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Aquatic and Terrestrial Humic Materials

Edited by

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CHAPTER 16

CONDITIONAL STABILITY CONSTANTS OF TRACE METALS AND NATURALLY OCCURRING HUMIC MATERIALS: APPLICATION IN EQUILIBRIUM MODELS AND VERIFICATION WITH FIELD DATA

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ABSTRACT

Ion-selective electrode techniques and Scatchard plots were employed to determine the conditional stability constants and number of binding sites for the trace elements Cu, Cd and Pb with naturally occurring organic matter isolated from several streams of the southeastern United States. The data obtained from these studies were used to (1) investigate the degree of binding of oxy-functional groups exhibited by these organic ligands, and (2) determine the usefulness of the values for stability constants and binding sites when employed in thermodynamic chemical equilibrium models. Field data describing the chemical speciation of Ca, Cd, Cu and Fe were used to verify model predictions and to estimate the conditional constants of both Ca and Fe with these organic ligands. The results of these studies demonstrate that large-molecular-weight organic matter plays a significant role in the complexing of metals and that the conditional stability constants determined for organic matter in the southeastern U.S. have applicability over a wide geographical range.

INTRODUCTION

A major goal of environmental biogeochemistry is to gain a sufficient understanding of the transport and fate of materials introduced into natural systems to allow the prediction of the short- and long-term impacts of these materials. Knowledge of the chemical form of an element in natural waters is essential to understanding and predicting an element's distribution between the various biotic and abiotic components of the system. Considerable progress has been made in determining the chemical form of trace metals in natural waters where inorganic ligands dominate the anionic component of the system. The formulation of thermodynamic equilibrium models using formation constants for these inorganic complexes has provided several potentially powerful tools for understanding the chemical form of elements in water [1]. However, while chemical equilibrium models have much potential, they do have limitations, not the least of which is their present inability to successfully predict the chemical forms of many trace metals in systems where naturally occurring organic compounds comprise a significant portion of the anions present [2]. This natural organic matter is often dominated by humic and fulvic acids [3] whose complex structures still continue to perplex investigators.

While the absolute structure of humic acids may evade investigators for some time to come, the role of these compounds in complexing metals is well known [4,5] and advances have been made in incorporating terms into equilibrium models to address natural organic matter/trace metal complexation [6]. Of particular interest is the quasiparticle model, which simplifies the complex metal-organic interactions of surface waters by replacing the actual assembly of organic compounds present with an assembly of hypothetical, identical macromolecules whose mole mass is the number average mole mass of the actual mixture and whose metal-complexation reactions closely mimic those of the real system [6]. This model allows for the incorporation of overall, conditional formation constants and stoichiometries determined by methods such as Scatchard plot analysis, while providing a generally applicable conceptualization of metal-organic binding which may be of value to predicting chemical speciation of metals in natural waters.

It is the purpose of this chapter to describe some of our work aimed at quantifying the binding of metals by naturally occurring organic matter, and to determine the applicability of the data for systems in the Southeast to other regions of the country. To this end, we have used many techniques of measurement, data analysis and chemical modeling that will not be detailed in this chapter, but which are or will soon be described in the literature. Our purpose is not to detail the minutiae of currently available analytical techniques, even though we feel that the importance of proper

analytical applications cannot be overstated; rather, we examine how current techniques may allow us to predict the chemical form of trace elements over a wide geographical area, for waters which contain significant concentrations of naturally occurring organic ligands.

METHODS

Water samples (50 litres) were collected from eight sites in the Southeast. The sites included: four rivers (the Caloosahatchee, Peace, and Suwannee rivers in Florida, and the Satilla River in Georgia), Banks Lake (a blackwater lake in south Georgia), and the Okefenokee Swamp. The limnological parameters of these waters have been discussed previously [7-9] and are summarized in Table I. The waters represent a wide range of pH, conductivity and dissolved organic carbon values.

The water samples were filtered through 0.45- μm membrane filters (Millipore Corp.) and organic matter was concentrated successively with two ultrafilters (Diaflo Hollow Fiber, Amicon Corp.). The ultrafilters used thus provided two organic size fraction concentrates, namely, 0.45 μm > fraction I > 50 Å and 50 Å > fraction II > 13 Å. Ultrafilters also may separate by charge characteristics of the molecules, so these fractions must be considered as operationally defined.

Each fraction was then analyzed for total exchangeable proton concentration and the concentration of carboxylic and phenolic protons per gram of organic matter was estimated [4]. In addition, the complexing capacity of each fraction was determined for Cd, Cu and Pb with ion-selective electrodes (Orion Corp.) [10]. Data from these titrations were analyzed after the method of Scatchard [5,11] to determine the conditional stability constants (pH = 5.0) of the metal-organic complexes as well as the number of sites active in binding metals with a specific stability constant.

All calculations of elemental distributions were conducted using the thermodynamic equilibrium models REDEQL2 [12] or GEOCHEM [13].

Table I. Ranges of Chemical Characteristics of Southeastern Waters Studied

pH	4.0-8.3
Conductivity ($\mu\Omega$)	36-1950
Alkalinity (mg/l)	0-3.0
DOC (mg/l)	11.4-47.3
% DOC removed by ultrafiltration (>5000 daltons)	44.5 \pm 18.5 (n = 8)

Finally, to determine the effect of competing ions on binding of these metals, the binding capacity measurements were carried out as before, except that the organic fraction being tested was placed into solutions containing the competing metal (Al, Ca or Mn) prior to titration with the metals of interest (Cd, Cu or Pb) [14]. Again ion-selective electrodes were employed to measure the metal activities.

RESULTS AND DISCUSSION

DOC Distribution and Nature

In Table I, it can be seen that there are a wide range of dissolved organic carbon concentrations (DOC, defined as that material which passes through a 0.45- μm filter) in the waters of this study. Also of interest is the fact that approximately 45% of the DOC is removed by ultrafiltration, indicating a large molecular size or colloidal form for this material. This observation is in agreement with others [3,15] who have shown that DOC may be to a large extent humic or fulvic material. However, 40.9% (± 19.2) of the total DOC is removed by the first ultrafilter, indicating a size range of 50 to 4500 Å, while only 3.8% (± 2.9) of the total DOC is removed by the succeeding ultrafilter (size range, 13 to 50 Å). These data, representing eight samples taken from six water bodies, agree with other data from the Southeast [7-10] which show that DOC can be fractionated by ultrafiltration techniques and that these fractions may represent different proportions of the total DOC depending on season and water type. These data emphasize that while DOC should be thought of as a continuum of organic material, it must be remembered that the distribution of carbon is not equal across the size spectrum.

Our primary concern in this chapter is determining the extent of the binding of metals to organic matter. To this end, a discussion of the distribution of carbon within organic fractions is of limited use as metals are bound to the carbon skeleton through heteroatoms such as N, O or S. Of these elements, S is in low concentrations in natural organic compounds and little is known of metal binding to organic compounds via this element in natural systems. In contrast, N is present in amounts adequate to make a significant impact on metal binding and has been implicated in metal binding in recent work [16]. However, the majority of the evidence at this point argues for oxygen binding to metals via carboxylic and phenolic groups [4,17].

We determined the total number of exchangeable protons in these organic fractions by means of the $\text{Ba}(\text{OH})_2$ precipitation technique [4] and found the values to range from 3.9 to 11.9 (meq/g ash-free dry wt of

organic matter). Furthermore, using the calcium acetate precipitation method [4], we observed that the exchangeable protons were equally divided between the carboxylic and phenolic functional groups (% carboxylic protons = 47.6 ± 15.9 for 16 samples). While Perdue [17] has correctly pointed out the limitations of the calcium acetate method, it is interesting that the percentage carboxylic nature of these organics is in such close agreement when the range of physical parameters observed for these waters is considered. Furthermore, the errors attributable to the calcium acetate method have little effect on the conclusions drawn for metal-to-organic binding.

Organic Binding of Cd, Cu and Pb

Using ion-selective electrodes [10] and the method of Scatchard [5,11], we approximated the conditional stability constants of the organic fractions with Cd, Cu and Pb. The Scatchard plot analysis was employed because it was developed to determine both stability constants (K) and number of binding sites (n) for metal-protein complexes. As these complexes often have the same difficulties in analysis (primarily undetermined molecular weights of the organics and stoichiometry of the complex), it was hoped that this method, which has been used for humic-metal complexes [18], would allow us to produce data which were comparable across a wide range of water types. Of particular interest was the prospect of determining the number of binding sites (n) per gram of DOC, as this value has eluded investigators in the past. The results of our analyses are given in Table II as the average log K values and average $-\log n$ values determined for the organic matter isolated by ultrafiltration from southeastern waters. The two fractions from each sample location have been combined so that the data reported in Table II are representative of the entire organic fraction

Table II. Conditional Stability Constants (log K) and Concentrations of Binding Sites ($-\log [n]$) for Natural Organic Matter Isolated from Southeastern United States Waters^a

	Cd ²⁺	Cu ²⁺	Pb ²⁺
K ₁	5.83 ± 0.35 (8)	6.52 ± 0.45 (8)	5.09 ± 0.46 (8)
n ₁	5.96 ± 0.56 (8)	5.62 ± 0.37 (8)	5.63 ± 0.63 (8)
K ₂	3.13 ± 2.45 (6)	4.89 ± 0.82 (8)	2.00 ± 3.36 (7)
n ₂	4.04 ± 1.66 (6)	4.94 ± 1.72 (8)	3.29 ± 1.26 (7)

^aValues in () = number of samples.

removed. Two points are apparent from the data: (1) for all three metals, there appear to be two sites for organic binding (K_1 , n_1 and K_2 , n_2 , respectively) at most of the locations sampled; (2) while some variation occurs, the agreement of the values between locations was quite good.

The presence of two binding sites is in agreement with previous work, which indicates phthalic and salicylic binding sites as the primary binding types for metals with humic acids [4,19]; however, some recent studies postulate that the two sites represent steric hindrance rather than differing functional groups [18]. The magnitude of the stability constants in Table II is in reasonable agreement with previously reported data [18,20,21]. Of interest is the fact that K_2 values for Cd and Pb are low, and that in some cases K_2 and n_2 values could not be measured. This observation indicates that the binding of Cd and Pb to organic matter may occur primarily through the stronger sites indicated by the K_1 and n_1 values, while Cu binding appears to occur at both sites in all cases studied.

At the outset of the study, we were concerned about the variation in n values, particularly with respect to different metals binding at similar sites, i.e., n_1 for Cd, Cu and Pb. This concern arose from our wish to employ predictive models. To accomplish this end, the n values for a given site would have to be similar for different metals. Only one n value per site may be entered in the computations, whereas any stability constant may be entered for a specific metal-organic complex. As can be seen from Table II, the agreement for n_1 values is quite good. While the agreement for n_2 values is not as good as for n_1 values, they are still usable since the variability indicates an overlap of the possible values. More importantly than allowing the use of this data in further computations is the good agreement among both n_1 and n_2 when the range of waters is considered. The agreement of the data, as noted by the relatively low standard deviations of the values, indicates that given a wide range of conditions and possible organic carbon sources, the organic fractions isolated by ultrafiltration do not vary greatly with respect to stability constants or number of binding sites available for metal binding. Thus, it may be possible to derive some general expressions for metal-organic binding on a regional basis.

An additional calculation may be made with the data derived for milliequivalents of carboxylic and phenolic acidities and the n_1 and n_2 values, which are expressed in $\mu\text{g atm/l}$. From these data and the mg C/l data, it is possible to calculate the percentage of carboxylic and phenolic sites that may be active in binding metals if one assumes that n_1 represents only carboxylic bonding of the phthalate type and n_2 represents bonding that incorporates phenolic bonds. With these calculations, it is found that 0.8 to 26% of the carboxylic groups may participate in n_1 -type binding, and 0.8 to >100% of the phenolic groups may participate in n_2 -type

binding. The ranges are generated by consideration of the standard deviations of the n values and hence the $>100\%$ values. It must be pointed out that while these calculations are interesting, they do not take into consideration the stoichiometry of the possible complexes, nor the degree of dissociation of the oxy-functional groups. However, the calculations do point out the internal consistency of the measurements and indicate the relative magnitudes of n_1 - and n_2 -type binding.

Equilibrium Models and Field Verification

As previously described, a valid test of the data is their applicability to various systems. In an attempt to determine the generality of our data, we incorporated our organic stability constant values into the chemical equilibrium, thermodynamic model GEOCHEM [13] and attempted to predict the chemical speciation of Cd and Cu from waters in Maine [10]. The field data were chosen because the pH and DOC values were within the range of values studied in the Southeast. In addition, the investigators had passed samples of centrifuged waters through anion and cation resins and analyzed the eluants so that the percent of anionic and cationic metals had been determined. Two lakes (Sunken Pond and Bog Pond) were chosen from these studies based on their pH and DOC values. Table III shows the pertinent chemical data from the ponds, and the percentage anionic and cationic character of four elements studied are reproduced in Table IV.

Table III. Chemical Characteristics of Two Ponds from Maine

	Bog Pond	Sunken Pond
pH	4.6	4.6
Alkalinity (mg/l)	1	1
DOC (mg/l)	19.3	13.7
Na (mg/l)	3.2	3.2
K (mg/l)	0.4	0.97
Ca (mg/l)	2.3	0.73
Cd ($\mu\text{g/l}$)	0.40	0.32
Cu ($\mu\text{g/l}$)	22.5	27.9
Fe ($\mu\text{g/l}$)	0.18	0.11
CO_3^{2-} (M)	4.5×10^{-13}	4.5×10^{-13}
SO_4^{2-} (M)	5.9×10^{-5}	8.8×10^{-6}

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Table IV. Percent Ca, Cd, Cu and Fe Removed from Two Pond Surface Waters by Ion Exchange Resins

	Bog Pond		Sunken Pond	
	% Cation	% Anion	% Cation	% Anion
Ca	>99	<1	>99	<1
Cd	65	37	56	55
Cu	<1	98	5	96
Fe	10	90	19	81

The model GEOCHEM was employed because it has provisions for fulvic acid ligands with stability constants, at least for K_1 -type binding with Cu and Cd. For this reason, GEOCHEM was used to predict the distribution of these two metals for Sunken Pond and Bog Pond and then compared those predictions to calculations in which the K_1 and K_2 values determined in southeastern waters had been inserted for the values in GEOCHEM. This latter model was called GEOPLAY. The n_1 and n_2 values from the Southeast were adjusted to the DOC of the ponds and used in both models as the concentrations of available sites. In addition, since the type I and type II binding sites are usually considered to be phthalate- and salicylate-type bonds respectively, the model REDEQL2 was also used to predict the chemical forms of Cd and Cu in the two Maine ponds. REDEQL2 is an earlier version of GEOCHEM that has a smaller thermodynamic data base and does not have fulvic acid-type ligands but does have phthalic acid and salicylic acid data. Hence REDEQL2 was used without alteration of the thermodynamic data but with the same corrected n_1 and n_2 values used in GEOCHEM and GEOPLAY as the concentration of phthalic and salicylic acids, respectively.

The results of the computations can be seen in Table V. For both metals, in the two ponds, the models with unaltered thermodynamic data predicted that >95% of the metals should exist as cations. The model GEOPLAY, which had had the K_1 and K_2 values from Table II inserted in the thermodynamic data base of the model, predicted that approximately 40% of the Cd in both ponds would be cationic, as would about 9% of the Cu. Comparison of the predictions from the models with the empirical data gathered in the field (Table IV) clearly shows that the predictions using the stability constants determined for organic matter from the Southeast give a much better agreement with measured distributions than do those of either of the other models.

The reason for the discrepancies can be seen with an examination

Table V. Percentage Cd and Cu Predicted by Chemical Models to be in Anion or Cation Forms in Two Maine Surface Waters

	Bog Pond			
	Cd		Cu	
	% Cation	% Anion	% Cation	% Anion
REDEQL2	99.0	<1	98.6	<1
GEOCHEM	97.7	0.8	95.9	2.9
GEOPLAY	41.1	58.3	9.9	90.0
	Sunken Pond			
	Cd		Cu	
	% Cation	% Anion	% Cation	% Anion
REDEQL2	99.8	<1	99.3	<1
GEOCHEM	98.9	1.1	95.5	3.5
GEOPLAY	40.1	59.8	9.2	90.8

of the stability constant data within the GEOCHEM thermodynamic data base. The data base has $\log K_1$ and $\log K_2$ values of 3.5 and 2.7, 4.3 and 2.5 for Cd and Cu, respectively, with fulvic material. Comparing these values with those from this study ($\log K_1 = 5.8$, $\log K_2 = 3.1$, for Cd; $\log K_1 = 6.5$, $\log K_2 = 4.9$, for Cu; Table II) shows a two log unit discrepancy for the K_1 values for both metals and a similar discrepancy for the $\log K_2$ value of Cu. Since models such as GEOCHEM are designed to solve sets of simultaneous, competitive equations by successive iterations, it is apparent that the two orders of magnitude difference in the value of a stability constant can have significant effects on the results, especially when many of the stability constants are similar. In the case of the thermodynamic data deck of GEOCHEM, of 36 metals (including H^+) only 9 metals have $\log K$ values listed. For $\log K_1$ the 9 values range from 3.1 for Mg^{+2} to 4.7 for Pb^{+2} , a range of only 1.5 log units for all complexes considered. When this information is considered, it is easy to understand how the differences in predictions arise.

Influence of Ca and Fe

The results of the computations shown in Table V would indicate that the stability constants for Cd and Cu with natural organics from the Southeast are a relatively good estimate of the values for similar complexes

from the Northeast. However, as has been noted, the models solve competitive equations. It has been pointed out previously that major ions such as Ca will be present in such quantities as to effectively compete for binding sites with the trace metals [22,23]. This is particularly true if the stability constants are similar, as we have seen in existing models. However, the stability constant values which best predict the field data for Cd and Cu may be as much as two orders of magnitude greater than those used for Ca-fulvic complexes in GEOCHEM. To investigate the effect of changing the stability constants for the Ca-fulvic complex, we again employed GEOCHEM and ran a series of calculations in which the Ca-fulvic stability constant values were increased to determine the magnitude of the log K_1 and log K_2 values which would be required to cause a deviation in the predicted value from that determined in the field (Table IV). The results of this study are seen in Figure 1.

In both cases, significant differences were noted at log $K_1 \sim 5$ and log $K_2 \sim 3$. These values represent approximately one log unit higher values than have been reported for the stability constants of Ca-humic compounds [21]. Values in excess of the literature data do not appear warranted in the case of calcium due to the observed cationic character of Ca in field studies (Table IV). Hence the values of log $K_1 = 3.6$ and log $K_2 = 1.7$ used in the model's data base were used in further calculations.

A similar exercise is warranted with respect to Fe. The field data indicate that, in both ponds, Fe is primarily anionic (Table IV). Examination of the thermodynamic data reveals that no stability constants exist for Fe⁺³-fulvic complexes, and that Fe⁺²-fulvic complexes are reported as log $K_1 = 4.4$ and log $K_2 = 2.7$, which appear to be too low for the measured distribution. Hence, the model GEOCHEM was again employed to approximate realistic stability constants for Fe⁺³-fulvic complexes. As before, the n_1 and n_2 values for southeastern systems were used as the concentrations of binding sites with K_1 and K_2 values, respectively. The stability constants were changed to higher values in successive runs of the model and the percentage cationic Fe was plotted against K values (Figure 2). For both systems, log $K_1 = 9.6$ and log $K_2 = 8.6$ values gave the best estimate of the field data (Table IV). Thus, it would appear that a divalent alkaline earth such as Ca has relatively low stability constants relative to metals Cd and Cu (3.5 and 1.5 vs ~ 6 and ~ 4 for Cd and Cu), and the trivalent Fe has stability constants higher than the divalent species (~ 9.5 and ~ 8.5). This would mean that under equilibrium conditions, the trivalent Fe would be expected to bind to organic matter more strongly than the divalent metals, which in turn would bind more strongly than the alkaline earths. Some support is provided for this argument by the studies of competitive binding of metals by organic matter.

Natural organic matter that had been isolated from southeastern waters

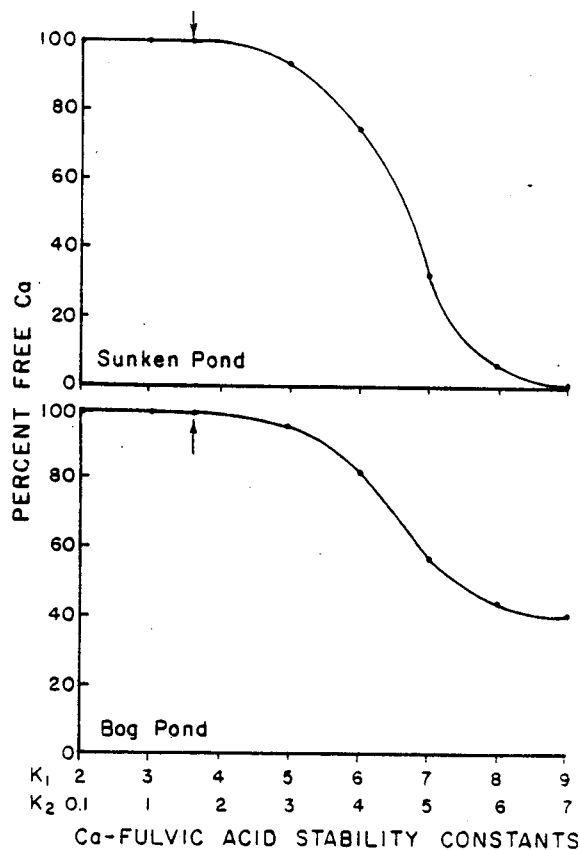


Figure 1. Percentage cationic Ca^{2+} predicted as a function of the two stability constants (K_1 and K_2) of the Ca-fulvic acid complex. Arrows represent values currently in the thermodynamic data base of the equilibrium model "GEOCHEM."

by ultrafiltration was allowed to react with various elements including Al^{+3} , Ca^{+2} and Mn^{+2} [14]. The binding capacities of these organics were then determined by titration with Cd^{+2} , Cu^{+2} and Pb^{+2} . The binding capacities determined in this manner were then compared to the binding capacities of separate samples of the organic matter which had not been allowed to react with the competing ions Al^{+3} , Ca^{+2} , Mn^{+2} . The results of a portion of this work are shown in Table VI. As can be seen, Ca^{+2} did not

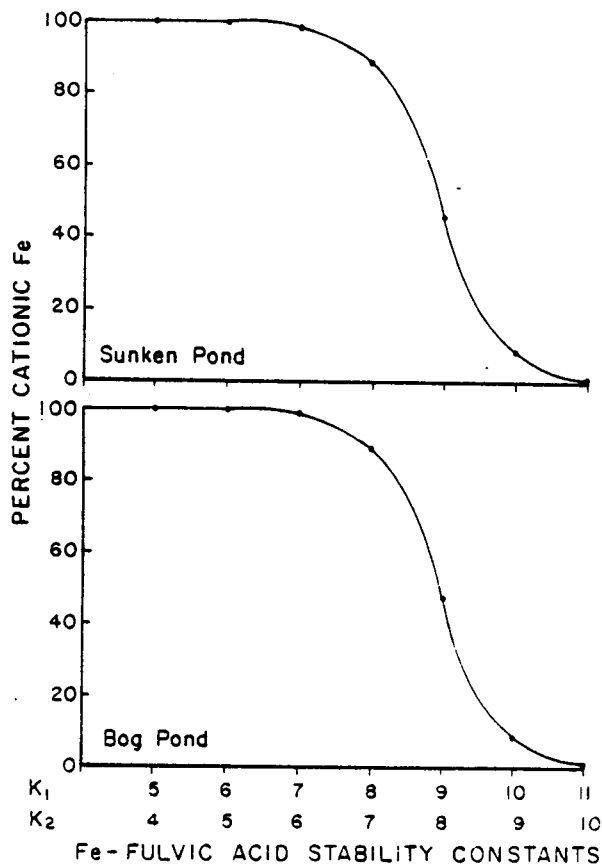


Figure 2. Percentage cationic Fe^{3+} predicted as a function of the two stability constants (K_1 and K_2) of the Fe-fulvic acid complex.

compete well with any of the divalent metals, whereas the trivalent Al was very effective at blocking the binding sites of the organic from reacting with divalent metals. The divalent Mn ion was intermediate in its ability to block sites, but appeared to be more effective against Cd and Pb, which have lower stability constants with organics (Table II) than does Cu. Recent studies [24] have arrived at similar results, although some discrepancies in order of reactivity do arise, particularly as a function

Table VI. Effect of Competing Ions on Cd, Cu and Pb Binding Capacities of Surface Water Organic Matter

Competing Ion	% of Original Binding Capacity Remaining in the Presence of Competing Ions		
	Cd ²⁺	Cu ²⁺	Pb ²⁺
Al ³⁺	3.2 ± 5.4 ^a	ND ^b	3.6 ± 5.4
Ca ²⁺	95.7 ± 4.8	39.3 ± 8.0	94.7 ± 4.6 ^a
Mn ²⁺	25.6 ± 16.5 ^a	51.3 ± 20.2	24.8 ± 19.4

^an = 9, all others n = 12.^bND = not determined.

of pH. While there are always difficulties in interpreting competition studies, the general trend supports the lower organic-metal stability constants of Ca²⁺ and the high values of Fe³⁺ relative to Cd and Cu.

Since as we have noted the model solves competitive reaction equations, we again used the model GEOPLAY to predict the distribution of chemical species of Maine lakes. In this effort, we incorporated the stability constants we had derived for Ca and Fe along with those for Cd and Cu and again used n₁ and n₂ as described above. The results of those calculations are compared to the field observations in Table VII. The agreement between calculated and observed distribution was quite good. The calculated values for Cu are less accurate with the incorporation of the Fe and Ca values; but, considering the cumulative errors possible in the data gathering and calculations, they must still be considered in good agreement. In addition, it must be remembered that other metal-organic

Table VII. Percentage Cationic Ca, Cd, Cu and Fe Predicted by Chemical Models and Found by Ion Exchange Resin in Maine Ponds

	Bog Pond		Sunken Pond	
	Found	Pred.	Found	Pred.
Ca ²⁺	>99	98.7	>99	99.4
Cd ²⁺	65	67.7	56	62.6
Cu ²⁺	<1	19.0	5	16.5
Fe ³⁺	10	19.5	19	18.1

interactions not considered in this treatment (i.e., Al^{+3} , Mg^{+2}) are required before fine tuning of these predictions can be considered.

SUMMARY

The work reported here shows that approximately 50% of the DOC of six southeastern waters can be extracted by ultrafilters designed to remove particles $>13 \text{ \AA}$ in diameter. In addition, despite a wide range of physical and chemical differences in these waters and possible differences in source terms, this organic matter has narrow ranges of stability constants and numbers of binding sites available for complexing with Cu, Cd and Pb. The number of exchangeable protons associated with this organic matter ranges from 3.9 to 11.9 meq/g ash-free dry wt organic matter, with approximately 50% of those protons being carboxylic and 50% being phenolic. However, it appears that only a relatively small portion of those proton exchange sites may be active in metal binding.

Computer model predictions in conjunction with field observations and laboratory data presented in this work indicate that trivalent ions have higher stability constants for binding with natural organic matter than do divalent heavy metals, which, in turn, form stronger bonds than do alkaline earths. More importantly, it appears that data gathered relative to metal-organic binding in the southeastern United States is applicable on a broad regional basis and may well be applicable across regions of the U.S. Hence, it may be possible to obtain accurate predictions of trace metal speciation in highly organic waters without the requirement of determining stability constants for each location, as has been suggested [21].

In conclusion, the quasiparticulate model is not a preferred or even theoretically appealing alternative to the complete description of the metal-ligand interactions, but may be the only pragmatic method of describing complex natural systems in a manner that allows the prediction of the free metal concentrations. Thus, it would appear that natural organic-metal interactions are not intractable, and many useful measurements and predictions of chemical speciation of metals in high organic concentration waters may be made using current techniques and knowledge.

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