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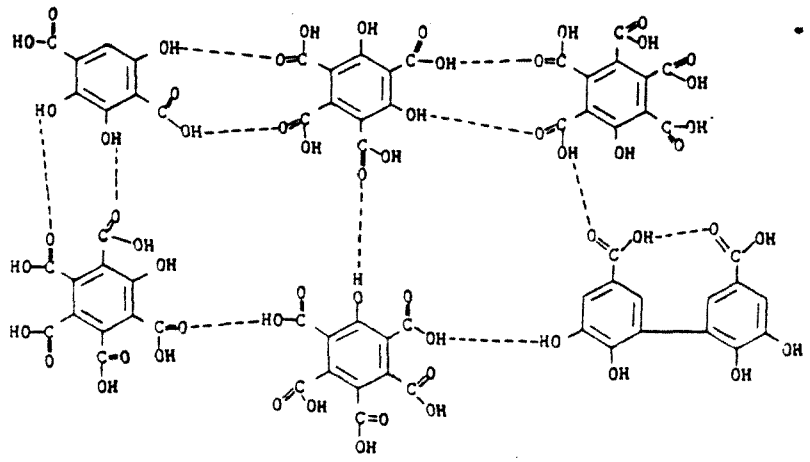
SEDIMENT QUALITY CRITERIA FOR METALS: III. REVIEW OF DATA ON COMPLEXATION OF TRACE METALS BY PARTICULATE ORGANIC CARBON



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SEDIMENT QUALITY CRITERIA FOR METALS: III. REVIEW OF DATA ON THE COMPLEXATION OF TRACE METALS BY PARTICULATE ORGANIC CARBON

Work Assignment 56, Task 4

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ABSTRACT

The approach to developing sediment quality criteria for trace metals is based on predicting the activity of the metal ion in interstitial water of the sediment and relating the concentration of the metal ion to the toxic level of the metal ion inferred from the water quality criteria for the metal. To predict the activity of the metal in the interstitial water, it is necessary to model the sorption of the metal to the sediment using a surface complexation adsorption model that relates the adsorption to the trace metal ion activity in solution and not to the total metal concentration. The resulting sediment quality criteria for trace metals will be based on the net adsorption of the metal to the three major sorption phases in sediment--iron oxides, manganese oxides, and reactive particulate organic carbon. This report is a review of the organic carbon adsorption literature.

Organic matter in soil can be classified as humic or nonhumic substances. The humic substances are in turn composed of three main groups--fulvic acid, humic acid, and humin. These groups are distinguished by their respective solubilities in dilute acid and dilute base. Abundant evidence exists for the complexation of trace metal cations with soil organic matter, mainly humic, and fulvic acids. Two methods have been used to evaluate the binding of metal ions to humic substances. The first and most common method is to consider the humic molecule as a ligand and the metal ion as the central atom. In the second method, the humic molecule is considered to act as the central atom and the metal cations as ligands. Several investigators have attempted to measure the stability constants for the binding of trace metals to humic substances; however, the constants appear to be dependent on the pH, metal concentrations, amount of organic matter, temperature, and ionic strength. Therefore, these constants are conditional constants.

An alternative approach to modeling the complexation of trace metals to humic substances is to consider that the substances are polyelectrolytes. Marinsky and colleagues used this method to overcome the difficulties in the determination of stability constants.

Tables of the published stability constants for trace metal complexation by humic acids and fulvic acids are included in the appendix of this report. The stability constants in the tables are used to evaluate the percent of

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TABLES

INTRODUCTION

The U.S. Environmental Protection Agency, Criteria and Standards Division, has initiated an effort to develop sediment quality criteria for nonpolar organic contaminants and trace metals. These sediment quality criteria will be used in conjunction with water quality criteria to protect U.S. freshwater and saltwater bodies and their uses. The approach chosen for developing sediment quality criteria for trace metals is based on predicting the activity of the metal ion in the interstitial water of the sediment and relating this concentration to the toxic level of the metal ion inferred from the water quality criteria for the metal (Jenne et al. 1986). Thus, the sediment quality criteria will be tied to the water quality criteria. The activity of the metal ion in the interstitial water is predicted from the adsorption of the metal to sediment using a surface complexation adsorption model. The surface complexation model relates the adsorption to the trace metal ion activity in solution and not to the total metal concentration, thus avoiding the limitations of the more classical distribution constant and adsorption isotherm approaches. To predict the adsorption of the metal on the sediment, the adsorption constants for the metals on the three major sorption phases in the sediment--iron oxides, manganese oxides, and reactive particulate organic carbon--and the quantity of each of these sorption phases in the sediment must be determined.

This report is a review of the organic carbon adsorption literature. It is one in a four-part series of reports reviewing the available literature on sorption constants for metals on iron oxides[a] and manganese oxides[b], and extraction methods for estimating the quantities of each of the sorption phases

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(a) Jenne, E. A. 1987. Sediment Quality Criteria for Metals: IV. Review of Surface Complexation and Acidity Constants for Modelling Adsorption of Cadmium and Zinc onto Iron Oxides. Submitted by Battelle, Washington Environmental Programs Office, Washington, D.C. to the U.S. Environmental Protection Agency, Criteria and Standards Division.

(b) DiToro, D. M., and B. Wu. 1986. Sediment Quality Criteria for Metals: V. Review of Data for Determining the Intrinsic Adsorption Constants for Manganese Dioxide. HydroQual Co., Inc. Submitted by Battelle, Washington Environmental Program Office, Washington, D.C. to the U.S. Environmental Protection Agency, Criteria and Standards Division.

BACKGROUND

Organic matter can be classified as two basic types, humic substances and nonhumic substances. Humic substances are amorphous, acidic, and polydisperse (i.e., exhibit a wide range in molecular sizes) with molecular weights ranging from several hundreds to tens of thousands (Schnitzer and Khan 1972). These substances are composed of three main groups that are distinguished by their solubilities in dilute acid and dilute base. The fulvic acid fraction (FA) is soluble in dilute base and dilute acid. The humic acid fraction (HA) is soluble in dilute base but is insoluble in acid solution. The humic fraction is insoluble in both acid and base solutions (see Figure 1).

The nonhumic substances have specific and identifiable chemical characteristics and include such substances as carbohydrates, proteins, amino acids, fats, and resins. These nonhumic substances are easily decomposed by microorganisms and thus have a relatively short residence time. Therefore,

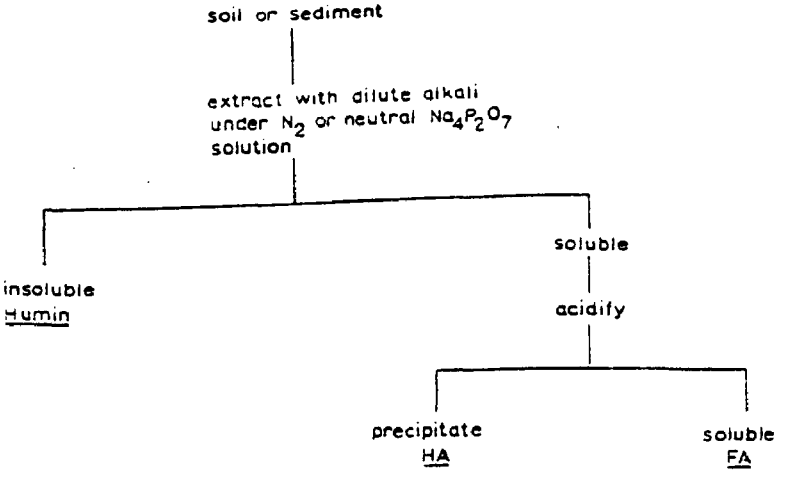

FIGURE 1. Extraction and Fractionation of Humic Material (Schnitzer 1976, p. 90)

phase may have altered the sediment surface and thus the adsorptive behavior of the organic particulate matter. The evidence, however, suggests that particulate organic matter is important in trace metal sorption.

CHARACTERIZATION OF HUMIC SUBSTANCES

Methods for characterizing humic substances fall into two general categories, the degradative and the nondegradative. The different methods for each category can be found in Table A.2 (Schnitzer 1976).

Elemental analysis of humic substances (Table A.3) has shown that the major constituents are carbon and oxygen (Schnitzer 1976). Functional group analysis of humic acid and fulvic acid from different soils can be found in Table A.4 (Schnitzer 1976) and Table A.5 (Schnitzer and Khan 1972). The carboxyl and phenolic functional groups are believed to be involved in trace metal binding. These tables show that fulvic acids have a greater oxygen content, whereas humic acids have a greater carbon content. Also in fulvic acids, a larger amount of the oxygen that is present is tied up in -OH, -COOH, and -C=O functional groups than in these same functional groups in the humic acid. Finally, fulvic acid is more acidic than humic acid.

Degradative methods for humic substance characterization have produced products that consist mainly of aliphatic carboxylic acids, benzene carboxylic acids, and phenolic acids. Other degradative products include n-alkanes, substituted furans, and dialkyl phthalates. Some of the compounds produced from these degradative products are shown in Table A.6 and in Figures 3-5 (Schnitzer 1976).

X-ray analysis and electron microscopy of fulvic acid (Kodama and Schnitzer 1967) has shown that this substance consists of a network of condensed aromatic rings perforated by holes that can trap organic and inorganic compounds. Combining this information and that gathered through other methods of degradative and nondegradative characterization, several general structures of humic and fulvic acids were proposed: Figure 6 (Stevenson 1982), Figure 7 (Stevenson 1982), Figure 8 (Stevenson 1982), Figure 9 (Schnitzer and Khan 1972), and Figure 10 (Stevenson 1982).

In summary, humic substances are complex mixtures whose exact composition varies as a function of the source and method of isolation.

PURIFICATION OF HUMIC SUBSTANCES

Once the humic materials are extracted from the sediment and divided into the different fractions (Figure 1), the fractions need to be purified to remove organic and inorganic impurities. To remove ash from humic acid (HA), Khan (1971) used dilute solutions of HCl/HF and dialyzed against distilled water in the presence of a hydrogen ion exchange resin. Gascho and Stevenson (1968) alternately dialyzed the HA against 0.3N HF and 0.02M $Na_4P_2O_7$. Dormaar et al. (1970) used successive precipitations with mineral acid followed by passage through an ion exchange resin to purify the HA fraction.

Organic impurities, such as lipids, can be removed from the HA with ether or an alcohol/benzene mixture. Hydrolysis with mineral acids, gel filtration, and phenol extraction can be used to remove carbohydrates and proteins from HA (Stevenson 1982).

For fulvic acid (FA), inorganic impurities can be removed by the use of cation exchange resins. Organic impurities can be removed by the process shown in Figure 2 (Stevenson 1982).

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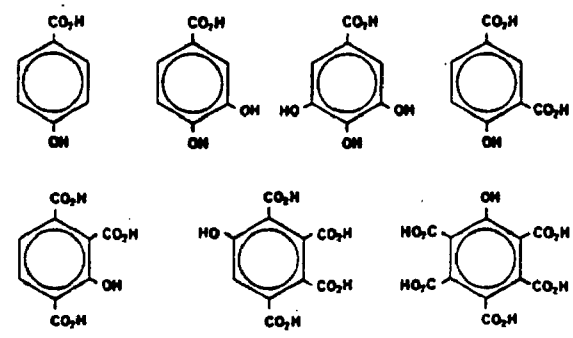

FIGURE 5. Major Phenolic Degradation Products (Schnitzer 1976, p. 96)

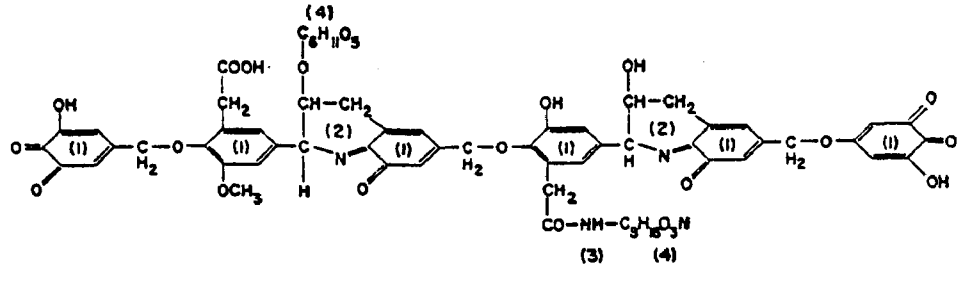

FIGURE 6. Dragunov's Structure of Humic Acid [Kononova shows (1) an aromatic ring of the di- and trihydroxybenzene type, part of which has the double linkage of a quinone group; (2) nitrogen in cyclic forms; (3) nitrogen in peripheral chains; and (4) carbohydrate residue (Stevenson 1982, p. 258)]

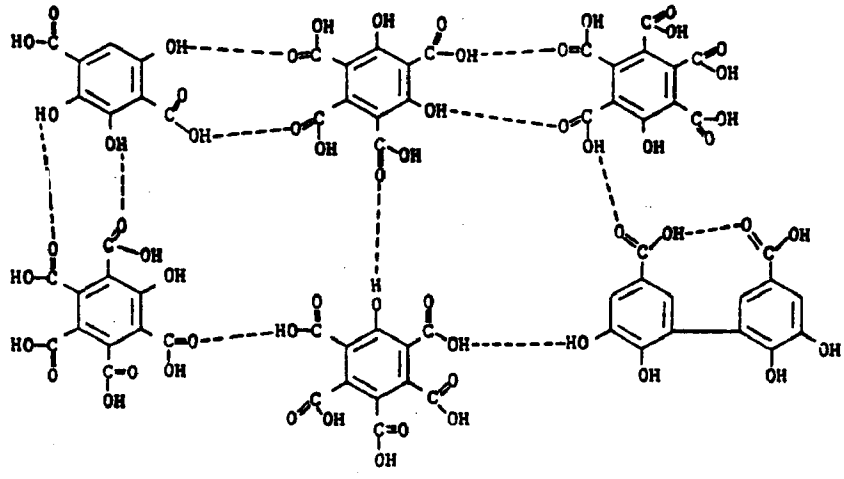

FIGURE 9. Structure of Fulvic Acid (Schnitzer and Khan 1972)

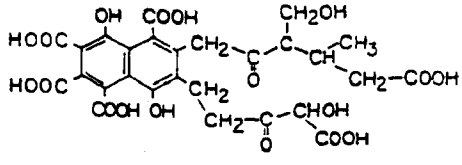

FIGURE 10. Model Structure of Fulvic Acid According to Buffle (Stevenson 1982, p. 261)

In the second method, the humic molecule is considered to act as the central atom, and the metal cations act as "ligands" permitting formation of metal-humic acid complexes with multiple metals (i.e., M_jA complexes where $j \geq 1$). Investigators attempted to measure the strength of binding of trace metals to humic substances or, in other words, the stability constants. The stability constants, K, as defined by Equations (1) and (2) are

$$k_1 = [MA^+]/[M^{+2}][A^-] \tag{3a}$$

$$k2 = [MA_2]/[MA^+][A^-] \tag{3b}$$

and for the overall reaction:

$$2A^- + M^{+2} \leftrightarrow MA_2 \tag{4}$$

$$K = k_1k_2 = [MA_2]/[M^{+2}][A^-]^2 \tag{5}$$

However, problems occur when determining stability constants. Stability constants, K, for the binding of trace metals to humic substances, measured under different experimental conditions, have different values. Stability constants are conditional constants because they appear to be dependent on such experimental conditions as pH, metal concentration, amount of organic matter, temperature, and ionic strength. For example, Saar and Weber (1979), in a study on soil and water fulvic acids that was previously prepared by Weber and Wilson (1975), found that the stability constants for fulvic-cadmium complexes decreased as the concentration of fulvic acid increased (Table A.7). Saar and Weber (1979) concluded that the decrease in the stability constant was a result of the conformational changes that occurred when the concentration of fulvic acid was increased. The conformational changes resulted in a blocking of some potential binding sites. Schnitzer and Skinner (1966) found that the stability constant was not dependent on the fulvic acid concentration for copper-fulvic complexes (Table A.8).

Saar and Weber (1979) also investigated the effect of pH on the value of the stability constants for cadmium-fulvic acid complexes and found that the

Finally, Sposito et al. (1979), in a study on complexation of copper by fulvic acid extracted from sewage sludge, found through Scatchard Plots that as the ratio of Cu^{+2} to FA increased (increased metal loading), the stability constant decreased. Bresnahan et al. (1978), in a study of copper-fulvic complexes, also found this relationship to be true. This decrease in the stability constant was attributed to the presence of different types of binding sites in the humic molecule. Therefore, because stability constant values are dependent on pH, ionic strength, and metal and FA concentrations, most of the reported stability constants can only be considered conditional constants.

Stability constants measured under different experimental conditions vary significantly for several reasons. Humic substances are polyelectrolytes that range in apparent molecular weights, solubilities, and acid strengths (Marinsky et al. 1983). These humic substances are heterogeneous in composition and thus have different functional groups in different chemical environments. As a result, the binding of trace metals at one site will affect the binding of trace metals at other sites. Aggregation of humic substances may also affect the number of sites available for binding. For polyelectrolytes, the surface charge on the humic molecule will vary with the degree of dissociation of the humic molecule, the ionic medium in which the molecule is present, and the amount of metal binding (Marinsky and Reddy 1984a,b). In previous work, these factors were not incorporated into the expression for the stability constant; consequently, stability constant values vary widely. A goal is to develop a model that will account for these conditions and also allow for the prediction of trace metal availability in aquatic systems.

Another factor that complicates the interpretation of data on metal-humic binding is that at least two types of metal ion-humic reactions were identified (Gamble et al. 1985): an electrostatic binding resulting from the charged surface on the humic material and an inner-sphere complex formation (inner sphere meaning the humic molecule ligand replaces water molecules bound to the hydrated metal cation) including chelation (more than one binding site on the humic molecule is bound to a single metal ion).

Marinsky and others tried to overcome these difficulties in the determination of stability constants. When considering the nature of humic substances, note that there are two general types (Gamble et al. 1985): a small low molecular weight polydisperse polymer (i.e., a fulvic acid), and a higher

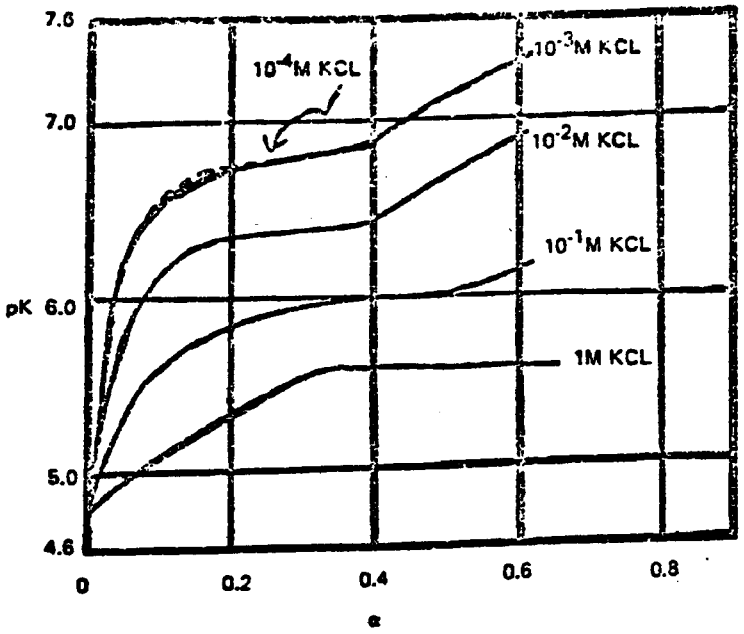

FIGURE 12. Potentiometric Titration of Polymethacrylic Acid (Gamble et al. 1985, p. 381)

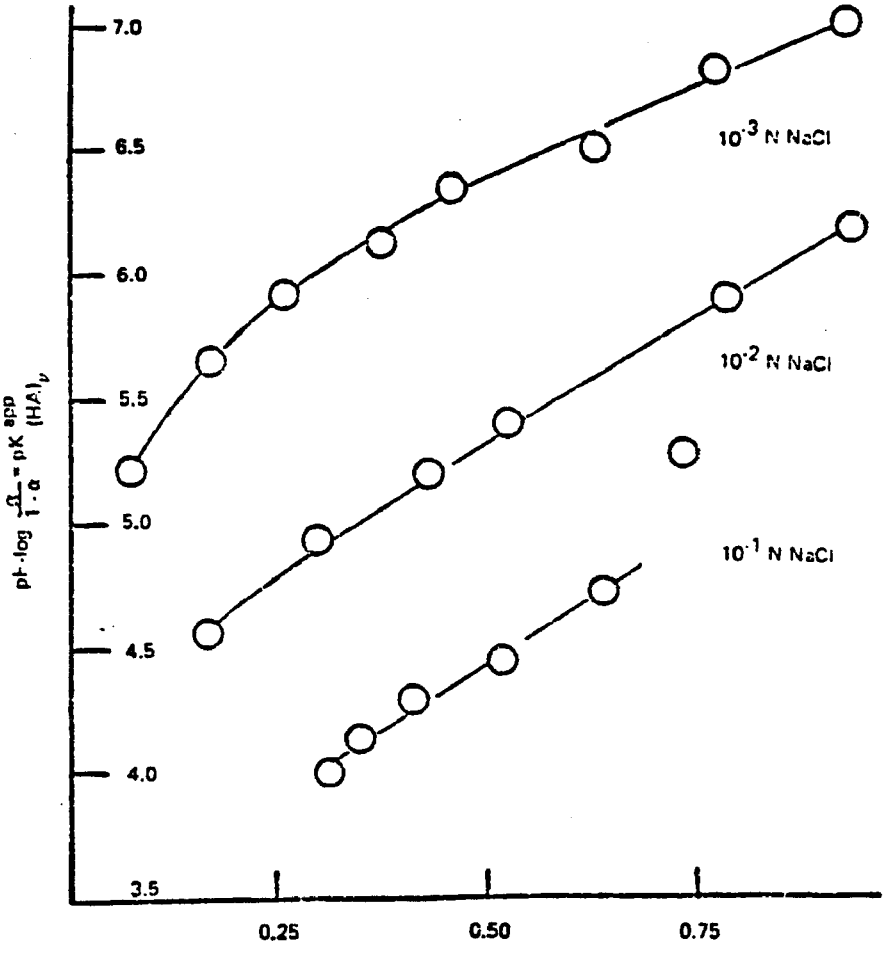

FIGURE 13. Potentiometric Titrations of Sphagnum Peat (Gamble et al. 1985, p. 382)

where $pK^{int}(HA)\gamma$ = the intrinsic acid dissociation constant of the repeating functional group γ of the humic acid gel

$y_{Na(g)}$ = activity coefficient of Na^+ in the gel

F = the electrostatic free energy of the system

psi(a) = the potential at the gel surface.

The apparent stability constant can be expressed in terms of experimentally measurable quantities:

$$pK^{app}(HA)\gamma = pH(s) - pNa(s) - \log\{C_{Na(g)} + A/V_g\} - \log\{\alpha/(1-\alpha)\} \quad (10)$$

where $C_{Na(g)}$ = concentration of sodium ion in the humic acid gel which is accessible through base titration

V_g = volume of the gel

A = dissociated humic acid

If a plot of $pK^{app}(HA)\gamma$ versus α is constructed and the line is extrapolated to $\alpha = 0$, the value of the y intercept is $pK^{int}(HA)\gamma$, and the intrinsic acid dissociation constant of the repeating functional unit γ. The y intercept is $pK^{int}(HA)\gamma$ because at low ionic strength there will be negligible NaX imbibement and at zero charge on the gel surface the deviations from ideality will vanish.

The distribution of a metal cation, M^{+z}, and a neutral salt (i.e., Na^+) between two phases can be determined by the same method used to determine the acidity constant (Gamble et al. 1985). The expression for the equilibrium distribution of Na^+ and the metal cation of interest, M^{+z}, between a gel and an aqueous phase can be written as

$$pM^{+z}(g) - pM^{+z}(s) = zpNa^+(g) - zpNa^+(s) \quad (11)$$

Expansion of Equation (11) and inclusion of $pK^{app}(MA)n(z-n)\gamma$ (apparent or conditional stability constant of the metal humic complex) gives

$$pM^{+z}(s) - zpNa(s) - z\log\{C_{Na(g)} + A/V_g\} - n\log\{(A/V_g)/(M_b/V_g)\} = pK^{app}(MA)n(z-n)\gamma \quad (12)$$

If one or the other species is dominant, this analysis will result in a constant value for D1, because the deviation terms in the numerator and denominator, exp(-2ϵ psi(a)/KT), will cancel out if the charge arises exclusively from the three-dimensionally situated sites of the gel matrix.

If both species are formed the expressions for D1 and D2 would be:

$$D2 = [\beta^{int}(MA2)\gamma / \{\beta^{int}(HA)\}^2] + [(V^g)\{\beta^{int}(MA^+)\gamma\}/(A)\{\beta^{int}(HA)\gamma\}^2] \qquad (18)$$

and

$$D1 = [\beta^{int}(MA^+)\gamma/\{\beta^{int}(HA)\gamma\}^2] + [(A)\{\beta^{int}(MA_2)\gamma\}/(V_g)\{\beta^{int}(HA)\gamma\}^2] \qquad (19)$$

By plotting D2 versus V_g/A and extrapolating to $V_g/A = 0$, the y intercept would be equal to $\beta^{int}(MA2)\gamma/\{\beta^{int}(HA)\gamma\}^2$. By plotting D1 versus A/V_g and extrapolating to $A/V_g = 0$, the y intercept would be equal to $\beta^{int}(MA^+)\gamma/\{\beta^{int}(HA)\gamma\}^2$.

where m_{SM} is the molal concentration of the chelated sites, m_{SH2} is the molal concentration of the protonated sites, and m_{SH} is the molal concentration of the free chelation sites. Similar relationships can be written for each of the components. The mole fraction of free chelation sites, χ_{SH}, for the ith component in the whole mixture is

$$(\chi_{SH})_i = m_{SiH}/C_s \tag{23}$$

where the material balance summed over all m_{SiH} is equal to m_{SH}. By including expressions for the mole fraction in Equation (23), for the material balance, and for the law of mass action; the average equilibrium constant function ($\bar{K}$) for the whole mixture is expressed as

$$\bar{K} = 1/\chi_{SH} \; \Sigma K_i \exp(-\Delta G^e_i/RT)(\chi_{SH})_i \tag{24}$$

The summation in Equation (24) may be replaced by an integral if $\bar{K}$ approximates a continuous function. A continuous function is expected because of the large numbers of individual K_i functions and because the electrostatic Gibbs energy will be an increasing function of the amount of electrostatic charge (free chelation sites, SH) on the molecules and aggregates.

Shuman et al. (1983) evaluated metal binding to humic substances by an "affinity spectrum" technique, as suggested by Hunston (1975). The binding relationship of bound metal to total ligand, γ, is rewritten for multiple sites as

$$\gamma = \sum_{i=1}^{m} (n_i K_i [M])/(1 + K_i [M]) \tag{25}$$

where i is the ith class with n_i sites and with binding constant, K_i. The total number of sites, n_o, when summed over all classes is

$$n_o = \sum_{i=1}^{m} n_i \tag{26}$$

Unger and Allen[a] have applied the Shuman affinity model to the binding of metals by sediments; they found that the data does not resemble normal or gaussian probability densities for humic substances, as suggested by Posner (1966) and Perdue and Lytle (1983b), but portrayed a positive skewness toward the higher log K values. Unger and Allen[b] found that the data followed a Maxwell-Boltzman distribution instead.

(a) Unger, M. T., and H. E. Allen. 1986. "Distribution Model of Metal Binding to Natural Sediments." Drexel University. (Submitted for Publication)

(b) Unger, M. T., and H. E. Allen. 1986. "Distribution Model of Metal Binding to Natural Sediments." Drexel University. (Submitted for Publication)

and Yoshida 1978). Data in Table A.16, appendix reference 16 (Unger 1984) compared with data in Table A.16, appendix reference 14 (Allen et al. 1982) show that log K values for Grand River bulk sediment and organic fraction measured by different experimental methods, but under comparable conditions were within an order of magnitude (log K = 7.14 for organic fraction appendix reference 16, compared to 6.15 and 7.01 for appendix reference 14)

Stability constants for copper-humic acid complexes were measured under the same experimental conditions by five different experimental methods (Table A.19). For four out of the five methods, the log K values were within experimental error: 6.54, 6.61, 6.72, 6.80 for experimental methods 5, 4, 16, and 8, respectively (Tuschall and Brezonik 1983; Tuschall 1983). The anodic stripping voltametry (ASV) method gave different log K values, probably resulting from the sorption of ligand onto the surface of the electrode. Therefore, it appears that the experimental method is not the major factor that results in the reported range in K values for metal humic acid complexes.

As with Cd-humic acid complexes, the log K of Cu-humic acid (Table A.19) and Zn-humic acid complexes (Table A.28) increases as the pH increases. The data in Table A.19 (Adhikari et al. 1977) and (Tan et al. 1971) and Table A.28 indicate that log K is not highly dependent on humic acid concentration. The data in Table A.19 also indicate that there are different binding sites on the humic acid molecule and that these sites have different K values (Tuschall and Brezonik 1983; Tuschall 1983).

For the binding of zinc to soil humic acids [Table A.28 (Matsuda and Ito 1970)] and sediments (Unger 1984), the log K values appear to be dependent on the soil sample (range of log K values is 4.20 to 10.33) but did not appear to be dependent on the sediment used (range in log K values is 7.67 to 8.27). Table A.28 also shows that log K values are independent of pH over the range 3.5 to 5.5 for Zn(II) complexes. However, most studies have shown metal-humic acid complexation to be highly pH dependent.

In summary, most of the data indicate that as pH increases, log K increases. The value of K appears to be dependent on the origin of the sample in some cases, yet, in other cases, it is not. Experimental method is not a major factor in the variability in log K values. Finally, the dependence of log K on ligand concentration cannot be ascertained from the data.

EVALUATION OF STABILITY CONSTANTS

The data in Tables A.16, A.19, and A.28 were carefully evaluated to determine the percent of cadmium, copper, or zinc that would be bound to humic acid at three different pH values (Tables A.29-A.31). Some of the data in Tables A.16, A.19, and A.28 were not included in Tables A.29-A.31. For example, the data in Table A.16 (Van de Meent et al. 1981) were omitted because only the binding of cadmium to the suspended sediment as a whole and not just to the humic acid present in the sediment, was measured. The data of Guy and Chakrabarti (1979) in Tables A.16, A.19, and A.28 were omitted because Malcolm (R. Malcolm, U.S. Geological Survey, Personal Communication, 1985) has indicated that Aldrich humic acid is structurally very different from natural soil or sediment humic acid. The data of Alberts and Giesy (1983), Shuman and Cromer (1979), and Buffle et al. (1977) in Table A.19 were omitted because they dealt with binding of metals to aquatic humic acid, which has also been shown by Malcolm to be different from soil or sediment humic acid. The data in Tan et al. (1971) in Tables A.19 and A.28 were omitted because it is not known if the sample chosen is similar in properties to soil or sediment humic acid. Finally, the data in Matsuda and Ito (1970) in Table A.28 were not used because of incomplete data; the j values were not given.

The percent metal bound was calculated by the following method. First, the degree of dissociation, α, of the humic acid was calculated. This value is pH dependent. The following equation was used to determine α at a specific pH:

$$pH = 5.05 - 1.93\log\{(1-\alpha)/\alpha\} \qquad (31)$$

This equation was determined by Stevenson (1976) from the curve that described the titration of a Leonardite humic acid with base (Figure 14).

If the reaction of metal with humic acid is represented by

$$M + L \leftrightarrow ML \qquad (32)$$

then the stability constant would be

Therefore, the ratio of bound metal to free metal, [ML]/[M], can be determined from the conditional stability constant, $K_{conditional}$, and the concentration of ligand, C_L.

To compute the ratio of bound to free metal, a humic acid concentration needs to be chosen. A typical humic acid concentration is 5 mg/L (Laxen 1983), and a typical humic acid molecular weight is 5000 Daltons (Schnitzer and Khan 1972). Therefore, the total concentration of undissociated ligand used in the calculations is $1x10^{-6}$M. Further, rearrangement of Equation (35) yields

$$[M] = [ML]/K_{conditional}C_L \tag{36}$$

and substitution into Equation (37),

$$[ML] + [M] = M_T \tag{37}$$

results in Equation (38)

$$[ML] + [ML]/(K_{conditional}C_L) = M_T \tag{38}$$

or

$$[ML](1 + 1/(K_{conditional}C_L)) = M_T$$

where M_T is the concentration of total metal. Therefore, the concentration of bound ligand is

$$[ML] = M_T/\{1 + 1/(K_{conditional}C_L)\} \tag{39}$$

The percent metal bound is $\{100 \times ([ML]/M_T)\}$. Substitution of Equation (39) into this expression gives the following equation:

$$\% \text{ Metal Bound} = 100 \times \{1 + 1/(K_{conditional}C_L)\}^{-1} \tag{40}$$

According to some references at a concentration of 0.005 g/L of humic acids, appreciable binding of the metal by the humic material is predicted. When a higher humic concentration (e.g., the 5 g/L level that is more typical of sediment-water systems is considered) the predicted extent of binding is very high.

CONCLUSIONS

Data available to quantify the extent of metal partitioning between the aqueous phase and the sediment-bound humic substances is insufficient. Most of the available literature constants do not account for the effects of hydrogen ions and different electrolytes on metal sorption by reactive particulate organic carbon.

The polyelectrolyte model appears to provide adsorption constants that are compatible with the surface complexation constants for inorganic adsorbents. Establishing sediment quality criteria for trace metals, using the approach of Jenne et al. (1986) requires the experimental development of a data base of complexation constants for trace metals with the reactive organic carbon on the sediments. These complexation constants must be determined for a number of oxic sediments representative of those sediments found in streams and lakes.

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APPENDIX

REPORT TABLES

APPENDIX

REPORT TABLES

Table.A.1. Reagents used for Extraction of Organic Constituents from Soil (Stevenson 1982, p. 37)

Type of Material	Extractant	Organic Matter Extracted (%)
Humic substances[a]	Strong bases	
	NaOH	To 80%
	Na_2CO_3	To 30%
	Neutral salts	
	$Na_4P_2O_7$,NaF	To 30%
	organic acid salts	To 30%
	Organic chelates	
	Acetylacetone	To 30%
	Cupferron	
	8-hydroxyquinoline	
	Formic acid (HCOOH)	To 55%
	Acetone/H_2O/HCl solvent	To 20%
Hydrolyzable compounds		
1. Amino acids, amino sugars	Hot 6 N HCl	25-45%
2. Sugars	Hot 1N H_2SO_4	5-25%
Polysaccharides	NaOH,HCOOH,hot water	<5%
Clay-bound biochemicals	HF	5-50%
"Free" biochemicals (amino acids, sugars)	H_2O, 80% alcohol, ammonium acetate	1%
Fats, waxes, resins	Usual "fat" solvents	2-6%

[a] Considerably higher amounts of organic matter can be extracted from Spodosol B horizons with most reagents.

TABLE A.3. Elemental Analysis of Humic and Fulvic Acids (Schnitzer 1976, p. 91)

Element	% dry, ash free wt	
	HA	FA
C	50-60	40-50
H	4-6	4-6
N	2-6	<1-3
S	0-2	0-2
O	30-35	44-50

TABLE A.5. Major Oxygen-Containing Functional Groups in Humic Substances (meq/g) (Schnitzer and Khan 1972, p. 38)

Total Acidity	Carboxyl	Phenolic OH	Alcoholic OH	Carbonyl	Methoxyl
			Soil HA's		
6.6	4.5	2.1	2.8	4.4	0.3
8.7	3.0	5.7	3.5	1.8	-
5.7	1.5	4.2	2.8	0.9	-
10.2	4.7	5.5	0.2	5.2	-
8.2	4.7	3.6	-	3.1	0.3
			Coal HA		
7.3	4.4	2.9	-	-	1.7
			Soil FA's		
14.2	8.5	5.7	3.4	1.7	
12.4	9.1	3.3	3.6	3.1	0.5
11.8	9.1	2.7	4.9	1.1	0.3
			Soil Humins		
5.9	3.8	2.1	-	4.8	0.4
5.0	2.6	2.4	-	5.7	0.3

TABLE A.7. Effect of Fulvic Acid Concentration on Cadmium-Fulvic Acid Conditional Stability Constants (Saar and Weber 1979, p. 1265)

Water FA $\times 10^4$ M[a]	K $\times 10^{-3}$	Soil FA $\times 10^4$ M[b]	K $\times 10^{-3}$
0.28	8.8	0.30	29
0.56	6.5	0.61	24
1.06	2.5	1.3	18
3.18	4.4	2.4	13
		4.1	14
		5.6	12

[a]Titrations done at pH 7.0 in 0.1M KNO_3

[b]Titrations done at pH in 0.1M KNO_3

TABLE A.9. Effect of pH on Cadmium-Fulvic Acid Conditional Stability Constants[a] (Saar and Weber 1979, p. 1265)

pH	$K \times 10^{-3}$	
	Water Fulvic Acid	Soil Fulvic Acid
4.0	1.4	1.7
5.0	3.0	6.3
6.0	4.8	12
7.0	8.1	21
8.0	12	43

a) All titrations have fulvic acid concentrations of 5 to 6×10^{-4} M and 0.1 M KNO_3 supporting electrolyte at 25 C.

TABLE A.11. Experimental Methods

Numerical Code	Experimental Method
1	Anodic Stripping Voltametry (ASV)
2	AA[a]- Vary Sediment Concentration
3	AA- Vary Metal Concentration
4	Competing Ligand
5	Continuous Ultrafiltration
6	Continuous Variation
7	Differential Pulse Anodic Stripping Voltametry(DPAS)
8	Fluorescence
9	Fluorescence Quenching
10	Gel Filtration
11	Ion Exchange
12	Ion Exchange-AA
13	Ion Exchange-DPAS
14	Ion Exchange-Scintillation Counting
15	Ion Exchange-Spectrophotometric
16	Ion Selective Electrode (ISE)
17	Liquid Scintillation Counting
18	Metal Titration-AA
19	Potentiometric Titration-Conventional
20	Potentiometric Titration-Constant pH
21	Potentiometric Titration-ISE
22	Stopped Flow Spectrometry
23	Titrimetric-ASV

a) AA=Atomic Absorption Spectroscopy

TABLE A.13. Stability Constants for Al(III)-Fulvic Acid and Al(III)-Humic Acid Complexes

Sample	Concentration	Temp.	pH	μ	log K	K Units	Experimental Method	Reaction	j	Reference
Armadale Podzol(1)			3.7	0.1N KCl	3.7	L/Moles	6	3	1	1
Armadale Podzol(1)			1.70	0.1N KCl	3.7	L/Moles	15	3	1	1
Armadale Podzol(1)			2.35	0.00	5.3	L/Moles	6	3	1	1
Armadale Podzol(1)			2.35	0.15N KCl	2.9	L/Moles	6	3	1	1
Chinsura-West Bengal(2)	2.0320 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal(2)	4.0640 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal(2)	6.0960 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal(2)	8.1280 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal(2)	10.1600 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal(2)		30 C	4.0		3.15*	(L/Moles)i	11	3	0.90	2
Chinsura-West Bengal(2)		30 C	5.5		3.38	(L/Moles)i	11	3	0.90	2
Broiler House Litter(3)	7 x10—5 M		3.5	0.1N KCl	2.93	(L/Moles)i	12	3	0.60	3
	14 x10—5 M		3.5	0.1N KCl	2.91	(L/Moles)i	12	3	0.60	3
	21 x10—5 M		3.5	0.1N KCl	2.93	(L/Moles)i	12	3	0.60	3
	28 x10—5 M		3.5	0.1N KCl	2.9	(L/Moles)i	12	3	0.60	3
	9.6 x10—5 M		5.5	0.1N KCl	3.99	(L/Moles)i	12	3	0.83	3
	19.2 x10—5 M		5.5	0.1N KCl	4.01	(L/Moles)i	12	3	0.83	3
	28.8 x10—5 M		5.5	0.1N KCl	3.99	(L/Moles)i	12	3	0.83	3
	38.4 x10 —5 M		5.5	0.1N KCl	3.93	(L/Moles)i	12	3	0.83	3
	48.0 x10—5 M		5.5	0.1N KCl	3.98	(L/Moles)i	12	3	0.83	3

(1) Fulvic Acid
(2) Humic Acid
(3) Organic Matter Extract (Both HA and FA)
*Average Value

References in Tables A.15 - A.34 are cited by number and can be found in numerical order at the end of this appendix.

TABLE A.15. Stability Constants for Cd(II)-Fulvic Acid Complexes

Sample	Concentration	Temp.	pH	μ	log k1	log k2	log K	K Units	Experimental Method	Reaction	Reference
Sewage Sludge	2 x10—3 M	25 C	5.0	0.1M KClO4	3.04 L/Moles	2.27 L/Moles	2.3	L/Moles	21	1	6
Water Fulvic Acid	5-6 x10—4 M	25 C	4.0	0.1M KCl			3.15	L/Moles	21	2	7
Water Fulvic Acid	5-6 x10—4 M	25 C	5.0	0.1M KCl			3.48	L/Moles	21	2	7
Water Fulvic Acid	5-6 x 10-4 M	25 C	6.0	0.1M KCl			3.69	L/Moles	21	2	7
Water Fulvic Acid	5-6 x10—4 M	25 C	7.0	0.1M KCl			3.91	L/Moles	21	2	7
Water Fulvic Acid	5-6 x10—4 M	25 C	8.0	0.1M KCl			4.08	L/Moles	21	2	7
Soil Fulvic Acid	5-6 x10—4 M	25 C	4.0	0.1M KCl			3.23	L/Moles	21	2	7
Soil Fulvic Acid	5-6 x10—4 M	25 C	5.0	0.1M KCl			3.8	L/Moles	21	2	7
Soil Fulvic Acid	5-6 x10—4 M	25 C	6.0	0.1M KCl			4.08	L/Moles	21	2	7
Soil Fulvic Acid	5-6 x10—4 M	25 C	7.0	0.1M KCl			4.32	L/Moles	21	2	7
Soil Fulvic Acid	5-6 x10—4 M	25 C	8.0	0.1M KCl			4.63	L/Moles	21	2	7
Water Fulvic Acid	0.28 x10—4 M	25 C	7.0	0.1M KNO3			3.94	L/Moles	10	1	8
Water Fulvic Acid	0.56 x10—4 M	25 C	7.0	0.1M KNO3			3.81	L/Moles	10	1	8
Water Fulvic Acid	1.06 x10—4 M	25 C	7.0	0.1M KNO3			3.40	L/Moles	10	1	8
Water Fulvic Acid	3.18 x10—4 M	25 C	7.0	0.1M KNO3			3.64	L/Moles	10	1	8
Soil Fulvic Acid	0.30 x10—4 M	25 C	6.0	0.1M KNO3			4.46	L/Moles	10	1	8
Soil Fulvic Acid	0.61 x10—4 M	25 C	6.0	0.1M KNO3			4.38	L/Moles	10	1	8
Soil Fulvic Acid	1.31 x10—4 M	25 C	6.0	0.1M KNO3			4.26	L/Moles	10	1	8
Soil Fulvic Acid	2.4 x10—4 M	25 C	6.0	0.1M KNO3			4.11	L/Moles	10	1	8
Soil Fulvic Acid	4.1 x10—4 M	25 C	6.0	0.1M KNO3			4.15	L/Moles	10	1	8
Soil Fulvic Acid	5.6 x10—4 M	25 C	6.0	0.1M KNO3			4.08	L/Moles	10	1	8

TABLE A.16. Continued

Sample	Concentration	Temp	pH	μ	log k1	log k2	Log K	K Units	Experimental Method	Reaction	j	Referen
Grand River Sediment												
Unfractionated		20 C	7.5				5.59	L/Moles	2	1		14
Organic		20 C	7.5				7.01	L/Moles	2	1		14
Grand River Sediment										1		14
Unfractionated		20 C	7.5				6.06	L/Moles	3	1		14
Organic		20 C	7.5				6.15	L/Moles	3	1		14
Swains Mills	2.0 x10—5 M		6.5				5.72	L/Moles	23	1		15
Chapel Hill	2.9 x10—6 M		5.7				4.87	L/Moles	23	1		15
	2.9 x10—6 M		6.0				4.99	L/Moles	23	1		15
	2.9 x10—6 M		6.5				5.15	L/Moles	23	1		15
	2.9 x10—6 M		7.0				5.2	L/Moles	23	1		15
Lake Waccamaw	9.1 x10—5 M		6.5				4.51	L/Moles	23	1		15
Black Lake	12.6 x10—5 M		6.5				4.81	L/Moles	23	1		15
Sediment Fractions:												
Des Plaines-												
Bulk		25 C	7.5				5.90	L/Moles	17	1		16
Oxidizables		25 C	7.5				8.02	L/Moles	17	1		16
Grand River-								L/Moles	17	1		16
Bulk		25 C	7.5				5.93	L/Moles	17	1		16
Oxidizables		25 C	7.5				7.14	L/Moles	17	1		16
Kanzaki-								L/Moles	17	1		16
Bulk		25 C	7.5				7.08	L/Moles	17	1		16
Oxidizables		25 C	7.5				8.91	L/Moles	17	1		16
L. Michigan								L/Moles	17	1		16
Bulk		25 C	7.5				6.17	L/Moles	17	1		16
Oxidizables		25 C	7.5				8.04	L/Moles	17	1		16
Wabash								L/Moles	17	1		16
Bulk		25 C	7.5				6.75	L/Moles	17	1		16
Oxidizables		25 C	7.5				9.08	L/Moles	17	1		16
Average Value								L/Moles	17	1		16
Bulk		25 C	7.5				6.36	L/Moles	17	1		16
Oxidizables		25 C	7.5				8.24	L/Moles	17	1		16
Sphagnum peat	.15 g/20ml						6.65(4)	L/Moles	17	4	1	17
(1) See reference for description of sample												
(2) Cd Water Complexes												
(3) Weighted for value of binding capacity (4) log K int												

TABLE A.18. Stability Constants for Cu(II)-Fulvic Acid Complexes

Sample	Concentration	Temp	pH	μ	log k1	log k2	log K	K Units	Experimental Method	Reaction	i	Reference
Sewage Sludge	2 x10—3 M	25 C	5.0	0 1 M KClO4	3 88 L/Moles	2.11 L/Moles	2.30	L/Moles	21	1		6
Lake Celyn-Wales		20 C	8.0	0 02	8 80 L/Moles	8 05 L/Moles	8.42	L/Moles	10	1		8
Soil Fulvic Acid			4.0	0.1 M KNO3	5.60 L/Moles	3.95 L/Moles	4.36	L/Moles	21	1		18
Soil Fulvic Acid			5.0	0 1 M KNO3	6.00 L/Moles	4.08 L/Moles	4.6	L/Moles	21	1		18
Soil Fulvic Acid			6.0	0.1 M KNO3	6.30 L/Moles	3.78 L/Moles	4.2	L/Moles	21	1		18
Water Fulvic Acid			4.0	0 1 M KNO3	5.48 L/Moles	4.00 L/Moles	4.49	L/Moles	21	1		18
Water Fulvic Acid			4.7	0 1 M KNO3	6.00 L/Moles	3.85 L/Moles	4.39	L/Moles	21	1		18
Water Fulvic Acid			5.0	0 1 M KNO3	5.95 L/Moles	3.70 L/Moles	4.08	L/Moles	21	1		18
Water Fulvic Acid			6.0	0 1 M KNO3	6.11 L/Moles	3.85 L/Moles	4.37	L/Moles	21	1		18
Armadale Podzol	3 x10—4 M	24 –0 1 C	3.5	0.1N KCl			5.78	(L/Moles)i	15	3	1.50	19
Armadale Podzol	6 x10—4 M	24 –0 1 C	3.5	0.1N KCl			5.79	(L/Moles)i	15	3	1.50	19
Armadale Podzol	9 x10—4 M	24 –0 1 C	3.5	0.1N KCl			5.75	(L/Moles)i	15	3	1.50	19
Armadale Podzol	12 x10—4 M	24 –0 1 C	3.5	0.1N KCl			5.78	(L/Moles)i	15	3	1.50	19
Armadale Podzol	15 x10—4 M	24 –0 1 C	3.5	0.1N KCl			5.80	(L/Moles)i	15	3	1.50	19
Armadale Podzol		24 –0.1 C		0 1N KCl			5.78*	(L/Moles)i	15	3	1.50	19
Armadale Podzol	1.2 x10—4 M	24 –0.1 C	5.0	0.1N KCl			8.67	(L/Moles)i	15	3	2.00	19
Armadale Podzol	1.5 x10—4 M	24 –0.1 C	5.0	0 1N KCl			8.67	(L/Moles)i	15	3	2.00	19
Armadale Podzol	1.8 x10—4 M	24 –0.1 C	5.0	0 1N KCl			8.66	(L/Moles)i	15	3	2.00	19
Armadale Podzol	2.1 x10—4 M	24 –0.1 C	5.0	0 1N KCl			8.76	(L/Moles)i	15	3	2.00	19
Armadale Podzol	2.4 x10—4 M	24 –0.1 C	5.0	0.1N KCl			8.7	(L/Moles)i	15	3	2.00	19
Armadale Podzol	3.0 x10—4 M	24 –0.1 C	5.0	0.1N KCl			8.67	(L/Moles)i	15	3	2.00	19
Armadale Podzol		24 –0.1 C	5.0	0 1N KCl			8.69*	(L/Moles)i	15	3	2.00	19
Armadale Podzol	2.24 x10—6 M	25 C	7.6	0.01M KNO3			7.82	L/Moles	13	1		20
Armadale Podzol			3.0	0.10M KCl			3.3	L/Moles	6	3	1	1
Armadale Podzol			5.0	0.10M KCl			4.0	L/Moles	6	3	1	1
Armadale Podzol			3.0	0.10M KCl			3.3	L/Moles	15	3	1	1
Armadale Podzol			5.0	0 10M KCl			4.0	L/Moles	15	3	1	1
Armadale Podzol			3.0	0 00			4.7	L/Moles	6	3	1	1
Armadale Podzol			3.0	0 15			2.6	L/Moles	6	3	1	1
Black Lake-NC	15mg/l						5.89	L/Moles	23	1		21
Black Lake-NC	30mg/l						5.43	L/Moles	23	1		21
Black Lake-NC	60mg/l						5.54	L/Moles	23	1		21
Soil Fulvic Acid	2.8 μM		5.0	0 1M KNO3			5.78	L/Moles	7	1		22
Soil Fulvic Acid	4.8 μM		5.0	0 1M KNO3			5.90	L/Moles	7	1		22
Soil Fulvic Acid	6.7 μM		5.0	0 1M KNO3			5.70	L/Moles	7	1		22
Soil Fulvic Acid			5.0	0.1M KNO3			5.78*	L/Moles	7	1		22
Soil Fulvic Acid	2.8 μM		6.0	0 1M KNO3			5.70	L/Moles	7	1		22
Soil Fulvic Acid	4.8 μM		6.0	0 1M KNO3			5.48	L/Moles	7	1		22
Soil Fulvic Acid	6.7 μM		6.0	0 1M KNO3			5.00	L/Moles	7	1		22
Soil Fulvic Acid			6.0	0 1M KNO3			5.48*	L/Moles	7	1		22
Soil Fulvic Acid	22.1 μM		5.0	0 1M KNO3			4.68	L/Moles	9	1		23
Soil Fulvic Acid	19.7 μM		6.0	0 1M KNO3			5.03	L/Moles	9	1		23
Soil Fulvic Acid	19.6 μM		7.0	0 1M KNO3			5.45	L/Moles	9	1		23

*Average Value

TABLE A.19. Continued

Sample	Concentration	Temp.	pH	μ	log k1	log k2	log K	K Units	Experimental Method	Reaction	j	Reference
Basin Swamp:												
v:												
0-0.025	5.8 x10—6 M		6.25	0.10N KNO3			6.04	L/Moles	1	1		24
0.026-0.125	5.8 x10—6 M		6.25	0.10N KNO3			5.30	L/Moles	1	1		24
0.126-0.4	5.8 x10—6 M		6.25	0.10N KNO3								24
0-0.025	2.1 x10—5 M		6.25	0.10N KNO3								24
0.026-0.125	2.1 x10—6 M		6.25	0.10N KNO3			5.70	L/Moles	8	1		24
0.126-0.4	2.1 x10—6 M		6.25	0.10N KNO3			4.87	L/Moles	8	1		24
0-0.025	1.4 x10—6 M		6.25	0.10N KNO3			7.82	L/Moles	16	1		25
0.026-0.125	1.4 x10—6 M		6.25	0.10N KNO3			6.85	L/Moles	16	1		25
0.126-0.4	1.4 x10—6 M		6.25	0.10N KNO3			6.26	L/Moles	16	1		25
0-0.025	1.2 x10—6 M		6.25	0.10N KNO3								25
0.026-0.125	1.2 x10—6 M		6.25	0.10N KNO3			6.67	L/Moles	5	1		25
0.126-0.4	1.2 x10—6 M		6.25	0.10N KNO3			5.56	L/Moles	5	1		25
0-0.025	1.3 x10—6 M		6.25	0.10N KNO3								25
0.026-0.125	1.3 x10—6 M		6.25	0.10N KNO3			6.72	L/Moles	4	1		25
0.126-0.4	1.3 x10—6 M		6.25	0.10N KNO3			5.54	L/Moles	4	1		25
S. E. US Waters(2)			5.0		6.52-0.45	4.69-0.82	5.76		16	1		12
Broiler House Litter(3)	14 x10—6 M		3.5	0.1N KCl			7.15	(L/Moles)i	12	3	1.44	3
Broiler House Litter(3)	28 x10—6 M		3.5	0.1N KCl			7.14	(L/Moles)i	12	3	1.44	3
Broiler House Litter(3)	42 x10—6 M		3.5	0.1N KCl			7.19	(L/Moles)i	12	3	1.44	3
Broiler House Litter(3)	56 x10—6 M		3.5	0.1N KCl			7.15	(L/Moles)i	12	3	1.44	3
Broiler House Litter(3)	19.2 x10—6 M		5.5	0.1N KCl			8.26	(L/Moles)i	12	3	1.66	3
Broiler House Litter(3)	28.8 x10—6 M		5.5	0.1N KCl			8.27	(L/Moles)i	12	3	1.66	3
Broiler House Litter(3)	38.4 x10—6 M		5.5	0.1N KCl			8.24	(L/Moles)i	12	3	1.66	3
Broiler House Litter(3)	48.0 x10—6 M		5.5	0.1N KCl			8.28	(L/Moles)i	12	3	1.66	3
Sample I-Pond Water		25 C	6.0	0.1M NaNO3	5.0	9.5		(L/Moles)i	16	4	1 & 2	26
Sample III-Black River		25 C	6.0	0.1M NaNO3	4.8	10.1		(L/Moles)i	16	4	1 & 2	26
Sphagnum Peat	1.5 g/200ml						7.65(4)	(L/Moles)i	3	4	1	17
Humic Acid							5.80(4)	(L/Moles)i	16	4	1	32
Humic Acid							8.55(4)	(L/Moles)i	16	4	2	32

(1) Both HA and FA
(2) Cu-Water Complexes
(3) Organic Matter Extract (Both HA and FA)
(4) Log K int
v = metal bound/total ligand
*Average Value

TABLE A.21. Stability Constants for Fe(III)-Fulvic Acid and Fe(III)-Humic Acid Complexes

Sample	Concentration	Temp.	pH	μ	log K	K Units	Experimental Method	Reaction	i	Referer
Armadale Podzol(1)			1.70	0.1N KCl	6.1	(L/Moles)i	6	3	1	1
Armadale Podzol(1)			1.70	0.00	7.6	(L/Moles)i	6	3	1	1
Armadale Podzol(1)			1.70	0.15N KCl	5.4	(L/Moles)i	6	3	1	1
Bh Horizon-Prince Edward Island(1)	3 x10—5 M	25.0 C	1.0	0.10 N NaClO4	4.45	L/Moles	22	1		27
Bh Horizon-Prince Edward Island(1)	3 x10—5 M	25.0 C	1.5	0.10 N NaClO4	4.18	L/Moles	22	1		27
Bh Horizon-Prince Edward Island(1)	3 x10—5 M	25.0 C	2.5	0.10 N NaClO4	4.18	L/Moles	22	1		27
Chinsura-West Bengal(2)	2.0320 x10—4 M	30 C	4.0				11	3	1	2
Chinsura-West Bengal(2)	4.0640 x10—4 M	30 C	4.0				11	3	1	2
Chinsura-West Bengal(2)	6.0960 x10—4 M	30 C	4.0				11	3	1	2
Chinsura-West Bengal(2)	8.1280 x10—4 M	30 C	4.0				11	3	1	2
Chinsura-West Bengal(2)	10.1600 x10—4 M	30 C	4.0				11	3	1	2
Chinsura-West Bengal(2)		30 C	4.0		3.56*	(L/Moles)i	11	3	1	2
Chinsura-West Bengal(2)		30 C	5.5		3.87	(L/Moles)i	11	3	1	2

(1) Fulvic Acid
(2) Humic Acid
*Average Value

TABLE A.23. Stability Constants for Mn(II)-Fulvic Acid Complexes

Sample	Concentration	Temp.	pH	μ	log K	K Units	Experimental Method	Reaction	I	Reference
Armadale Podzol	0.6 x10—3 M	24- 0.1 C	3.5	0.1N KCl	1.46	(L/Moles)]	12	3	0.55	5
Armadale Podzol	1.8 x10—3 M	24- 0.1 C	3.5	0.1N KCl	1.47	(L/Moles)]	12	3	0.55	5
Armadale Podzol	3.0 x10—3 M	24- 0.1 C	3.5	0.1N KCl	1.48	(L/Moles)]	12	3	0.55	5
Armadale Podzol	4.5 x10—3 M	24- 0.1 C	3.5	0.1N KCl	1.47	(L/Moles)]	12	3	0.55	5
Armadale Podzol	5.5 x10—3 M	24- 0.1 C	3.5	0.1N KCl	1.47	(L/Moles)]	12	3	0.55	5
Armadale Podzol		24- 0.1 C	3.5	0.1N KCl	1.47*	(L/Moles)]	12	3	0.55	5
Armadale Podzol	0.6 x10—3 M	24- 0.1 C	5.0	0.1N KCl	3.78	(L/Moles)]	12	3	1.10	5
Armadale Podzol	1.8 x10—3 M	24- 0.1 C	5.0	0.1N KCl	3.82	(L/Moles)]	12	3	1.10	5
Armadale Podzol	3.0 x10—3 M	24- 0.1 C	5.0	0.1N KCl	3.8	(L/Moles)]	12	3	1.10	5
Armadale Podzol	4.5 x10—3 M	24- 0.1 C	5.0	0.1N KCl	3.73	(L/Moles)]	12	3	1.10	5
Armadale Podzol	5.5 x10—3 M	24- 0.1 C	5.0	0.1N KCl	3.78	(L/Moles)]	12	3	1.10	5
Armadale Podzol		24- 0.1 C	5.0	0.1N KCl	3.78*	(L/Moles)]	12	3	1.10	5
Armadale Podzol			3.0	0.1N KCl	2.1	(L/Moles)]	6	3	1	1
Armadale Podzol			5.0	0.1N KCl	3.7	(L/Moles)]	6	3	1	1
Armadale Podzol			3.0	0.1N KCl	2.2	(L/Moles)]	15	3	1	1
Armadale Podzol			5.0	0.1N KCl	3.7	(L/Moles)]	15	3	1	1
Armadale Podzol			3.0	0.00	2.9	(L/Moles)]	6	3	1	1
Armadale Podzol			3.0	0.15	1.7	(L/Moles)]	6	3	1	1
*Average Value										

TABLE A.25. Stability Constants for Pb(II)-Fulvic Acid Complexes

Sample	Concentration	Temp	pH	μ	log k1	log k2	log K	K Units	Experimental Method	Reaction	i	Reference
Sewage Sludge	2 x10—3 M	25 C	5	0.1M KClO4	4.22 L/Moles	2.62 L/Moles	2.77	L/Moles	21	1		6
Armadale Podzol	0.6 x10—3 M	24 –0.1 C	3.5	0.1N KCl			3.1	(L/Moles)i	12	3	0.75	5
Armadale Podzol	1.2 x10—3 M	24 –0.1 C	3.5	0.1N KCl			3.07	(L/Moles)i	12	3	0.75	5
Armadale Podzol	1.8 x10—3 M	24 –0.1 C	3.5	0.1N KCl			3.09	(L/Moles)i	12	3	0.75	5
Armadale Podzol	2.4 x10—3 M	24 –0.1 C	3.5	0.1N KCl			3.09	(L/Moles)i	12	3	0.75	5
Armadale Podzol	3.0 x10—3 M	24 –0.1 C	3.5	0.1N KCl			3.08	(L/Moles)i	12	3	0.75	5
Armadale Podzol							3.09*	(L/Moles)i		3	0.75	5
Armadale Podzol	0.6 x10—3 M	24 –0.1 C	5.0	0.1N KCl			6.14	(L/Moles)i	12	3	1.50	5
Armadale Podzol	0.9 x10—3 M	24 –0.1 C	5.0	0.1N KCl			6.13	(L/Moles)i	12	3	1.50	5
Armadale Podzol	1.2 x10—3 M	24 –0.1 C	5.0	0.1N KCl			6.12	(L/Moles)i	12	3	1.50	5
Armadale Podzol	1.5 x10—3 M	24 –0.1 C	5.0	0.1N KCl			6.13	(L/Moles)i	12	3	1.50	5
Armadale Podzol	1.8 x10—3 M	24 –0.1 C	5.0	0.1N KCl			6.15	(L/Moles)i	12	3	1.50	5
							6.13*	(L/Moles)i		3	1.50	5
Armadale Podzol			3.0	0.1N KCl			2.6	L/Moles	6	3	1	1
Armadale Podzol			5.0	0.1N KCl			4.1	L/Moles	6	3	1	1
Armadale Podzol			3.0	0.1N KCl			2.7	L/Moles	15	3	1	1
Armadale Podzol			5.0	0.1N KCl			4.0	L/Moles	15	3	1	1
Armadale Podzol			3.0	0.00			3.6	L/Moles	6	3	1	1
Armadale Podzol			3.0	0.15			2.1	L/Moles	6	3	1	1
Soil Fulvic Acid		25 C	4.0	0.1M KNO3	4.0 L/Moles				21	3	1 and 2	28
Soil Fulvic Acid		25 C	4.5	0.1M KNO3	4.3 L/Moles	9.1 L2/Moles2			21	3	1 and 2	28
Soil Fulvic Acid		25 C	5.0	0.1M KNO3	4.9 L/Moles	9.5 L2/Moles2			21	3	1 and 2	28
Soil Fulvic Acid		25 C	6.0	0.1M KNO3	6.3 L/Moles	10.1 L2/Moles2			21	3	1 and 2	28
Water Fulvic Acid		25 C	4.5	0.1M KNO3	3.7 L/Moles	8.8 L2/Moles2			21	3	1 and 2	28
Water Fulvic Acid		25 C	5.0	0.1M KNO3	4.7 L/Moles	9.3 L2/Moles2			21	3	1 and 2	28
Water Fulvic Acid		25 C	6.0	0.1M KNO3	5.1 L/Moles	10.1 L2/Moles2			21	3	1 and 2	28

* Average Value

TABLE A.27. Stability Constants for Zn(II)-Fulvic Acid Complexes

Sample	Concentration	Temp.	pH	μ	log K	K Units	Experimental Method	Reaction	j	Reference
Lake Celyn-Wales		20 C	8.00	0.02	5.14	L/Moles	10	1		8
Armadale Podzol	3.0 x10—4 M	24 -0.1 C	3.5	0.1 N KCl	1.72	(L/Moles)j	15	3	0.58	19
Armadale Podzol	6.0 x10—4 M	24 -0.1 C	3.5	0.1 N KCl	1.74	(L/Moles)j	15	3	0.58	19
Armadale Podzol	9.0 x10—4 M	24 -0.1 C	3.5	0.1 N KCl	1.73	(L/Moles)j	15	3	0.58	19
Armadale Podzol	12.0 x10—4 M	24 -0.1 C	3.5	0.1 N KCl	1.73	(L/Moles)j	15	3	0.58	19
Armadale Podzol	15.0 x10—4 M	24 -0.1 C	3.5	0.1 N KCl	1.74	(L/Moles)j	15	3	0.58	19
Armadale Podzol		24 -0.1 C	3.5	0.1 N KCl	1.73*	(L/Moles)j	15	3	0.58	19
Armadale Podzol	3.0 x10—4 M	24 -0.1 C	5.0	0.1 N KCl	2.34	(L/Moles)j	15	3	0.56	19
Armadale Podzol	6.0 x10—4 M	24 -0.1 C	5.0	0.1 N KCl	2.34	(L/Moles)j	15	3	0.56	19
Armadale Podzol	9.0 x10—4 M	24 -0.1 C	5.0	0.1 N KCl	2.34	(L/Moles)j	15	3	0.56	19
Armadale Podzol	12.0 x10—4 M	24 -0.1 C	5.0	0.1 N KCl	2.34	(L/Moles)j	15	3	0.56	19
Armadale Podzol	15.0 x10—4 M	24 -0.1 C	5.0	0.1 N KCl	2.33	(L/Moles)j	15	3	0.56	19
Armadale Podzol		24 -0.1 C	5.0	0.1 N KCl	2.34*	(L/Moles)j	15	3	0.56	19
Armadale Podzol			3.0	0.1 N KCl	2.4	(L/Moles)j	6	3	1	1
Armadale Podzol			5.0	0.1 N KCl	3.7	(L/Moles)j	6	3	1	1
Armadale Podzol			3.0	0.1 N KCl	2.2	(L/Moles)j	15	3	1	1
Armadale Podzol			5.0	0.1 N KCl	3.6	(L/Moles)j	15	3	1	1
Armadale Podzol			3.0	0.00	3.2	(L/Moles)j	6	3	1	1
Armadale Podzol			3.0	0.15 N KCl	2	(L/Moles)j	6	3	1	1
Soils(1)-										
32		Room	7	0.1N KCl	5.79	(L/Moles)j	14	3	not given	29
2		Room	7	0.1N KCl	4.62	(L/Moles)j	14	3	not given	29
31		Room	7	0.1N KCl	7.49	(L/Moles)j	14	3	not given	29
12		Room	7	0.1N KCl	5.36	(L/Moles)j	14	3	not given	29
19		Room	7	0.1N KCl		(L/Moles)j	14	3	not given	29
38		Room	7	0.1N KCl	7.59	(L/Moles)j	14	3	not given	29
33		Room	7	0.1N KCl	4.53	(L/Moles)j	14	3	not given	29
18		Room	7	0.1N KCl	6.5	(L/Moles)j	14	3	not given	29
26		Room	7	0.1N KCl	9.3	(L/Moles)j	14	3	not given	29
8		Room	7	0.1N KCl	8.34	(L/Moles)j	14	3	not given	29
1		Room	7	0.1N KCl	6.65	(L/Moles)j	14	3	not given	29
30		Room	7	0.1N KCl	8.2	(L/Moles)j	14	3	not given	29
25		Room	7	0.1N KCl	6.89	(L/Moles)j	14	3	not given	29
3		Room	7	0.1N KCl	5.75	(L/Moles)j	14	3	not given	29
20		Room	7	0.1N KCl	7.25	(L/Moles)j	14	3	not given	29
4		Room	7	0.1N KCl		(L/Moles)j	14	3	not given	29
5		Room	7	0.1N KCl	6.98	(L/Moles)j	14	3	not given	29
39		Room	7	0.1N KCl	7.01	(L/Moles)j	14	3	not given	29
24		Room	7	0.1N KCl	5.85	(L/Moles)j	14	3	not given	29
22		Room	7	0.1N KCl		(L/Moles)j	14	3	not given	29

TABLE A.28. Stability Constants for Zn(II)-Humic Acid Complexes

Sample	Concentration	Temp.	pH	μ	log K	K Units	Experimental Method	Reaction	i	Reference
Aldrich	20μg/l		6.8		5.00	l/mg HA	18	2		9
Yolo Clay loam	7.84 -39.2 mg		3.6	0.1N KCl	4.42	L/Moles	15	3	1	31
Yolo Clay loam	7.84 -39.2 mg		5.6	0.1N KCl	6.18	L/Moles	15	3	1	31
Yolo Clay loam	7.84 -39.2 mg		7.0	0.1N KCl	6.80	L/Moles	15	3	1	31
Chinsura-West Bengal	2.4880 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal	4.9759 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal	7.4637 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal	9.9520 10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal	12.4395 x10—4 M	30 C	4.0				11	3		2
Chinsura-West Bengal		30 C	4.0		2.63*	(L/Moles)i	11	3	1.09	2
Chinsura-West Bengal		30 C	5.5		3.60	(L/Moles)i	11	3	1.09	2
Garden Peat(1)		20 C	8.00	0.02	4.83	L/Moles	10	1		8
Broiler House Litter(2)	14 x10—6 M		3.5	0.1N KCl	5.32	(L/Moles)i	12	3	1.04	3
Broiler House Litter(2)	21 x10—6 M		3.5	0.1N KCl	5.40	(L/Moles)i	12	3	1.04	3
Broiler House Litter(2)	28 x10—6 M		3.5	0.1N KCl	5.43	(L/Moles)i	12	3	1.04	3
Broiler House Litter(2)	35 x10—6 M		3.5	0.1N KCl	5.45	(L/Moles)i	12	3	1.04	3
Broiler House Litter(2)	42 x10—6 M		3.5	0.1N KCl				3		3
Broiler House Litter(2)	56 x10—6 M		3.5	0.1N KCl				3		3
Broiler House Litter(2)	9.6 x10—6 M		5.5	0.1N KCl	5.75	(L/Moles)i	12	3	1.06	3
Broiler House Litter(2)	19.2 x10—6 M		5.5	0.1N KCl	5.72	(L/Moles)i	12	3	1.06	3
Broiler House Litter(2)	28.8 x10—6 M		5.5	0.1N KCl	5.72	(L/Moles)i	12	3	1.06	3
Broiler House Litter(2)	38.4 x10—6 M		5.5	0.1N KCl	5.72	(L/Moles)i	12	3	1.06	3
Broiler House Litter(2)	48.0 x10—6 M		5.5	0.1N KCl	5.74	(L/Moles)i	12	3	1.06	3
Soil Samples(3)-										
32		Room	7	0.1N KCl	10.31	(L/Moles)i	14	3	not given	29
2		Room	7	0.1N KCl	7.74	(L/Moles)i	14	3	not given	29
31		Room	7	0.1N KCl	9.26	(L/Moles)i	14	3	not given	29
12		Room	7	0.1N KCl	8.00	(L/Moles)i	14	3	not given	29
19		Room	7	0.1N KCl	8.62	(L/Moles)i	14	3	not given	29
38		Room	7	0.1N KCl	7.46	(L/Moles)i	14	3	not given	29
33		Room	7	0.1N KCl	6.99	(L/Moles)i	14	3	not given	29
18		Room	7	0.1N KCl		(L/Moles)i	14	3	not given	29
26		Room	7	0.1N KCl	7.76	(L/Moles)i	14	3	not given	29
8		Room	7	0.1N KCl		(L/Moles)i	14	3	not given	29
1		Room	7	0.1N KCl	7.34	(L/Moles)i	14	3	not given	29
30		Room	7	0.1N KCl	6.50	(L/Moles)i	14	3	not given	29
25		Room	7	0.1N KCl	9.57	(L/Moles)i	14	3	not given	29
3		Room	7	0.1N KCl	8.87	(L/Moles)i	14	3	not given	29

TABLE A.29. Percent Cadmium Bound by 0.005 g/L of Humic Acid

Reaction Number (a)	Percent Cadmium Bound pH 3	pH 4	pH 6	Reference
1 1:1 complex	0.03	0.1	0.3	11
1	33	57	82	14
1	97	99	100	16
3 1:2 complex	<.00001	<.0001	0.0007	11
4 1:2 complex	<.00001	<.0001	0.0001	10
4 1:1 complex	26	49	77	17

(a) Reactions given in Table A.12.

TABLE A.31. Percent Zinc Bound by 0.005 g/L of Humic Acid

Reaction Number (a)	Percent Zinc Bound pH			Reference
	3	4	6	
1	0.005	1	5	8
1	88	95	99	16
3	0.03	0.09	0.3	2
3	20	41	71	31
4 1:1 complex	35	60	84	17

(a) Reactions given in Table A.12.

TABLE A.33. Log K Values for Copper-Humic Acid Complexes at Specific pH Values

pH			K Units	Reference
3	4	6		
1.00	1.44	1.98	L/g	32
2.07	2.31	2.60	L/g	2
2.41	2.85	3.39	L/g	24, 25
2.85	3.29	3.83	L/g	17
3.06	3.50	4.04	L/g	8
-2.03	-1.15	-0.07	L2/g2	10
-1.04	-0.17	0.91	L2/g2	32

Table A.35. Chosen Stability Constants for Metals

	pH		
Metal	3	4	6
Cd	2.0	2.3	3.0
Cu	2.8	3.2	3.8
Zn	2.0	2.3	3.0

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