

# CADMIUM INTERACTIONS WITH NATURALLY OCCURRING ORGANIC LIGANDS

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1. Introduction	237
2. Nature of Cadmium in Natural Waters	239
3. Binding Capacity of Cadmium-Organic Complexes	241
4. Factors Affecting Cadmium Interactions with Organic Ligands	247
Acknowledgment	253
References	253

## 1. INTRODUCTION

The physical and chemical state of cadmium is dependent on inorganic water quality and must be considered when assessing cadmium toxicity and availability to aquatic biota. For example, water hardness has an antagonistic effect on cadmium toxicity to zooplankton (McKee and Wolf, 1963). Similarly, Pickering and Henderson (1966) found increases in Cd 96-hr LC<sub>50</sub> values with increasing water hardness for all fish tested, and Kinkade and Erdman (1975) reported that organisms accumulated cadmium more slowly from harder water. These results indicate that divalent cationic cadmium is the most toxic form, as is the

**Table 1. Binding Capacities of Nominal Molecular Weight Organic Fractions from Three Surface Waters in the Southeastern United States**

Station and Nominal Molecular Weight Fraction	Cadmium (ng-atoms/l)	Cadmium (ng-atoms/mg OC)	Cadmium Binding Capacity (mg-atoms/mg OC)	Saturation (%)
<b>Upper Three Runs</b>				
I > 300,000	1.8	1.9	0.15	1.1
300,000 > II > 10,000	0.18	9.0	0.0042	4.2
10,000 > III > 500	1.1	1.0	0.06	1.8
IV < 500	1.8	0.48	1.9	0.10
Total	4.9 <sup>a</sup>	—	2.1 <sup>a</sup>	—
<b>Skinface Pond</b>				
I > 300,000	6.3	2.9	0.28	2.3
300,000 > II > 10,000	0.4	2.2	0.012	0.33
10,000 > III > 500	6.5	1.4	0.32	2.0
IV < 500	1.2	0.13	4.6	0.25
Total	14.0 <sup>a</sup>	—	5.2 <sup>a</sup>	—
<b>Fire Pond</b>				
I > 300,000	2.8	2.7	0.11	2.6
300,000 > II > 10,000	0.4	2.0	0.0074	5.4
10,000 > III > 500	0.01	0.014	0.098	0.09
IV < 500	1.3	0.56	1.4	0.1
Total	4.5 <sup>a</sup>	—	1.6 <sup>a</sup>	—

<sup>a</sup> Particulates  $\geq 0.15 \mu\text{m}$  removed.

case for copper (Brown et al., 1974; Pagenkopf et al., 1974). Inorganic solubility chemistry would predict that most of the cadmium introduced into the soft-acid waters of the southeastern United States, northeastern United States, and Scandinavia would exist as the free divalent cation ( $\text{Cd}^{2+}$ ) or as aquated ions ( $\text{CdOH}^+$ ,  $B = 1.5 \times 10^4$ ;  $\text{CdO}_2^-$ ,  $B = 5.8 \times 10^8$ ) (Weber and Posselt, 1974).

Although extracellular organics from plants and animals may affect cadmium speciation in natural waters, this discussion will deal primarily with the colored, refractory polyphenolic compounds known variously as humics, fulvics, and tannins. These compounds are thought to be the result of chemical polymerization and microbial decomposition and synthesis from components of plants such as lignin (Flaig, 1964). Information available in the literature regarding interactions between cadmium and naturally occurring organic ligands is ambiguous. Weber and Posselt (1974) reported that cadmium can form stable complexes with naturally occurring organics, whereas Hem (1972) stated that the amount of cadmium occurring in organic complexes is generally small and that this element is less tightly bound than zinc by most organic ligands. Pittwell (1974) reported that cadmium would be complexed by organic carbon under all pH conditions encountered in normal natural waters, and Levi-Minzi et al. (1976) found cadmium sorption in soils to be correlated with soil organic matter content.

## 2. NATURE OF CADMIUM IN NATURAL WATERS

McGlynn (1974) observed that between 40 and 60% of the total cadmium dissolved in natural surface waters existed in the free divalent form, while Mantoura et al. (1978) found less than 11% of the cadmium to be complexed by humic materials. Allen et al. (1978) concluded that little of the cadmium in Lake Michigan exists in the free ionic form and that approximately 75% of a  $50 \mu\text{g Cd/l}$  addition to Lake Michigan water would be bound. Gardiner and Stiff (1975) found that between 10 and 25% of the cadmium complexing capacity of the river waters studied could be attributed to humic materials. Riffaldi and Levi-Minzi (1975) reported that approximately 50% of the total cadmium was bound to humics in coordination complexes, while 50% was in the readily exchangeable form. Ultrafiltration (Table 1) and ion exchange (Table 2) information indicates that more than 80% of the soluble cadmium in some waters of the southeastern United States is tightly bound to organics. Bahan et al. (1978) found that cadmium showed relatively little tendency to associate with the fulvic acid fractions of sewage sludge extract. Cadmium, a relatively weak Lewis acid, was more readily complexed by  $\text{Cl}^-$  than fulvic acid.

The relative amount of cadmium bound in natural waters examined by ion

**Table 2. Percent Cadmium Removed from Water Passing through UM-05 Ultrafilters by Anionic and Cationic Ion Exchange Resins**

Sample	Cadmium Removed by Ion Exchange Resins (%)	
	Cationic Dowex 50W)	Anionic Dowex 1-8X)
Upper Three Runs, S. C.	17	80
Skinface Pond, S. C.	15	92
Fire Pond, S. C.	50	61
Shaker Pond, Me.	<i>a</i>	<i>a</i>
Great East Lake, Me.	48	51
Mousum Lake, Me.	54	46
Deering Pond, Me.	>99	<1
Salmon Falls River, Me.	51	48
Beaver Dam Pond, Me.	>99	<1
Sunken Pond, Me.	56	55
Estes Lake, Me.	<i>a</i>	<i>a</i>
Saco River, Me.	69	21
Little Pond, Me.	91	9
Bog Pond, Me.	65	37
Sebago Lake, Me.	<i>b</i>	<i>b</i>

*a* Below detection limit.

*b* Contamination or interference.

exchange techniques ranges from less than 17% to greater than 90% (Table 2). Although not all of this can be attributed to organic binding, inorganic solubility product chemistry predicts that in Upper Three Runs Creek, South Carolina, essentially all of the cadmium would exist as the free  $\text{Cd}^{2+}$  ion. In Upper Three Runs, a coastal plain stream of high organic content, 80% of the total cadmium was removed onto anionic exchange resin. Approximately 63% of the total cadmium was in association with portions greater than a nominal diameter of 0.9 nm (as measured by ultrafiltration).

Whitfield (1975) stated that values reported for the degree of cadmium complexation by organics in seawater range from 0 to 80%. Duinker and Kramer (1977) found no cadmium-organic complexes in North Sea water, using anodic stripping voltametry. Conversley, Batley and Florence (1976) reported that 75% of the cadmium present in seawater was bound as labile organic complexes removed by Chelex-100 ion exchange resin. This indicates that chloro complexes are relatively unimportant and organic complexes important in the speciation

of cadmium in the marine environment, but that the organic-cadmium complexes formed are relatively weak.

Giesy and Briese (1977) found cadmium associated with all ultrafiltration fractions of organics in Okefenokee Swamp water. Approximately 30% of the cadmium was in portions that passed both PM-10 (10,000 M.W.) and UM-05 (500 M.W.) ultrafilters. The distribution of cadmium in ultrafilter fractions was bimodal, with the element associated with the largest and smallest fractions. The Cd/organic C ratio was greater in larger molecular weight portions, indicating preferential binding by this class of organics. Giesy and Briese (1978a), working in an upper coastal plain stream in the southeastern United States, found that the relative proportions of cadmium associated with ultrafilter fractions fluctuated with stream discharge and origin of organics. The percentage of cadmium associated with organics greater than 300,000 nominal molecular weight was highest in January, when organics were flushed from the floodplain and sloughs because of high water; the percentage associated with this portion decreased continually between January and July, with a concomitant increase in a percentage associated with smaller ultrafilter fractions. Approximately 25% of the cadmium in Upper Three Runs Creek was associated with particulates greater than  $0.15 \mu\text{m}$  in nominal diameter after large rainfalls. Reductions in the ash-free dry weight in the suspended solids fractions resulted in a concomitant decrease in cadmium content, indicating that cadmium was associated with the organic component of the suspended solids fraction.

### 3. BINDING CAPACITY OF CADMIUM-ORGANIC COMPLEXES

Many attempts have been made to determine the binding capacities of metal-organic complexes (Martell and Calvin, 1952; Chaberek and Martell, 1959; Martell, 1975; Stevenson, 1977; Buffle et al., 1977). One way of circumventing the problems of defining the type of complexes formed is to define a binding capacity (Giesy et al., 1978; Allen pers. com.). The binding capacity can be defined as the amount of  $\text{Cd}^{2+}$  bound by titrating receiving water with  $\text{Cd}^{2+}$  solution (Figure 1) or the maximum amount of  $\text{Cd}^{2+}$  reduction by titrating standards with receiving water:

$$\text{BC} = \frac{(C_i)(V_s) - (C_f)(V_s + V_t)}{V_t} \quad (1)$$

where  $C_i$  is the initial free ion concentration ( $\mu\text{g-atoms/ml}$ )

$V_s$  is the volume of standard solution (ml)

$C_f$  is the final free ion concentration ( $\mu\text{g-atoms/ml}$ )

$V_t$  is the volume of titrant (natural water of interest) added (ml)

BC is the binding capacity ( $\mu\text{g-atoms/ml}$ )

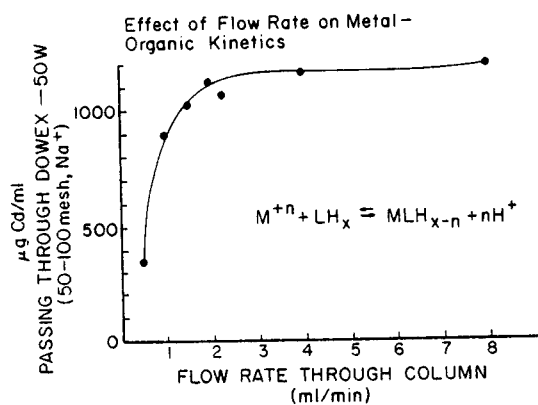


Figure 1. Maximum binding capacity as a function of flow rate through ion exchange columns.

Both techniques have given the same maximum binding capacities for all of the waters in which they have been compared. With this method the free metal can be determined by selective ion electrode or anodic stripping voltametry (ASV). However, selective ion electrodes are not available for all metals of interest, and dissolved organics may interfere with ASV determinations.

Another method utilizes atomic absorption to determine total metal concentrations with free metal removed from solution by ion exchange. A number of authors have used ion exchange resins in equilibrium with a competing ligand under Schubert conditions (Wahlgren et al., 1972; Stevenson and Ardakani, 1972; Beck et al., 1974; Crosser and Allen, 1977).

Calculation of binding capacities will be affected by the kinetics of metal-ligand reactions; thus a flow rate of metal-ligand mixture through exchange columns must be established. The flow rate through the ion exchange columns used in our laboratory is 4 to 6 ml/min (Figure 2).

Binding capacities are easy to determine, and they give insight into the relative amount of metal that can be bound by surface waters. These methods estimate maximum binding capacity per volume, which is prerequisite to assessing the impacts of metals released to surface waters (Guy and Chakrabarti, 1976), without multiple titrations. The selective ion electrode method gives maximum binding capacity values very close to those obtained by ion exchange methods (Giesy, unpublished data) and avoids problems involved in differentiating between the onset of free metal ions in solution and minimum selective ion electrode sensitivity. Binding capacities, as defined above, can be used in conjunction with statistical analyses to determine the relative importance of various mechanisms of divalent cation reduction in surface waters. Binding capacities are not dy-

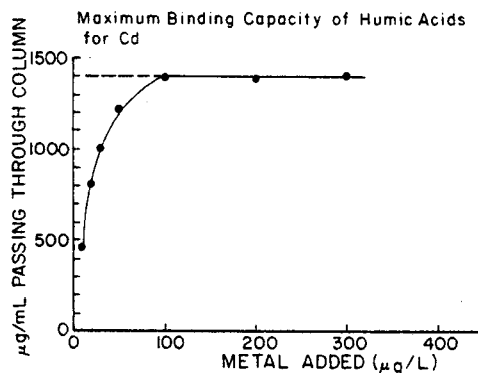


Figure 2. Maximum binding capacity determined by column ion exchange equilibrium.

namic, however, and do not give a measure of the relative strength of metal-organic associations.

The binding capacity of most surface waters for cadmium is less than that for copper and lead (Sunda and Lewis, 1976; Giesy et al., 1978). Binding capacities for naturally occurring organics extracted from several southwestern waters are given in Table 1. Skinface Pond has the highest organic carbon content of the three waters reported on here. In all cases the greatest binding capacity per unit weight of organic carbon was observed in the fraction containing the organic carbon of the smallest nominal molecular weight. The percent saturation of available cadmium binding sites by previously bound cadmium was always low.

Gardiner (1974) used equation 2 to express the relative amount of cadmium that was complexed by humics:

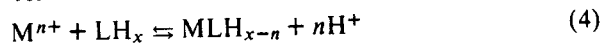
$$\frac{[\text{Cd complex}]}{[\text{Cd}^{2+}]} \propto \frac{[\text{ligand}]^{0.64}}{[\text{H}^+]^{0.20}} \quad (2)$$

and gave the following expression for calculating the degree of cadmium complexation by humic material:

$$\log \frac{[\text{Cd complex}]}{[\text{Cd}^{2+}]} = 0.64 \log A_{400} + 0.20 \text{ pH} - 1.14 \quad (3)$$

where  $A_{400}$  is the absorbance of a filtered solution at 400 nm in a 40-mm cell. Using this relationship, he found the amount of cadmium bound by humics to be dependent on both pH and organic ligand concentration. Other conclusions of this work were that the organic ligand was unprotonated and that some of the ligand molecules complexed more than one cadmium ion.

The affinity of a metal for a particular ligand has traditionally been represented by a stability constant ( $K_{stab}$ ), defined as a competitive reaction between the metal ion and  $H^+$  for reactive sites:



$$K_{stab} = \frac{(MLH_{x-n})(H^+)^n}{(M^{n+})(LH)} \quad (5)$$

where  $K_{stab}$  is the overall stability constant  
 $M^{n+}$  is the metal ion  
 $H^+$  is the hydrogen ion  
 $L$  is the organic ligand  
 $x$  is the number of protons released from the complexing ligand

Because of subtle stereochemical considerations, the order of filling of binding sites, and the molecular weights of naturally occurring organics there exist a large number of possible metal-organic bonds and thus binding energies and stability constants. Metals may be bound to refractory organics as mononuclear or polynuclear complexes, with different organics acting differently (Buffle et al., 1977). The calculation of thermodynamic and stoichiometric stability constants has been successful for metal complexes and chelates with ligands of known molecular weight and structure (Buffle et al., 1977). However, the calculation of theoretically correct overall formation constants is not possible for the complex mixture of organic ligands found in natural waters (Stevenson and Ardakani, 1972; Gardiner, 1974) because of the heterogeneous nature of the binding sites of humic acids and inability to determine molar ligand concentrations (Stevenson, 1977). Conditional stability constants have been calculated by comparing the metal binding capacity of a metal with a ligand of unknown structure to that of the same metal with a model ligand of known structure. A ratio of bound to unbound metal can be calculated at any equilibrium of added metal. However, because the binding between many of the organic-metal pairs is essentially irreversible (Zunino and Martin, 1977; Petruzzelli et al., 1977; Giesy and Briesse, unpublished data), a nonequilibrium situation exists unless all binding sites of the medium are saturated.

Conditional stability constants ( $K$ ) can be calculated using the Scatchard plot analysis (Scatchard, 1949; Mantoura and Riley, 1975; Guy and Chakrabarti, 1976; Mantoura et al., 1978). One cannot determine from Scatchard plot analyses whether a particular type of complex is formed or whether there exists a mixture of 1:1 complexes with different stability constants. However, overall estimates of conditional stability constants can be determined (equation 6).

$$\frac{\bar{V}}{M_f} = K_i(n_i - \bar{V}) \quad (6)$$



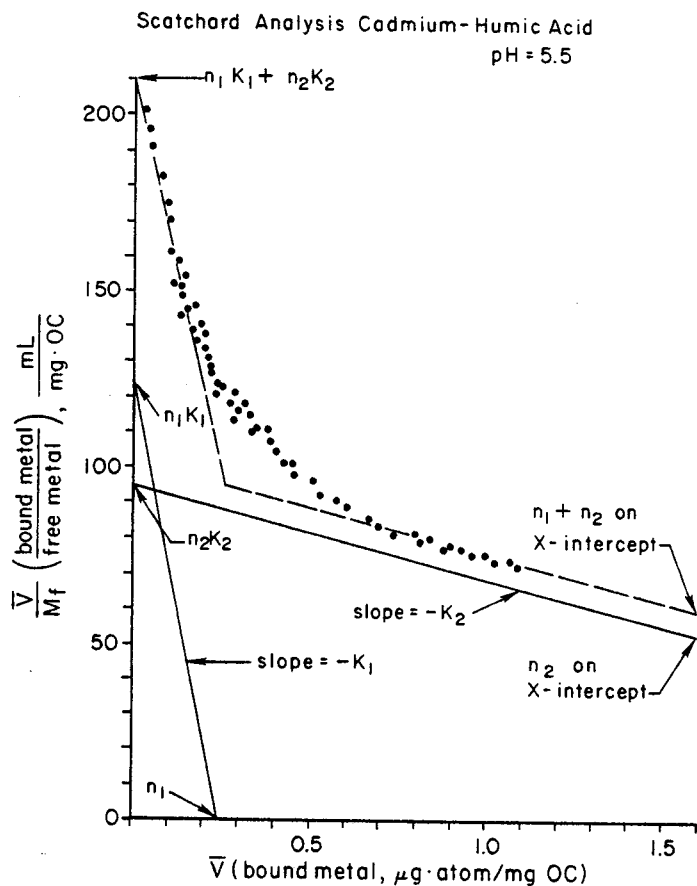


Figure 3. Scatchard plot of cadmium binding by humic acids.

where  $\bar{V}$  is the bound metal-organic concentration  
 $K_i$  are stability constants  
 $n_i$  is the number of binding sites per molecule of organic substance  
 $M_f$  is the metal unbound to ligand

An example of this method is given by using Aldrich\* humic acids† as a model compound which is accessible to other workers. The cadmium-humic interactions were studied at pH = 5.5 and humic concentration of 7 mg/l (dry weight), which

\* Aldrich Chemical Company, Milwaukee, Wisconsin.

† H 1675-2; Lot #082091.

are typical conditions in waters of the coastal plain of the southeastern United States. A plot of  $\bar{V}/M_f$  as a function of  $M_f$  can be used to determine  $n_i$  and  $K_i$  graphically (Figure 3). If this plot results in a straight line, only one type of binding site is present and the slope of this line =  $-K$  and the  $\bar{V}$ -intercept =  $n$ . However, if the resulting plot is curvilinear, as in Figure 3, the cadmium is bound by more than one type of site. When more than one type of site is indicated, the values for  $K_i$  and  $n_i$  can not be resolved graphically by extrapolating the linear regions of the curve because each type of site contributes in the nearly linear portion at both ends of the curve. The values of  $K_i$  and  $n_i$  can be calculated iteratively using equation 7.

$$\bar{V} = M_f \left[ \sum_i \frac{K_i n_i}{(1 + K_i M_f)} \right] \quad (7)$$

with partial derivatives of the form:

$$\frac{d\bar{V}}{dn_i} = \frac{K_i}{1 + K_i M_f} \quad (8)$$

$$\frac{d\bar{V}}{dK_i} = \frac{n_i}{(1 - K_i M_f)^2} \quad (9)$$

A Marquardt iterative nonlinear least squares technique was used to calculate the estimates of  $K$  and  $n$  for the data presented in Figure 3. The curve resolved into two types of binding sites (Table 4). The strength of binding is approximately 20 times as great at the stronger site, however there are approximately 1/10 as many of these sites available. The values obtained by the author for humic acids agree closely with those which Allen (personal communication) determined for cadmium in nearshore Lake Michigan water.

If computer programs are not available to solve nonlinear equations by numerical methods and one has reason to believe that two types of sites are involved in binding cadmium, good estimates of  $K_i$  and  $n_i$  can be obtained by assuming that  $-K_1$  and  $-K_2$  are represented by the slopes of the near-linear portions of the curve. Then  $n_1$  and  $n_2$  can be calculated by equations 10 and 11.

$$n_i = I_x - N_2 \quad (10)$$

$$n_2 = \frac{I_y - K_1 I_x}{K_2 - K_1} \quad (11)$$

where

$I_x = n_1 + n_2$  = the  $x$ -intercept of the line with the lesser slope

$I_y = K_1 n_1 + K_2 n_2$  = the  $y$ -intercept of the line with the greater slope

The maximum binding capacity (BC) is equal to the sum of  $n_i$ .

**Table 3. Effects of Competing Ions on Cadmium Binding Capacity in Three Southeastern Surface Waters**

Competing ions tested are listed from left to right in decreasing order of effect on cadmium binding capacity. Percent of cadmium binding capacity remaining in presence of competing ions is listed for each competing ion.

Upper Three Runs Creek					
FI	Al	Mg	Mn	Ni	Ca
	0	30	38	45	94
FII	Ca				
	100				
FIII	Al	Mg	Mn	Ni	Ca
	0	0	0	0	89
FIV	Al	Mg	Mn	Ni	Ca
	0	8	8	9	89
Skinface Pond					
FI	Al	Mg	Mn	Ni	Ca
	13	33	44	67	100
FII	Ca				
	100				
FIII	Al	Mg	Mn	Ni	Ca
	3	29	48	48	100
FIV	Al	Mg	Mn	Ni	Ca
	0	8	27	28	91
Fire Pond					
FI	Al	Mg	Mn	Ni	Ca
	12	16	18	34	100
FII	Ca				
	100				
FIII	Al	Mg	Mn	Ni	Ca
	0	1	32	33	97
FIV	Al	Mg	Mn	Ni	Ca
	0	8	15	22	91

#### 4. FACTORS AFFECTING CADMIUM INTERACTION WITH ORGANIC LIGANDS

The relative affinity of cadmium for organics in the presence of competing cations has been determined by titrating organics with cadmium in the presence of 37, 12, 41, 18, and 17 mg-atom/l of Al, Ca, Mg, Mn, and Ni, respectively. All of the metals tested were able to compete successfully with cadmium for some binding sites (Table 3). However, calcium did not compete very actively with cadmium. Aluminum was able to outcompete cadmium for binding sites with

**Table 4. Conditional Stability Constants and Number of Binding Sites for Cadmium-Humic Complexes.**

Aldrich humic acids (7.14 mg/l) constant pH = 5.5. Estimate  $\pm$  asymptotic 95% confidence interval. Non-linear least squares regression  $F_{4,65} = 722$ .

$K_1^a$	$K_2$	$n_1$	$n_2$
l/g-atom		$\mu\text{g-atom/mg HA}$	
$5.0 \pm 0.003 \times 10^5$	$2.6 \pm 0.002 \times 10^4$	$2.5 \pm 0.002 \times 10^{-1}$	$3.6 \pm 0.002$

<sup>a</sup> Units of ml/ $\mu\text{g-ATOM Cd}$ , assume density of water = 1 to cancel units.

all the organics studied and often resulted in no organic binding of cadmium. In general, Mg, Mn, and Ni reduced cadmium binding by a similar amount, suggesting they were competing for the same binding sites. Organic-specific competition was exhibited. For example, competition for cadmium binding sites was similar for Mg, Mn, and Ni for any particular organic, even though the amount of competition varied between organics.

Stumm and Bilinski (1973) suggested that metal-organic complexes are unimportant in most aquatic systems because of competition for binding sites by calcium, which is generally present in high concentrations. O'Shea and Mancy (1978) have reported that calcium inhibits labile complexation between cadmium and humic acids. At pH 3.5, Cu, Fe, Ni, Pb, and Cd all form more stable complexes with fulvic acids than does calcium (Stevenson and Ardakani, 1972). The results presented here demonstrate that calcium does not effectively compete with cadmium for many of the potential binding sites associated with naturally occurring organics. Calcium, which is present at high concentrations in most surface waters, had a total concentration of only 13  $\mu\text{g-atom/l}$  in Skinface Pond and only 3.6  $\mu\text{g-atom/l}$  in Fire Pond.

Calcium was associated with each of the fractions isolated from all three waters studied here, as well as Okefenokee Swamp water (Giesy and Briese, 1977), indicating that it is bound to organics in these fractions. The amount of calcium associated with each fraction varied among collection sites. Koljonen and Carlson (1975) reported that calcium in Finish humic lakes is associated with humus and causes coagulation and precipitation of these organics, while Beck et al. (1974) reported that calcium was not complexed or was only weakly complexed by organics in the Satilla River, Georgia. More than 99% of the calcium present in FIV of Upper Three Runs Creek could be removed by cationic exchange resins, while less than 1% was removed by anionic exchange resin. This is similar to results obtained by Benes et al. (1976) for Norwegian surface waters and indicates that the calcium in this fraction existed as  $\text{Ca}^{2+}$  or was loosely bound in labile complexes. Approximately 80% of the dissolved calcium in Upper

Table 5. Conditional Stability Constants for Cadmium Organic Complexes

Sample	K	pH	Reference
Peat	$3.7 \times 10^4$	8.0	Mantoura et al. (1978)
Lake	$3.7 \times 10^4$	8.0	Mantoura et al. (1978)
	$5.0 \times 10^4$	8.0	Mantoura et al. (1978)
Loch	$8.9 \times 10^4$	8.0	Mantoura et al. (1978)
	$7.4 \times 10^4$	8.0	Mantoura et al. (1978)
Seawater	$4.9 \times 10^4$	8.0	Mantoura et al. (1978)
Soil	$1.2 \times 10^5$	8.0	Mantoura et al. (1978)
Peat	$1.2 \times 10^5$	4, 5, 6	Stevenson (1977)
Leonardite humic acid	$1.2 \times 10^6$	4, 5, 6	Stevenson (1977)
Soil humic acid	$1.1 \times 10^6$	4, 5, 6	Stevenson (1977)
Humic acid	$1.1 \times 10^5$	6.8	Guy and Chakrabarti (1976)
Tannic acid	$1.8 \times 10^4$	6.8	Guy and Chakrabarti (1976)
Lake Michigan			
Nearshore	$1.2 \times 10^8$	—	Allen et al. (pers. comm.)
Offshore	$8.2 \times 10^7$	—	

Three Runs water was bound, while more than 50% of the total calcium was retained by ultrafilters of greater than 0.0009-mm nominal pore diameter in all cases. Calcium binding sites were all filled, but the humics still exhibited binding capacity for cadmium. Calcium may be displaced from organics by cadmium or may be bound by different mechanisms, thus not competing for the same sites.

Both relative electronegativity and ionic radius are important parameters in determining the stability of metal-organic complexes (Jameson, 1976). The low affinity of naturally occurring organics for  $\text{Ca}^{2+}$  can be explained by its large ionic diameter and low relative electronegativity. Aluminum, which was a highly successful competitor of cadmium, has the smallest ionic radius and highest relative electronegativity of the ions studied. Aluminum also has a "rare-gas" octet structure due to its completely filled *d* shell and forms stable complexes with oxygen-donor ligands (Jameson, 1976). As a trivalent ion, aluminum may also have a greater affinity for organics.

Stability constants reported for cadmium-organic complexes in surface waters range over several orders of magnitude (Tables 4 and 5) and are generally lower than those for copper and lead. True stability constants should be valid for all cadmium concentrations encountered because the ratio of complexed to uncomplexed cadmium is independent of the total concentration of the element, provided that the ligand is in excess. Since humic acids are a mixture and different fractions may have different complexing properties, low concentrations

**Table 6. Number of Cadmium Atoms Bound ( $N_i$ ) Expressed as Total, Carboxylic, and Phenolic Acidity**

Fraction	Total Acidity		Carboxylic Acidity		Phenolic Acidity	
	$n_1^a$	$n_2^a$	$n_1$	$n_2$	$n_1$	$n_2$
Par Pond humic acids						
Total	0.00065	0.0020	0.0017	0.0052	0.0010	0.0032
FI > 300,000	0.0055	0.065	0.0094	0.108	0.013	0.0156
FII < 300,000	0.013	0.025	0.026	0.051	0.025	0.049
Aldrich humic acids						
Total	0.0045	0.13	0.032	0.95	0.0052	0.156
FI > 300,000	0.002	0.18	0.011	0.93	0.003	0.23
FII < 300,000	0.0036	0.136	0.023	0.88	0.0042	0.160

<sup>a</sup> Values of  $n$  reported as mg-atoms Cd/mequiv humic acid.

of metals may be more highly complexed at a given humic acid concentration than at higher metal concentrations when less active sites are used (Gardiner, 1974; Jenne and Luoma, 1975). Trace metals in natural waters are often not in a state of equilibrium with the organic and inorganic ligands present, thereby greatly complicating equilibrium treatments of metal ions and complexes (Martell, 1975). Gardiner (1974) concluded that the humic concentration was largely unimportant in the range studied (6.6 to 86 mg/l). On the contrary, MacCarthy and Smith (1978) suggested that conditional stability constants for metal-humic interactions are ligand dependent. It is suggested that studies of cadmium-organic interactions be made at several ligand concentrations in the range expected in the environment of interest. Gardiner (1974) found that the fraction of cadmium complexed by humics was only slightly dependent on pH. Hydrogen ion effects are not surprising since we have assumed a competitive interaction between  $H^+$  and  $M^{2+}$  (equations 4 and 5).

Binding capacity studies have indicated that the amount of cadmium bound by organics is often small. Guy and Chakrabarti (1976) reported  $n_i$  values of 3 and 11 nmol Cd/g organic for the tannic and humic acids listed in Table 5.

When  $n_i$  is reported as gram-atoms per gram equivalent weight of total, carboxylic, and phenolic acidity, it can be seen that cadmium does not occupy many of the potential binding sites (Table 6) as compared to lead and copper, which occupy essentially all of the acidic functional groups, when possible binding sites are saturated. Theoretically, if 1:1, 2:1, or mixed complexes are formed, two equivalents should be required to bind  $Cd^{2+}$ . Thus, if all of the acidic functional groups were used, a maximum of 0.5 g-atom Cd/g-equiv humics could

Table 7. Pairwise Correlations for Surface Waters in the Northeastern United States ( $n = 12$ )

Parameter	[Cd] <sup>a</sup>	[Cd BC] <sup>b</sup>
pH	-.55 ***	.68 ***
OC <sup>b</sup>	.43 ***	-.49 *
Cu BC	.46 *	-.55 **
Pb BC	.00 NS	.00 NS
Cu	.57 **	-.41 NS
Ca	-.47 *	.72 ***
Cd BC	-.78 ***	

<sup>a</sup> \*  $p < .10$ , \*\*  $p < .05$ , \*\*\*  $p < .01$ , NS = not significant.

be bound, as is the case for lead. If an  $n_i$  value is much greater than 0.5, such as that for  $n_2$  calculated for Aldrich humics on a carboxylic acidity basis, that type of functional group model alone is not sufficient to explain the metal binding observed. When a very small number relative to 0.5 is observed, as with the total acidity model for Par Pond humics (Table 5), very few of the model functional groups are actually possible binding sites for cadmium.

Heavy transition elements to the right of the periodic table generally show smaller coordination numbers than do their lighter counterparts, which have greater apparent ionic radii, presumably because their directional valence demands are more stringent. The ionic radius of cadmium (0.92) is large enough that this element does not readily substitute in crystalline structures of clay but is bound to the soil humus fraction directly (Anderson, 1977). Thus, the large difference between lead and cadmium in the number of potential binding sites probably cannot be explained by lead binding to clays that are associated with the humics. Cadmium, however, does have a lower relative electronegativity (1.46) than either copper (1.75) or lead (1.55).

We have discussed cadmium binding by organics in the laboratory and in the unique surface waters of the southeastern United States, but we need to address the broader question of whether organics are important in determining the speciation of cadmium in other surface waters. To address this question binding capacities have been measured and correlated with chemical parameters of the

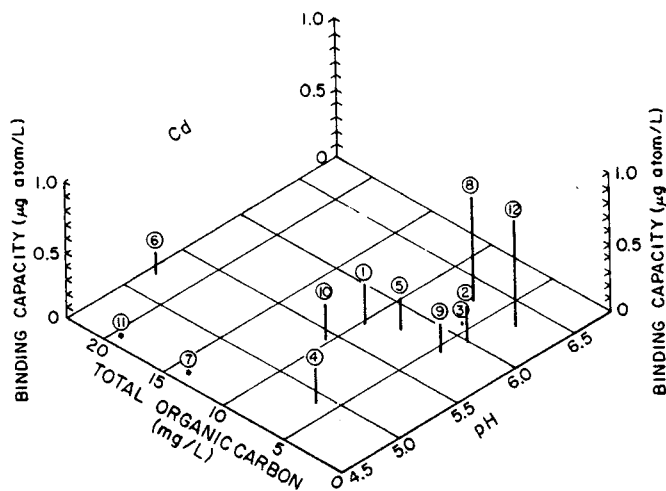


Figure 4. Cadmium binding capacities of surface waters as a function of pH and organic carbon.

surface waters of interest in the northeastern United States (Giesy et al., 1978) and in northwestern Europe (Giesy and Briese, 1978b).

Cadmium binding capacity (Cd BC) in surface waters from the northeastern United States was found to be inversely related to organic carbon (OC) and positively correlated with pH (Table 7). This result, due in part to the fact that pH and OC are inversely correlated in these waters, indicates that Cd BC was controlled by inorganic compounds over wide ranges of pH and OC (Figure 4). Thus, inorganic species are the most important in determining cadmium speciation, and OC is not at all important for the waters studied in the northeastern United States. Organic carbon was also unimportant in explaining a significant amount of the variability in cadmium binding capacity of northern European waters (Giesy and Briese, 1978b). A linear multiple regression model, using  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  as independent variables, resulted in the prediction equation

$$\text{Cd BC} = -5.7 \times 10^{-1} + 1.2 \times 10^5 [\text{CO}_3^{2-}] + 1.08 \times 10^1 [\text{SO}_4^{2-}]$$

with a coefficient of determination ( $R^2$ ) of .97. Gardiner (1974) reports that for naturally occurring organic ligands to be effective at complexing cadmium at a concentration of  $10^{-8}$  M it would have to have a stability constant of approximately  $10^8$ . The relative importance of naturally occurring organics in regard to cadmium speciation in surface waters is regionally specific, and no completely accurate generalization can be made about all waters.

Gardiner (1974) suggested that, because a substantial proportion of the total



dissolved cadmium is expected to be present as the free ion, availability and toxicity in biota can be assessed with reasonable accuracy from a knowledge of total cadmium concentration without reference to the degree of complexation, unless the toxicity of cadmium complexes present is much greater than that of free  $Cd^{2+}$ . Giesy et al. (1977) studied the effects of naturally occurring organics on the toxicity of cadmium to the cladoceran *Simocephalus serrulatus* and found that all nominal molecular size organics bound cadmium measurably at the concentrations in which they were observed in the environment. All nominal size organics reduced cadmium toxicity except those less than 0.9 nm (500 M.W., when compared to globular proteins), which increased cadmium toxicity relative to controls. This synergism may be due to cadmium-organic complexes that are more available to these relatively small molecular weight organics by reason of juxtapositioning and uptake facilitation.

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