the two curves overlap in the range of pH less than 3.5.

Table 43

Distribution of Copper in Solubilized Humic Acid

Size Fraction (nm)	Copper in Fraction (%)
> 5.1	47
> 3.2	8
> 2.4	7
> 1.9	23
< 1.9	14

Table 44

Sorption of Metal Ions onto Particulates in Presence of Humic Acid

Particulate	Metal Ion Sorbed (μ moles/gram)			
	Lead		Copper	
	with HA	without HA	with HA	without HA
clay	41	120	47	80
Humic Acid	380	540	370	440
MnO ₂	390	490	290	430

* Soluble humic acid concentration was 10 μ g/ml

Figure 51: A. Sorption of lead onto clay. B. Distribution of lead in solution.

● 10 μg/ml humic acid solution ▲ no humic acid

6.3 x 10⁻⁵ M copper was used in both experiments

Figure 52: A. Sorption of Cu ion onto clay B. Distribution of copper in solution
● 10 μg/ml humic acid solution ▲ no humic acid in solution

A comparison of the lead-clay sorption (curve A) with that of the dialyzable lead (curve B) in solution indicates that in the pH region less than 3.7, the lead ion is present as free ion, whereas, above pH 3.7 some of the lead ion is present as a humic acid complex. It is evident therefore, that the decrease in the sorption of lead ion is a result of complexation of the lead ion. Figure 52 presents similar behaviour for the copper ion. However, since the concentration of free ion is greater than that of the lead ion, a maximum is not observed in the copper curve.

The metal ion-clay-soluble humic acid systems are good examples of the effect of a complexing agent on the ion exchange distribution ratio. In Chapter 2, the equation describing the effect of a ligand on the distribution ratio was given:

$$6-9 \quad \log (\lambda_0 / \lambda - 1) = \log K + x \log (\text{ligand})$$

where λ , λ_0 are the distribution ratios with and without the complexing agent, K is the complex stability constant, and x is the number of ligands bound to the metal ion. It is evident from this equation that as K decreases because of the lowering of pH (that is, the conditional stability constant decreases), the ratio λ_0 / λ approaches 1. The stability constants of the metal humates determined in Chapter 4 indicated that at the same pH, the stability constants decreased in the order lead > copper > cadmium $\geq$ zinc, and therefore, the effect of organics on the distribution of metal ion is more prevalent for lead than copper. The other complexing agent of interest, tannic acid, had no effect on the distribution ratio because in the pH range less than 5,

the metal complex is not stable.

A set of experiments was performed to determine the release of copper ion into solution by organic acids. Three acids--humic, tannic and EDTA--were equilibrated with copper-spiked bentonite, humic acid, and MnO_2 particulates. As noted earlier, the mechanism of release would be ion exchange, followed by complexation of the released ion. The release of copper from bentonite as a function of the concentration of tannic acid is shown in Figure 53. Two points are evident: first, with no tannic acid present, 0.8 μmoles of copper ion was released, and that this released copper ion was dialyzable; secondly, as the concentration of tannic acid was increased, more copper ion was solubilized but the concentration of dialyzable copper remained constant. This indicates that the exchangeable copper is complexed by the tannic acid, which shifts the equilibrium given in equation 6-1 to the right.

The soluble metal concentration depends on the relative magnitudes of K_1 and K_2 . In Table 45, the concentration of soluble copper ion is given for different organics and natural water samples. The results in Table 45 indicate that appreciable concentrations of soluble copper ion are possible in natural waters and that a fraction of the copper species is large in size. The ratio of metal ion released to the ligand concentration present in solution is as follows:

ligand	ligand conc.	metal conc.	ratio
EDTA	25 μM	25.8 μM	1.03
tannic acid	220 μM	62.5 μM	0.28
humic acid	40 μM	17.6 μM	0.44

Figure 53: Release of copper ion from bentonite .

- Total soluble copper ion
- ▲ Dialyzable copper ion

Table 45

Release of Copper Ion from Bentonite

Solution	Soluble Copper (M)	Dialyzable Copper (%)
2.5×10^{-5} M EDTA	2.58×10^{-5}	100
20 μ g/ml TA	6.25×10^{-5}	6
20 μ g/ml HA	1.76×10^{-5}	0
Rideau River water	2.20×10^{-5}	48
Lac Phillippe water	3.92×10^{-5}	43
Pinks Lake water	2.27×10^{-5}	76
Meach Lake water	2.96×10^{-5}	62

where for tannic and humic acid the concentration of binding sites was taken from Table 33. It is evident from the above that the ratio decreases in the order $\text{EDTA} > \text{HA} > \text{TA}$, and this is the same order as the metal complex stability constants. The comparison of the amount of metal released with the number of binding sites present in the solution indicates that a binding capacity determined by saturating the ligand (and then determining the free copper ion) during a titration (cf. binding capacity measurements in Chapter 4) bears no relation to the solubilizing capacity of the solution because the amount of metal ion solubilized depends on the metal complex stability constants.

The size of the released copper species was investigated further by ultrafiltration; three natural waters and a humic acid solution were equilibrated with copper-spiked bentonite, and the solutions analyzed by ultrafiltration/flame atomic absorption spectroscopy. Table 46 presents the results of the fractionation experiments. It is evident from the results in Table 46 that in the humic acid solutions and Meach Lake water, the size of the complexed species is greater than 3.1 nm. The Rideau and Meach waters contain some ions in species of size less than 1.9 nm. To determine whether the small species were free metal ions or small complexes (note that both CuCO_3 and CuEDTA pass through the filter), they were investigated by potentiometry with ion selective electrodes. Figure 54 presents the concentration of free copper ion as a function of pH for the Rideau River # 3 water sample, and for copper ion in the presence of $1.0 \times 10^{-3} \text{ M NaHCO}_3$. It is evident that for the Rideau River sample #3, the ion-filterable through the 1.9 nm filter was present as CuCO_3 ; and similarly, for Rideau River

Table 46

Fractionation of Copper Released from Bentonite

Pore size (nm)	Copper in Fraction (% of total)*					
	HA 1	HA 2	Rideau 1	Rideau 2	Rideau 3	Meach
> 5.1	32	79	29	11	64	80
> 3.1	67	11	-	-	-	-
> 2.4	-	-	10	-	-	-
> 1.9	-	10	-	-	19	-
< 1.9	-	-	65	89	17	20
Total Conc. (μ M)	0.79	8.66	13.5	11.8	22.4	17.3

* HA 1 was a solution of 50 ng/ml copper in 50 μ g/ml humic acid, for comparison. Rideau 1 and 2 sites were 50 miles apart. The sample from Rideau 3 was collected after a rainfall.

Figure 54: Concentration of free copper ion (measured by ISE) as a function of pH

● Rideau River water sample #3

▲ 1.0×10^{-3} M NaHCO_3 and $1 \mu\text{g/ml}$ copper ion

samples # 1 and 2 and the Meach Lake water sample, the filterable species was also CuCO_3 . It is interesting to note that for Rideau River sample # 3 (which was collected after a rainfall), the copper ion was present in species of size greater than 5.1 nm. This indicates that significant amounts of large sized species must have been washed into the water.

Table 47 presents the results of the experiments comparing the amount of copper released from clay, MnO_2 , and humic acid particulates by EDTA, tannic acid, and humic acid. If the solubilization of manganese is taken into account, then the order of copper release is,

which is the same as that observed by McClaren and Crawford (34) for isotope-exchangeable copper. Secondly, if one compares the order of solubilizing capacity of the ligands the order is the same as noted earlier, that is $\text{EDTA} > \text{HA} > \text{TA}$. The release of copper ion from humic acid by EDTA would be expected to give a ratio of the moles of copper ion released to the moles of EDTA present of 1; however, the observed ratio was 0.28. There could be two reasons for this--the EDTA may form a complex with Cu^{+2} and be sorbed onto the humic acid particulate, as follows:

This effect was duplicated for the release of copper from Rexyn 101,

Table 47

Release of Copper Ion From Particulates

Ligand ^{@, *}	Copper Ion Released (μ moles)		
	MnO ₂ [*]	Humic acid	Clay
EDTA	0.51	0.51	1.80
Tannic acid	0.19	0.04	1.95
Humic acid	0.32	0.35	0.88

[@] tannic acid, 625 μ g; EDTA 1.8 μ moles; humic acid 1.0 mg

^{*} manganese released

EDTA	0.78 μ moles
TA	1.70 μ moles
HA	2.08 μ moles

^{*} number of complexing sites present:

EDTA 1.8 μ moles TA 6.8 μ moles, HA 2.0 μ moles

where the ratio was 0.32, and for the release of copper from Rexyn 102, where the ratio was 0.38. The example of Rexyn 102 is similar to ligand exchange, where the water molecules complexing the copper ion on the resin are replaced by ligands in solution (114,115). The second possible explanation is that the metal ion may be adsorbed inside the particulate and unavailable for interaction with ligands in solution.

It is evident from the previous experiments that the organics can release metal ions from the particulates by ion exchange and subsequent complexation. A system composed of hydrous MnO_2 , tannic acid and copper ion was investigated as a function of pH. Figure 55 presents the results obtained using dialysis and graphite furnace atomic absorption spectroscopy. Two points are of interest in Figure 55a: first, tannic acid maintains a higher concentration of copper ion in solution by complexation (e.g., at pH greater than 5, 60% of the soluble copper is in a nondialyzable form), and since the copper-tannic acid complex is unstable below pH 5, the curves in the presence and absence of tannic acid overlap. Secondly, the concentration of free copper ion is the same with and without tannic acid present, which is a good evidence for the release of copper ion solely by ion exchange (for example, if the copper ion was being released by decomposition of the oxide, the two curves would not be expected to overlap). In Figure 55b it is evident that the tannic acid releases the manganese ion from the oxide at pH values where complexation would not be possible (i.e., the manganese-tannic acid complex is unstable at pH values less than 5.5), and the manganese ion released is over 10 times greater in the presence of tannic acid than in its absence. This effect of

Figure 55: Copper-tannic acid-MnO₂

A Δ Total copper $\square$ Dialyzable copper $\circ$ Total copper w/o tannic acid
 B $\bullet$ Total manganese with tannic acid $\blacktriangle$ Total manganese w/o tannic acid

pH on the release of manganese ion from MnO_2 by tannic acid raises the question of whether a redox reaction is occurring.

Several authors (27,116-119) have reported the solubilization of oxides by organic acids. Hem (27,116) reported that tannic acid can keep Mn(II) and Fe(II) in solution at pH values where the corresponding oxide normally precipitates. Kee and Bloomfield (117) noted that fermenting plant materials can solubilize both MnO_2 and Fe_2O_3 . Goodman and Chesire (118) investigated the bonding of vanadium with humic acids by EPR spectroscopy and found that vanadate ion (VO_3^-) was reduced to the vanadyl ion (VO^{+2}). If the electrochemical potentials of the various redox couples are compared:

it can be seen that it should be relatively easy to reduce hydrous MnO_2 (because MnO_2 in an acid medium is a relatively strong oxidizing agent). To investigate the action of polyhydric phenols on the hydrous oxides, pyrogallol (A), gallic acid (B), and tannic acid (C), were equilibrated with hydrous MnO_2 and hematite. In Figure 56 are shown

Figure 56: Soluble metal as a function of pH for organic acid--metal oxide systems

□ pyrogallol ▲ gallic acid ● tannic acid

the concentrations of soluble manganese and iron as a function of pH for the different acid and solid combinations. A comparison of the solubilization of the iron and manganese indicates that at pH 2, eight times more manganese is released than iron, which reflects the ease of reduction of Mn(IV) compared to that of Fe(III). One can therefore expect manganese to be more soluble than iron in a reducing environment. Another piece of information available from Figure 56 is that in the iron system a pronounced minimum occurs at pH 5 whereas in the manganese system no such minimum occurs. The studies reported in Chapter 4 indicated that iron formed a stronger complex with tannic acid than did manganese, and at pH 5, the iron-tannic acid complex is unstable. It is thus seen that above pH 5 iron is solubilized by complexation, and below pH 5 redox reactions become important in solubilization.

The values of E^0 for several organics are presented in Table 48. Table 49 presents the amount of manganese released by the different couples. It is evident from Table 49 that the capacity of the natural organics to reduce manganese dioxide is of the same order as that of 0.1 M quinone/hydroquinone.

The strong pH-dependence of the release of manganese shown in Figure 56 needs some explanation. Hem (116) indicates that the capacity of tannic acid to reduce KMnO_4 is 6 times greater at pH 2 than at pH 9. The oxidation of phenols has been studied by many workers; the products of the reduction are complicated by phenolic coupling; for example, the air-oxidation of catechol yields (121):

Table 48

 E^0 for Redox Couples (120)

Reduced Organic	E^0 (V)
Pyrogallol	0.713
Gallic acid	0.799
Catechol (pH 2)	0.55
(pH 8)	0.19
0.6992

Table 49

Release of Manganese from MnO_2 by Organics

Organic*	Manganese Released (μ moles)
0.1 M quinone/hydroquinone	54.5
20 μ g/ml pyrogallol	21
20 μ g/ml gallic acid	18
20 μ g/ml tannic acid	14
1.0×10^{-3} oxalate	4.5

* 100 ml solution, pH 8.0

whereas, pyrogallol yields D and gallic acid E (122):

among other products. It is evident, therefore, that the oxidation of polyhydric phenols is complicated by formation of polymeric species. It is interesting to note that the oxidation of gallic acid by basic H_2O_2 yields (123):

where F can be expected to be a complexing agent at pH less than 5 (similar to humic acids). Tannic acid is hydrolyzed and oxidized by nitric acid to yield oxalic acid (124), and therefore, one can expect oxalic acid to be present in the redox experiments described earlier. Figure 57 presents a comparison of the solubilization of MnO_2 by both oxalic acid and tannic acid as a function of pH. The curves in Figure 57 have the same general shape and suggest that below pH 5 the reducing action may be due to the oxalic acid formed by oxidation and

Figure 57: Release of manganese from MnO₂ by organic acids

● 10 μg/ml tannic acid

▲ 1.0 x 10⁻³ M K₂C₂O₄

hydrolysis of tannic acid.*

SUMMARY

The release of metal ions sorbed onto particulates is by ion exchange between soluble ions and sorbed metal ions and, if an organic acid is present, the subsequent complexation reaction shifts the ion exchange equilibrium to the right. The order of release of metal ions is clay > MnO_2 > humic acid. The release of metal ions from the particulates in the presence of organic acids depends on the magnitude of the stability constant of the metal-organic complex. The action of polyhydric phenols on the oxides of manganese and iron indicate that manganese is solubilized more readily than iron. The tannic acid- MnO_2 system shows a strong pH-dependence, which is thought to result from acid hydrolysis of the tannic acid to oxalate, which then reduces the hydrous oxide.

CONCLUSIONS

The objectives of the research were to define the minimum criteria for determining the metal ion species in natural waters, to apply these criteria in evaluating the available analytical techniques for metal ion speciation, to develop methodology for analysis, and to use the methodology to investigate metal ion chemistry in the aquatic environment. The aspects of aquatic chemistry of special interest were the interactions of metal-organic acids, the interactions of metal ions with sediment, and finally, the interactions of the metal ions sorbed onto sediments with organic acids in solution. To accomplish these objectives it was decided that simple model systems should be developed to test analytical procedures and to permit meaningful studies of metal ion chemistry. The components were metal ions, organic acids, and representative sediment components.

The minimum criteria for a successful speciation scheme are:

1. The analytical techniques for determination of the metals must be sensitive enough to detect metal ions at the concentrations present in natural waters.
2. The analytical technique must be free from interferences or the interferences be well defined, readily identifiable, and amenable to correction.
3. The results obtained be easily interpretable in terms of the possible metal species, such as free metal ion, organic complexes,

and colloidal species containing the metal ion. Three techniques have sufficient sensitivity to be promising in metal ion speciation--anodic stripping voltammetry, potentiometry with ion selective electrodes, and atomic absorption spectroscopy.

Anodic stripping voltammetry differentiates between the metal species by differences in the kinetics of the electrochemical reactions; for example, a metal complex that is not reducible and dissociates "slowly" to the free metal ion can be differentiated from the free metal ion that is reducible. The term "slowly" dissociates must be interpreted in the context of the ASV experiment; for example, if the plating time is one minute then a dissociation with a half life of several minutes will be slow. To apply ASV to the speciation of metal ions, it is necessary that the slow electrochemical step not be induced by a nonreacting component. The studies of the model systems indicated that organic molecules such as gelatin, cysteine, tannic acid, and humic acid adsorbed onto the hanging mercury drop and slowed down the reduction of the copper-EDTA complex. Current-time curves of the reduction of the Cu-EDTA complex at the HMDE indicated that species present in Rideau River waters also induced the decrease in the Cu-EDTA reduction current. Therefore, the conclusion was that ASV must be applied with extreme caution to the speciation of metal ions in natural waters with appreciable organic content.

Potentiometry with ion selective electrodes can differentiate between free metal ions and other species. If the metal species are pH-dependent, then a series of measurements at different pH values provides the activity of free metal ion at the pH of natural waters.

the total metal ion concentration, and a plot of the concentration of free metal ion as a function of pH. The limitations of ion selective electrodes are poor sensitivity (for example, only the copper electrode is suitable for nonpolluted waters), interferences from other ions (for example, sulphide, silver, and ferric ion interfere with the copper ion selective electrode), and electrodes for many elements, such as zinc, cobalt, iron are not commercially available.

Atomic absorption spectroscopy is a sensitive technique for determining the concentration of total metal. To apply atomic absorption spectroscopy to metal speciation, a preliminary separation is necessary. Three procedures for the preliminary separations were evaluated--ultrafiltration, dialysis, and ion exchange. Ultrafiltration was capable of separating the species into different size fractions ranging from less than 1.9 nm to greater than 5.1 nm; however, it was found that sorption of species onto the membrane and its porous backing can cause a shift in the distribution of species to larger size fractions. Dialysis can separate the metal species into two size fractions, and a combination of different membranes can produce a fractionation scheme similar to that given by the ultrafiltration procedure. The dialysis procedure also suffers from the problem of species sorption onto the dialysis membrane and onto the container walls. Ion exchange as a means of separating cationic, anionic and neutral species, was investigated, and it was found that limitations imposed by distribution ratios did not permit a workable speciation scheme.

The distribution of metal ions in natural waters may be viewed as that of species along a size continuum such as,

free ions < inorganic complexes < small organic complexes (such as metal citrates) < metal-humic acid complexes < colloids; this suggests that a combination of dialysis/atomic absorption spectroscopy, ion selective electrodes, and a pH titration may provide a suitable speciation scheme. The scheme can be applied as follows: ion selective electrodes are employed to measure the activity of the metal ion (which is equated to the concentration of free metal ion in the dilute aqueous solution used in this study); the difference between dialyzable metal and free metal ion is the concentration of small complexes (which include hydroxy species such as CuOH^+); the nondialyzable fraction would be metal ions associated with large organic molecules and colloidal species. The concentration of dialyzable metal as a function of pH provides a "fingerprint" for the water sample and may also serve to characterize the sample (for example, natural water pH tends to be between 6 and 8 and the dialyzable metal at pH 6 is normally available for conversion to free metal ion in the natural water pH range, whereas, the metal dialyzable only at pH 2 is not available for conversion to free metal ion under normal natural water conditions.

The speciation scheme based on size separations has two applications: in the study of the distribution of metal species between the soluble and particulate forms, and in the study of the toxicity of metal ion species to aquatic biota. The distribution of metal ion was investigated from two viewpoints: the distribution of metal species in solution, and the effect of the soluble organics on the removal of metal ions from the sediments. The distribution of the soluble metal

was investigated to determine the characteristics of interactions between the metal ion and the organic acid. The competition for binding sites on the humic acid indicated the following order of complexing: $Pb^{+2} > Cu^{+2} > Cd^{+2} > Zn^{+2}$. Scatchard plots of the metal ion distribution as a function of metal ion concentration indicated that the humic acid molecules have two different types of binding sites with a difference in metal complex stability constants of about 10. A study of the distribution of the four metal ions in the presence of humic acid over the pH range 2-8 indicated that below pH 3.5 all the metal was present as the free ion, between 3.5 and 6.5 the metal was distributed between humic acid species and the free ion, and above pH 6.5 competition between humic species and carbonate and hydroxy species increase the dialyzable concentration of ions. At the metal concentrations typical of natural waters (for example, 20-50 ng/ml) in the pH region 6-8, with 1.0×10^{-3} M $NaHCO_3$ and 20 μ g/ml humic acid, it was found that all of the metal ion was present in the metal-humic acid species. The studies of metal ion-humic acid solutions by ultrafiltration indicated that the metal ions were concentrated in the larger molecular size fractions, especially those larger than 3.1 nm.

The studies of the sorption of metal ions onto the sediment components indicated that metal ions are concentrated in the sediment phase and the capacity of the solids to sorb metals decreased in the order:

and the metal ions were sorbed in the order:

- The hydrous oxides and humic acid interact with metal ions by specific sorption; for example, metal ions are sorbed onto humic acids by complex formation on the surface:

The pH characteristics of the different solids indicated the following increasing order of pH for the release of metal ions from the particulates:

All of the solids investigated can sorb metal ions at the pH levels of natural waters. This observation has two immediate consequences: first, at the pH levels of natural waters metal ions are sorbed onto the sediments before formation of the carbonate and hydroxide precipitates, and secondly, the speciation scheme of Piro (4), where all ions released above pH 6 were attributed to colloidal species, is wrong since both hydrous oxides and clay colloids release metal ions below pH 2.

The Donnan equilibrium prevents the release of metal ions into solution without the intervention of another cation, and therefore, it was necessary to define a mechanism for the release of metal ions into solution in the presence of organic acids. The organic acids

release sorbed metal ions by shifting the ion exchange equilibrium as follows:

in which the metal distribution depends on the relative magnitudes of K_1 and K_2 . If the organic ligand was fixed (i. e., K_2 is constant), then the order of release of the copper ion from the solid was:

The release of copper ion from humic acid by EDTA was not stoichiometric, that is, the amount of copper ion released to the amount of EDTA present was not in the 1:1 ratio; this was explained using a ligand exchange reaction:

The hydrous oxides of manganese and iron may be solubilized by a redox reaction by the organics present in the solution. Tannic acid, pyrogallol, and gallic acid were found to release more manganese from MnO_2 than iron from hematite. This was in agreement with the redox potentials necessary to reduce the two oxides (i.e., iron oxide is more difficult to reduce than MnO_2).

FUTURE RESEARCH

Future research in the speciation of trace metals in the aquatic environment should include studies designed to relate the metal species in solution with the species that are toxic to aquatic biota. Hutchinson and Stokes (86) have investigated metal toxicity to algae and found that the total copper concentration of the water sample as determined by atomic absorption spectroscopy has not shown any correlation with its toxicity. Stiff (62) has reported that the toxicity of copper is decreased in hard water, which leads one to suspect that the toxic species is the free copper ion. The fractionation scheme proposed earlier in this thesis can differentiate between free metal ions, inorganic complexes, and large organic species. It is of interest to apply this scheme (including the pH titration) to the problem of heavy metal toxicity to algae. In the study of heavy metal toxicity in natural waters, a correlation between the results of algal assays (86,125) and the dialyzable metal concentrations would lend support to the adoption of a method of chemical analysis (which can be completed in 24 hours) as opposed to biological assays (which may take from 48-168 hours).

An aspect of the metal distribution between free ions and humic acid complexes that was not covered in this thesis was the question of whether the metal distribution is under kinetic or thermodynamic control. The rate constants of the complex formation and dissociation reactions may be studied by using one of the following

two techniques. Shuman and Michael (126) have employed anodic stripping voltammetry at a ring disc electrode to measure rates of formation and dissociation of metal-organic complexes. The procedure involves plating the metal ion of interest into the amalgam at the disc, transferring the electrode to the complexing media; and then stripping the amalgam and monitoring the disc current. If a second-order reaction (between the ligand L and the metal ion) is occurring, then the collection efficiency ($i_{\text{ring}}/i_{\text{disc}}$) will be lower than that in a noncomplexing media, and will depend on the velocity of rotation of the disc. By varying the angular velocity of the disc, the rate constant of the complex formation reaction can be determined. The main problem with this approach will be the adsorption of organics onto the electrode surface.

An alternate procedure is to employ the stopped-flow technique. Langford and Gamble (69) have employed the stopped-flow technique to investigate the Fe(III)-fulvic acid system, and were able to directly measure k_f ; using the conditional stability constant ($K = k_f/k_d$) they deduced k_d . A comparison of the rates of association of metal ion with different sizes of humic acid and the final distribution of metal ion should provide some insight into whether the distribution of metal ion is controlled by kinetics or thermodynamics.

Two aspects of the metal ion-particulate interactions need further investigation. The particulates employed in this study were bulk solids whereas in the aquatic environment, the humic acids and hydrous oxides occur as a coating on clay colloids. It is evident, therefore, that this study is only a first-order approximation of the

real systems, and it is desirable that similar studies be performed with clay coatings. Hem (127), for example, has produced a manganese coating on clays by exchanging Mn^{+2} for K^{+} and then performing an air oxidation under basic conditions. Similarly, Rashid et al. (8) have coated humic acids onto clays. Studies may then be undertaken to determine the effect of the clay matrix on the solubilization of metal humates, and the reduction of hydrous oxides by the organics.

The amount of metal sorbed by a particulate will depend both on its surface area and on its maximum capacity; it would be of interest to study mixtures of particulates to determine their competition for metal ions. To obtain information on the competition by particulates, one must be able to determine on which particulate the ion is bound (whether the metal ion is on the clay or MnO_2 or humic acid). This task requires a workable fractionation scheme to separate the different adsorbed ions. Several workers (6,128) have devised fractionation schemes for sediments and soils. McBain (129) evaluated the different extraction procedures and concluded that chemical procedures could not unequivocally distinguish between the particulate species. It appears that an instrumental technique, such as, field ion microscopy (130), scanning electron microscopy combined with X-ray fluorescence (131), or ESCA (132), is needed. The problems with these instrumental techniques are high cost and inadequate sensitivity, which would seriously limit the usefulness of these techniques.

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