

# Distribution of Dissolved Organic Carbon and Metal-Binding Capacity Among Ultrafilterable Fractions Isolated from Selected Surface Waters of the Southeastern United States

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**ABSTRACT** / The binding capacities of surface waters for Cd, Cu, and Pb were determined for eight water samples representing four rivers and two swamps from Florida and Georgia in the southeastern United States. The binding capacity ranges were CdBC = 0.04 to 0.79  $\mu\text{g atm/L}$ , CuBC = 1.0 to 5.4  $\mu\text{g atm/L}$ , and PbBC = 5.0 to 17.8  $\mu\text{g atm/L}$ . Binding capacity values from the southeastern United

States are shown to be in good agreement with values reported from the northeastern part of the country and northern Europe. The CdBC was due primarily to inorganic ligand binding, while PbBC was predominantly a result of organic matter. The CuBC was due to a complex function of both organic and inorganic binding. Significant portions of the CuBC and PbBC could be removed from the waters by ultrafiltration of particles between 0.45  $\mu\text{m}$  and 52  $\text{\AA}$  in diameter. Ultrafiltration, even to removing particles  $> 13 \text{\AA}$  diameter, did not affect the CdBC. Distributional studies of the dissolved organic carbon in these systems reveal that significant fractions of the DOC are present in the ultrafilterable fraction which contains significant portions of the CuBC and PbBC.

## Introduction

The chemical speciation of trace metals in aquatic systems is widely studied because of its importance in the prediction of transport, bioavailability, and fate of metals (Stumm and Morgan 1981; Forstner and Wittmann 1981; Jenne 1979). Since the chemical form and overall charge of trace metal species can affect important mechanisms such as solid/solution exchange reactions and biological toxicity, a knowledge of chemical species and their interconversion rates is critical to our understanding of trace metals in aquatic systems. Similarly, it is important to know how much stress, in the form of trace metal additions, aquatic systems are capable of accommodating. One measure of the ability of systems to buffer trace metal additions is the metal-binding capacity of the water. Unfortunately, metal-binding capacity is defined by variable operational techniques rather than by a widely agreed upon standard protocol (Truitt and Weber 1981). However, the concept is useful in establishing limits of buffering capacities for specific metals in waters. If care is taken, it allows intercomparison of this buffering capacity in waters among geographical regions.

Several investigators have estimated metal-binding capacities in a wide variety of waters using a diversity of analytical methods (Neubecker and Allen 1983). This large matrix of methods and waters has naturally led to a considerable variety of binding capacity estimates for certain metals and caused differences of opinion as to the relative importance of various ligands in determining binding capacities. One of the more important controversies regards the role of organic ligands in determining the binding capacity of metals relative to inorganic

ligands. This is certainly not a trivial question as the nature of the complex can greatly affect the overall charge of the complex as well as the rates of interconversion between complexes.

Here we present binding capacity estimates for the metals Cd, Cu, and Pb from several surface waters of Florida and Georgia. These data should add to the data base of metal-buffering capacities by providing representative values for waters normally characterized by, but not limited to, low pH and high dissolved organic carbon concentrations. In addition, by choosing the metals and techniques for estimating these binding capacities, we are able to compare and contrast our results with published data from other geographical regions with a minimum of variation due to methodological differences. Finally, we will discuss the relative importance of organic versus inorganic ligands in determining binding capacities for these metals over a wide range of physicochemical parameters but from a relatively small geographic region.

## Collection Sites and Methods

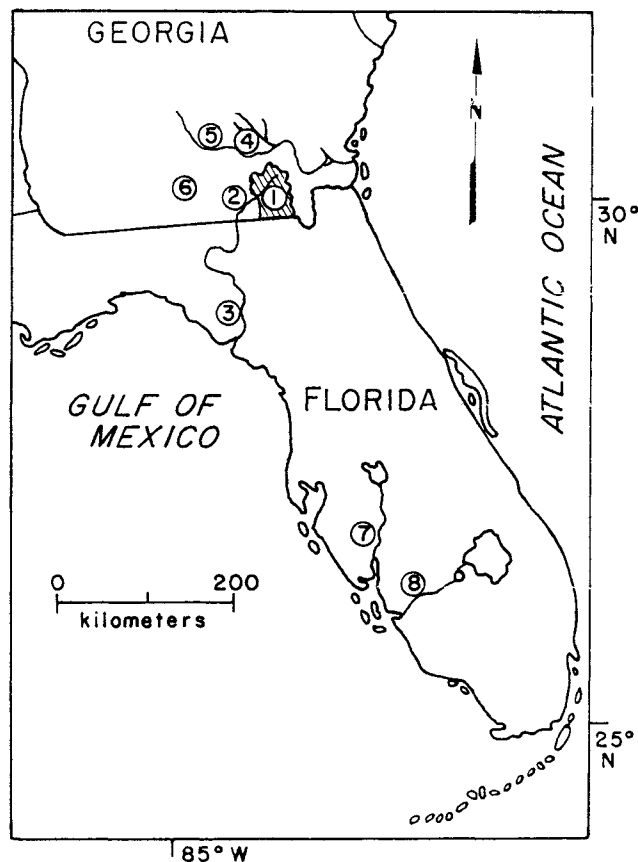
Surface water samples ( $\sim 50 \text{ L}$ ) were collected at eight locations from six waters in Georgia and Florida, between November 26 and 28, 1979 (Fig. 1). Locations were chosen where major highways crossed rivers: Caloosahatchee River at Florida State Highway 31 near Olga, Florida; Peace River at Florida State Highway 70 near Arcadia, Florida; Suwanee River at U.S. Highway 19 near Chiefland, Florida; Suwanee River at U.S. Highway 441 near Fargo, Georgia; the Satilla River at U.S. Highway 441 near Douglas, Georgia; and the Satilla River at Georgia State Highway 82 near Waycross, Georgia. In addition, the Okefenokee Swamp was sampled at Billy's Lake near the Stephen C. Foster State Park at Fargo, Georgia, and Banks Lake was sampled at Georgia State Highway 37 near Lakeland, Georgia.

Samples were filtered on the day of collection (0.45- $\mu\text{m}$  membrane filters, Millipore Corp.). Temperature, dissolved

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**Figure 1.** Locations of southeastern United States rivers and swamps sampled November 26–28, 1979.

oxygen, pH, and conductivity were determined using a model 8000 Surveyor System (Hydrolab Corp.). Alkalinity (American Public Health Association 1976) was determined in the field. Aliquots of the filtered water were reserved for dissolved organic carbon (DOC, Beckman model 915 Total Carbon Analyzer), dissolved sulfate (Baumann 1976), chloride (American Public Health Association 1976), and trace element analysis. The latter were fixed with Teflon® distilled  $\text{HNO}_3$  and stored cold in acid-washed polyethylene bottles. Upon return to the laboratory, two liters of the filtered water samples were reserved for binding capacity determinations. The remaining water samples were ultrafiltered sequentially through two Diaflo® Hollow Fiber Bundles (H10X100 and H10P5, Amicon Corp.) to retain colloidal matter of  $>52$  and  $>13$  Å diameter, respectively. Aliquots of the filtrates were reserved for binding capacity determinations, while additional aliquots of both the filtrates and the concentrates were kept for DOC analyses.

Binding capacities of the whole waters and the ultrafiltered waters were conducted for Cd, Cu, and Pb using ion-selective electrodes (Orion Corp.) and the method outlined by Giesy and others (1978). All water samples on which binding capacities were determined were adjusted to  $\text{pH } 4.70 \pm 0.10$  with Teflon® distilled  $\text{HNO}_3$ . Elemental analyses of the major elements Na, K, Ca, and Mg were determined with a Jarrell-Ash Plasma Autocomp 750 ICP Emission Spectrometer. Minor element analyses—As, Cd, Cu, Fe, Mn, Pb—were performed with a Perkin-Elmer model 306 Atomic Absorption Spectrophotometer equipped with an HGA-2100 Graphite Furnace.

Statistical analyses were conducted using the Statistical Analysis System (Helwig and Council 1979).

## Results and Discussion

### Water Chemistry and Organic Carbon Distribution

The waters examined in this study represent a broad range of physicochemical characteristics (Table 1) and include high organic concentration, soft waters such as the Okefenokee Swamp (0); the Suwanee River at Fargo, Georgia (F); the Satilla River at Douglas (D) and Waycross, Georgia (W); and Banks Lake (B), which are characterized by low pH and low conductivities. They also include the harder waters of the Suwanee River at Chiefland, Florida (Ch); the Peace River (P) and the Caloosahatchee River (Ca), which have neutral to basic pH values, higher conductivities, and appreciable  $\text{CaCO}_3$  alkalinities. All the waters sampled are well aerated and contain substantial ( $\geq 11.4$  mg/L) DOC concentrations.

Four of the rivers examined in this work have been analyzed previously (Alberts and Evans 1979). Comparison of the physical and chemical data from this study with data taken in 1978 indicates that the Peace River and the Suwanee River at both Fargo and Chiefland have changed very little with regard to major cations, while DOC has increased significantly in the Suwanee system. This increase in DOC may be the result of differences in season represented by the sampling periods and may be due to decomposition of vegetation in the Okefenokee Swamp, which acts as the headwaters for the river. The Caloosahatchee River exhibited the greatest change between the two sampling periods with a doubling of the DOC concentration, a five-fold increase in conductivity, and a ten-fold increase in Na and Mg concentrations. These dramatic changes are largely due to an influx of major ions from tidal influences in the estuary, since the sampling site is close to the mouth of the river. The two-fold increase in DOC can not be explained from the current data but may represent a flushing of organic matter from the citrus groves along the river's course.

The station on the Satilla River at Waycross, Georgia, was

Table 1 Physicochemical parameters of eight southeastern United States waters

	O	F	Ch	D	W	B	P	Ca
C°	18.5	18.6	20.0	15.4	18.6	20.9	22.6	24.6
pH	4.0	4.1	7.6	5.9	5.6	5.4	7.0	8.3
DO (mg/L)	8.9	9.0	8.9	9.4	9.6	7.9	8.4	7.7
Alkalinity (mg CaCO <sub>3</sub> /L)	—	—	2.15	0.08	0.04	—	0.86	3.0
Cond (μmhos)	76	74	304	61	65	36	404	1950
DOC (mg/L)	29.1	47.3	23.6	14.3	14.6	11.4	11.7	32.8

Table 2 Concentrations (p[M])<sup>a</sup> of specific cations and anions of waters studied<sup>b</sup>

	O	F	Ch	D	W	B	P	Ca
Na	3.72	3.80	3.54	3.70	3.66	3.82	3.15	1.80
K	5.09	5.25	4.66	4.15	4.34	5.25	4.17	3.42
Ca	4.66	4.80	3.05	4.89	5.05	4.62	3.12	2.82
Mg	4.46	4.48	3.51	4.11	4.25	4.59	3.18	2.59
As	8.55	8.51	7.36	7.80	7.80	8.05	7.42	7.32
Cd	9.15	9.10	8.70	9.36	9.05	9.05	8.89	8.92
Cu	7.36	7.80	7.19	7.68	7.72	7.85	7.40	7.09
Fe	5.11	4.96	5.54	5.09	4.85	5.96	5.72	5.85
Mn	6.26	6.24	6.85	5.89	5.96	6.06	6.44	7.42
Pb	8.42	7.77	8.80	9.11	8.24	8.74	8.68	8.35
Cl <sup>-</sup>	3.57	3.64	3.60	3.47	3.54	3.70	3.18	1.74
SO <sub>4</sub> <sup>-2</sup>	4.17	4.13	3.82	4.72	4.17	4.21	3.13	2.92
OH <sup>-</sup>	10.0	9.89	6.40	8.10	8.40	8.62	7.00	5.70
CO <sub>3</sub> <sup>-2</sup>	>13	>13	7.06	10.2	10.7	>13	8.05	6.21

<sup>a</sup>p[M] = -log[M].

<sup>b</sup>[CO<sub>3</sub><sup>-2</sup>] calculated assuming air equilibration at measured pH value.

also sampled in both studies. It was noted (Alberts and Evans 1979) that the data from 1978 had high pH and major cation concentrations relative to data collected in 1969 (Beck and others 1974). The data from this study, 1979, show that the pH values and major element concentrations have decreased relative to those reported in 1978 (Tables 1 and 2) but are still high compared to the work of Beck and others (1974). This increase in pH and major elemental concentration over the period of ten years is substantiated by the data from the Satilla River at Douglas taken in 1979 (Tables 1 and 2) which agree with the data from the Waycross station and also show an increase over the same location in 1969 (Beck and others 1974). While it is difficult to state that the Satilla River has changed during the ten years between 1969 and 1979, our observations show that the pH and major element concentrations have increased. However, it can not yet be demonstrated that these changes are due to changes in usage of the river and its watershed or that they simply reflect seasonal variations in composition. Also, care must be exercised when making generalizations about changes in river water chemistry based on isolated samples. It is interesting to note that the two stations on the Satilla River

have similar physicochemical parameters, whereas the two stations on the Suwanee River (Fargo, Georgia, and Chiefland, Florida) have significantly different values of these parameters. The marked differences in the Suwanee River result from passage through a region of phosphate deposits in middle Florida. Thus, it appears that if the Satilla River is being altered, the process is occurring over a large area of the river basin rather than being due to an isolated source as in the case of the Suwanee River.

The water chemistry of Banks Lake shows that the pH of the system has increased by one unit and that the DOC has increased from 8 to 11 mg/L since 1972 (Schindler and Alberts 1974). The Ca and Mg concentrations have remained approximately constant during that time period. In addition, the physicochemical parameters from the Okefenokee Swamp have changed little between 1975 and 1979 (Giesy and Briese 1977) with the exception of Ca, which has decreased from 5.9 to 0.9 mg/L.

The DOC concentrations at the sample sites, along with the distribution of the DOC in ultrafiltered fractions, are shown in Table 3. Recoveries of DOC for five of the eight locations are

Table 3 Distribution and percent recovery<sup>a</sup> of DOC (mg/L) among ultrafiltration fractions

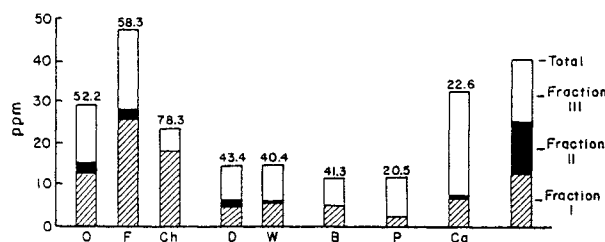
Location	DOC <4,500 Å	Fraction <sup>b</sup> I	DOC <52 Å	Fraction <sup>b</sup> II	DOC <13 Å	% Recovery
O	29.1	18.5	16.2	3.4	13.9	123
F	47.3	1.0	21.8	1.8	19.7	47.6
Ch	23.6	2.1	5.0	0.2	5.4	32.6
D	14.3	5.6	9.6	0.5	8.1	99.3
W	14.6	5.3	9.2	0.1	8.7	96.6
B	11.4	3.1	6.8	0.7	6.7	92.1
P	11.7	1.4	9.5	0.2	9.3	93.2
Ca	32.3	4.7	25.6	1.5	25.0	96.6

<sup>a</sup>Percent recovery = (Fraction I + Fraction II + DOC <13 Å) 100/(DOC <4500 Å).

<sup>b</sup>Fraction I = material <0.45 μm, but >52 Å; Fraction II = material <52 Å, but >13 Å.

quite good. However, recoveries for the two samples coming from the Suwanee River system are low while the sample from the Okefenokee is enriched in DOC. There is no ready explanation for the observed pattern of recoveries. The single high recovery value could be the result of compounding a small positive error in estimation of the DOC of the concentrated Fraction I which would be magnified when the volumes of the concentrate are corrected back to the volume of the sample. Low recovery values would indicate the interaction of the filter with a portion of the DOC in a nonreversible manner. However, if the filters were undergoing such a reaction, it would be expected that low recoveries would be observed in all cases. The fact that low recoveries are only observed at two locations and that those locations are in the same river system indicates that either the proposed interaction is not occurring or that it is only occurring with selected organic components of the Suwanee River. Finally, the apparent discrepancies in recoveries appear to occur only in the Fraction I concentrate, since the Fraction II concentrate provides a reasonable mass balance between the DOC values for material <52 Å and <13 Å. Whatever the reason for the discrepancies in the percent recoveries, we feel that the error lies in the values given for the Fraction I concentrates and that the values for the filtrates are reliable within experimental error.

Based on the values obtained for the DOC concentrations in the ultrafiltrates, the distribution of DOC among size classes and within the study sites is shown in Fig. 2. In all of the systems studied, some portion of the DOC can be retained by the ultrafilters. The amount of material that can be separated in this manner ranges from 20.5 to 78.3% of the DOC, which is defined as the carbon that passes a 0.45-μm membrane filter. Many authors have noted that DOC can be fractionated into size classes using various separation techniques. However, since all of these techniques differ in their definition of size separation and more importantly in the way in which they interact with a sample, it is difficult to compare the data



**Figure 2.** Distribution of dissolved organic carbon among ultrafiltrable fractions of eight southeastern United States waters sampled November 26–28, 1979. Fraction I = material <0.45 μm but >52 Å; Fraction II = material <52 Å but >13 Å; Fraction III = material <13 Å; percent of total DOC in Fractions I + II is indicated in numbers above bars.

gathered in this study with published data using other methodologies. Thus, valid comparisons between the distribution of DOC with earlier work by Beck and others (1974) on the Satilla River and Giesy and Briese (1977) in the Okefenokee Swamp, or Schindler and Alberts (1974) on Banks Lake is questionable. Valid comparison can be made to the work of Alberts and Evans (1979) in which the same techniques were employed on some of the same sampling locations. If such a comparison is undertaken, it is observed that the DOC in both the Suwanee River at Fargo, Georgia, and in the Caloosahatchee River have approximately doubled between 1978 to 1979, while the DOC in the Satilla River at Waycross, Georgia, has increased by 4.8 mg/L and the Peace River has decreased by 3.9 mg/L DOC. Furthermore, in 1978, the ultrafilter Fractions I and II accounted for less than 20% of the total DOC in all rivers examined, with most of the ultrafilterable DOC in Fraction II. In 1979, a higher percentage of DOC was removed by ultrafiltration in the rivers, with a preponderance of ultrafilterable DOC in Fraction I, e.g., the larger size class.

What is the cause of these large changes in DOC distribution within the same river systems, sampled by the same

Table 4 Measured<sup>a</sup> and calculated<sup>b</sup> binding capacity values for Cd, Cu, and Pb

	CdBC		CuBC		PbBC	
	Measured	Predicted	Measured	Predicted	Measured	Predicted
O	0.36	0.23	2.7	2.9	17.8	12.7
F	0.20	0.23	4.1	4.5	16.6	18.1
Ch	0.20	0.23	1.5	1.9	8.5	11.0
D	0.30	0.23	1.0	1.4	8.5	8.2
W	0.04	0.23	1.3	1.7	7.2	8.3
B	—	0.23	1.0	1.4	5.0	7.4
P	0.30	0.24	3.0	3.4	9.7	7.4
Ca	0.79	0.79	5.4	5.8	13.7	13.8

<sup>a</sup>Binding capacity in  $\mu\text{g atm/L}$ .

<sup>b</sup> $\text{CdBC} = 2.22 \times 10^{-7} + 3.16 \times 10^{-5}[\text{Cl}^-]$ ,  $R^2 = 0.810$ .  $\text{CuBC} = 1.81 \times 10^{-7} + 8.62 \times 10^{-8}[\text{DOC}] + 3.26 \times 10^{-3}[\text{SO}_4] - 6.29[\text{OH}^-] + 18.18[\text{CO}_3^-]$ ,  $R^2 = 0.999$ .  $\text{PbBC} = 3.93 \times 10^{-6} + 3.0 \times 10^{-7}[\text{DOC}]$ ,  $R^2 = 0.686$ .

techniques? The samples we are comparing are separated by a year in time and represent September versus November in the annual cycle. In addition, the pH values in some of the systems have changed. The pH of the Caloosahatchee River has increased from 7.3 to 8.3, while the pH of the Satilla River at Waycross has decreased from 6.5 to 5.6. Both the Peace River and the Suwanee River at Fargo have had relatively constant pH values of 7.0 and 4.2, respectively. It may be postulated that since humic acids behave as polydisperse systems at pH values below 6 and above 8, and as monodisperse systems at neutral pH values (Wershaw and Pinckney 1971) these pH shifts may be instrumental in the observed differences, since the separation technique involves size exclusion. However, while the Peace River exhibited approximately the same distribution of material at the two sampling times, the Suwanee River at Fargo, which did not change pH between the two years, exhibited a shift from 19.7% ultrafilterable DOC in 1978 to 58.3% ultrafilterable DOC in 1979. Furthermore, in 1978 only 1.8% of the ultrafilterable material was in Fraction I, while 53.9% occurred in Fraction I in 1979. Similarly, the Caloosahatchee River pH increased by a whole pH unit, yet the total percent ultrafilterable DOC did not change significantly, while the distribution of material among Fraction I and Fraction II did shift to larger material. Finally, the Satilla River at Waycross, Georgia, showed a one pH unit decrease during the intervening year with a concomitant increase in ultrafilterable DOC such as would be predicted by the concept of changing dispersion as a function of pH.

It is apparent that changes in the size distribution of DOC within natural waters is variable and complex. The changes in DOC distribution observed here can be the result of seasonal changes in source material, metabolic activity changes within the aquatic system, or changes in the physicochemical properties of the systems. However, we cannot as yet determine the importance of the various causes. Comparisons previously

made using different separation techniques in different systems further complicate our understanding. It is obvious that further work will be required to understand the changes in relative DOC pools as a function of seasonal cycles, within specific waters.

#### Binding Capacity Measurements

The term *binding capacity* in waters usually refers to the ability of a water sample to buffer the free ionic concentration of an added metal. This parameter is of considerable use in attempting to predict the transport, bioavailability, and reactivity of metals introduced into aquatic systems. Since the actual value derived for a binding capacity is a function of the analytical technique employed (Neubecker and Allen 1983; Truitt and Weber 1981), care must be taken in comparing and interpreting these data. However, it has been shown that several techniques, which do not rely on voltametric measurements, can be intercompared (Tuschall and Brezonik 1983; Neubecker and Allen 1983; Weber 1983). In this work, we employ selective ion electrodes to estimate the binding capacities of the surface waters for Cd, Cu, and Pb.

With the exception of Cd in Banks Lake, all the waters studied had measurable binding capacities for all three elements (Table 4). Furthermore, the binding capacities reported in this work have similar magnitudes and the same trend of relative strength, i.e.,  $\text{PbBC} > \text{CuBC} > \text{CdBC}$ , as data gathered in surface waters of Maine (Giesy and others 1978). Other investigators have determined binding capacities for some of these metals in various waters in the eastern United States and it is informative to compare these data (Table 5).

The values in this work as well as those from Maine and South Carolina were all generated using the same technique, while the data from New Hampshire were measured using a dialysis filtration method. The data from Florida are part of a study to compare several techniques including the selective ion

Table 5. Measured binding capacities<sup>a</sup> of Cd, Cu, and Pb reported for various surface waters of the eastern United States.

Study area	CdBC	CuBC	PbBC
Maine <sup>b</sup>	0.28 ± 0.25 (12)	2.43 ± 3.16 (12)	9.5 ± 4.2 (12)
New Hampshire <sup>c</sup>	3.9 ± 3.5 (5)	7.79 ± 5.23 (7)	NR
Florida <sup>d</sup>	3.77 ± 2.09 (2)	33.8 ± 29.4 (10)	NR
South Carolina <sup>e</sup>	NR	13.9 ± 5.7 (4)	32.6 ± 16.6 (4)
Florida and Georgia <sup>f</sup>	0.31 ± 0.22 (7)	2.5 ± 1.6 (8)	10.9 ± 4.6 (8)

<sup>a</sup>Mean values ( $\mu\text{g atm/L}$ )  $\pm$  1 STD deviation; (number of observations); NR = not reported.

<sup>b</sup>Giesy and others 1978.

<sup>c</sup>Truitt and Weber 1981.

<sup>d</sup>Tuschall and Brezonik 1983.

<sup>e</sup>Alberts and Collins 1980.

<sup>f</sup>This work.

electrodes and the dialysis methods with respect to copper-binding capacities. However, the sample size of ten actually refers to five different methodological determinations of copper-binding capacity on only two water samples. Agreement between the methods was such that all values of the binding capacity were used to determine the mean. In addition, the Cd-binding capacity values were generated using a dialysis-type technique and hence from a strict methodological standpoint should only be compared to the work from New Hampshire. However, examination of the data in Table 5 indicates that the range of binding capacity values for all metals is remarkably narrow. This observation is supported by the variation in pH values in the different studies, e.g., Maine, 4.6–6.3; New Hampshire, 5.7–7.4; Florida, 6.1–6.2; South Carolina, 5.3–8.9; this work, 4.0–8.3. Weber (1983) has demonstrated that binding capacities increase with increasing pH. Therefore, some of the discrepancies observed may be due to this effect. Similarly, the water quality parameters from the study sites often differ greatly. Truitt and Weber (1981), studying seven rivers in New Hampshire, concluded that inorganic ligands were responsible for the observed binding capacities in those waters; while Giesy and others (1978), studying twelve waters in Maine, concluded that inorganic ligands accounted for the Cd-binding capacity, organic complexing was the predominant factor in copper binding, and organic and sulfate binding appeared to determine the Pb-binding capacity. Hence, while binding capacity values can be determined with some consistency among waters over a large geographical region, the factors responsible for the metal-buffering capacity of these waters may differ as a complex function of physicochemical parameters.

In an effort to ascertain important components of the metal-binding capacities in the waters of this study, Pearson Product Moment correlation analyses were conducted. Examination of the correlation matrix (Table 6) shows that all of the

Table 6. Pearson pairwise correlations ( $R$ ,  $n = 8$ )<sup>a</sup>

	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	OH <sup>-</sup>	CO <sub>3</sub> <sup>-2</sup>	CdBC	CuBC	PbBC
DOC	0.30 NS	0.10 NS	0.30 NS	0.31 NS	0.26 <sup>b</sup> NS	0.72 **	0.83 **
Cl <sup>-</sup>		0.85 ***	0.98 ***	0.99 ***	0.90 <sup>b</sup> ***	0.73 **	0.25 NS
SO <sub>4</sub> <sup>-2</sup>			0.84 ***	0.83 **	0.81 <sup>b</sup> **	0.74 **	0.17 NS
OH <sup>-</sup>				0.99 ***	0.87 <sup>b</sup> **	0.69 *	0.20 NS
CO <sub>3</sub> <sup>-2</sup>					0.88 <sup>b</sup> ***	0.70 *	0.22 NS
CdBC						0.73 <sup>b</sup> *	0.39 <sup>b</sup> NS
CuBC							0.72 **

<sup>a</sup>\*,  $P < 0.10$ ; \*\*,  $P < 0.05$ ; \*\*\*,  $P < 0.01$ ; NS, not significant

<sup>b</sup> $n = 7$

anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>-2</sup>) are highly intercorrelated. Cadmium-binding capacity is highly correlated with all of the anions, but not with DOC, while Pb-binding capacity is only correlated with DOC. Copper-binding capacity appears to be highly correlated with both DOC and the anions present. The CdBC correlations agree with the findings of Giesy and others (1978) for waters in Maine, but do not agree with the data of Truitt and Weber (1981) from New Hampshire, who see no trends in cadmium-binding capacity with indicators of inorganic ligands. However, as the latter authors point out, the trends in their cadmium-binding capacity analyses may have been obscured. The lack of any significant correlation between PbBC and the anions is contrary to the findings of Giesy and others (1978), who found an effect of sulfate ions in controlling PbBC in addition to DOC. Finally, both Giesy and others (1978) and this work found DOC to be significantly correlated with CuBC, while Truitt and Weber (1981) found no signifi-

Table 7 Principal components analysis for Cd, Cu, and Pb binding capacities

Principal component	Weightings for ligands					Variance of principal component	% of total variation explained
	DOC	OH <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	CO <sub>3</sub> <sup>-2</sup>	Cl <sup>-</sup>		
PC1	0.090	0.257	0.232	0.257	0.257	3.842	76.8
PC2	0.992	-0.040	-0.274	-0.024	-0.037	0.941	18.8
PC3	0.468	-0.632	1.920	-0.723	-0.539	0.195	3.9
PC4	0.047	3.970	0.238	1.293	-5.501	0.021	0.4
PC5	-0.755	-149.2	9.714	200.6	-60.15	<0.000	<0.1

Table 8 Regression of the Cd, Cu, and Pb binding capacities on the computed principal components.

Model: CdBC = -0.063 + 0.850 PC1 - 0.006 PC2				
Source	df	Mean Square	F	P
PC1	1	4.812	16.56	≤0.015
PC2	1	<0.000	0.00	≤0.980
Model: CuBC = 4.28 × 10 <sup>-17</sup> + 0.782 PC1 + 0.436 PC2				
Source	df	Mean Square	F	P
PC1	1	4.280	15.42	≤0.011
PC2	1	1.333	4.80	≤0.080
Model: PbBC = 1.47 × 10 <sup>-16</sup> + 0.285 PC1 + 0.753 PC2				
Source	df	Mean Square	F	P
PC1	1	0.568	1.15	≤0.332
PC2	1	3.964	8.03	≤0.037

cant correlation between the two variables. Since the correlation analysis did point out the highly significant intercorrelation of the anions in the systems, it was felt that the use of principal components analysis might be helpful in determining the importance of specific variables in controlling binding capacities.

An extended discourse on the principal components analysis technique is beyond the scope of this report. The interested reader is encouraged to examine a more thorough discussion of this topic (Morrison 1976). Briefly, principal components analysis transforms the five possible ligand parameters (DOC, OH<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, CO<sub>3</sub><sup>-2</sup>) into five new, orthogonal parameters identified as PC1, PC2, PC3, PC4, PC5, which summarize the information contained in the original intercorrelated data set. The relative importance of the original ligands to these new parameters may be examined by comparing the correlations among them (Table 7).

Two principal components explain >95% of the total variability of the data set. The first component, PC1, which explains 76.8% of the variability, is composed of the anions (Cl<sup>-</sup>, OH<sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, and CO<sub>3</sub><sup>-2</sup>), with approximately equal weighting for each anion. The second component, PC2, explains an additional 18.8% of the variability and is composed entirely of DOC. The remaining components, PC3, PC4, and PC5, represent <5% of the total variability and contain

Table 9 Ratio of total metal concentration to metal-binding capacity.

Site	Cd/CdBC	Cu/CuBC	Pb/PbBC
O	1.97 × 10 <sup>-3</sup>	1.63 × 10 <sup>-2</sup>	2.17 × 10 <sup>-4</sup>
F	4.0 × 10 <sup>-3</sup>	3.90 × 10 <sup>-2</sup>	1.02 × 10 <sup>-3</sup>
Ch	1.0 × 10 <sup>-2</sup>	4.33 × 10 <sup>-2</sup>	1.88 × 10 <sup>-4</sup>
D	1.47 × 10 <sup>-3</sup>	2.10 × 10 <sup>-2</sup>	9.06 × 10 <sup>-5</sup>
W	2.23 × 10 <sup>-2</sup>	1.46 × 10 <sup>-2</sup>	7.92 × 10 <sup>-4</sup>
B	—	1.40 × 10 <sup>-2</sup>	3.60 × 10 <sup>-4</sup>
P	4.33 × 10 <sup>-3</sup>	1.33 × 10 <sup>-2</sup>	2.16 × 10 <sup>-4</sup>
Ca	1.52 × 10 <sup>-3</sup>	1.52 × 10 <sup>-2</sup>	3.28 × 10 <sup>-4</sup>

information regarding interaction terms between the ligands that is not contained in PC1 and PC2.

Regression of the metal-binding capacities on the principal components PC1 and PC2 is shown in Table 8. The CdBC was only statistically significantly correlated with the PC1, which agrees with the pairwise correlation analysis (Table 6) and most likely represents the known chloro complexes of Cd. Copper-binding capacity was statistically accounted for by both PC1 and PC2, indicating that in these systems both DOC and inorganic ligands are important in determining the CuBC. In the case of PbBC, only PC2 accounted for a statistically significant fraction of the PbBC, which indicates that DOC but not SO<sub>4</sub><sup>-2</sup> was important in determining PbBC.

Principal components represent a normalization of the original data. Hence, the models produced by regression of principal components are not appropriate for predicting binding capacities. Backward elimination regression analysis of the nontransformed data produce best-fit models, which were then used to predict the binding capacities in the study sites (Table 4). With these models, we are able to explain all of the variability of the CuBC data with a four-component equation including DOC, SO<sub>4</sub><sup>-2</sup>, OH<sup>-</sup>, and CO<sub>3</sub><sup>-2</sup>. A one-component model based on the Cl<sup>-</sup> concentration explains 81% of the variability of the CdBC; while PbBC is described by a model based only on DOC, which explains 69% of the variability. The predicted values of CdBC and CuBC are in reasonable agreement with the measured. The agreement between PbBC

Table 10 Means of the ratio of metal concentration to metal-binding capacity <sup>a</sup>

Study location	Cd/CdBC	Cu/CuBC	Pb/PbBC
Maine <sup>b</sup>	$9.63 \times 10^{-3} \pm 7.33 \times 10^{-3}$ (7) <sup>a</sup>	$1.99 \times 10^{-1} \pm 4.60 \times 10^{-1}$ (9)	$3.64 \times 10^{-2} \pm 3.30 \times 10^{-2}$ (2)
New Hampshire <sup>c</sup>	$6.76 \times 10^{-3} \pm 8.05 \times 10^{-3}$ (4)	$7.11 \times 10^{-3} \pm 1.52 \times 10^{-2}$ (7)	ND <sup>d</sup>
Northern Europe <sup>d</sup>	$6.37 \times 10^{-3} \pm 1.53 \times 10^{-2}$ (7)	$3.19 \times 10^{-2} \pm 8.19 \times 10^{-2}$ (9)	$8.43 \times 10^{-3} \pm 1.79 \times 10^{-2}$ (10)
Florida and Georgia <sup>e</sup>	$6.51 \times 10^{-3} \pm 7.57 \times 10^{-3}$ (7)	$1.77 \times 10^{-2} \pm 1.14 \times 10^{-2}$ (8)	$4.02 \times 10^{-4} \pm 3.29 \times 10^{-4}$ (8)

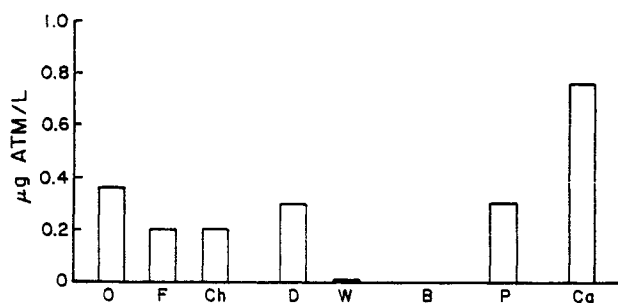
<sup>a</sup>Mean values  $\pm$  1 STD deviation; (number of observations); ND = not determined.

<sup>b</sup>Giesy and others 1978.

<sup>c</sup>Truitt and Weber 1981

<sup>d</sup>Giesy and Briese 1980.

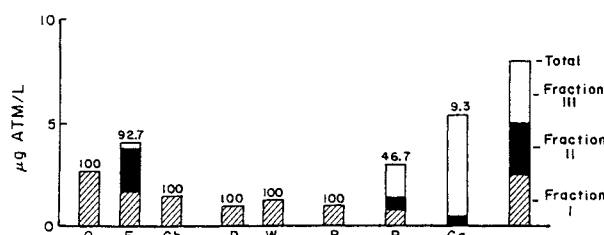
<sup>e</sup>This work.



**Figure 3.** Distribution of CdBC in eight southeastern United States waters sampled November 26-28, 1979.

measured and predicted values is less acceptable than for either CdBC or CuBC, indicating that we still do not have a completely satisfactory understanding of the factors controlling PbBC in these systems. However, the PbBC predicted values are still useful in a qualitative sense and may be acceptable in a semi-quantitative manner depending on the application.

The calculated ratios of metal concentration in the water versus the binding capacity of the water for that metal are low (Table 9). This would indicate that the total buffering capacity of these waters for the metals of interest is not saturated. Generally, the Cu:CuBC ratio is highest, with Cd:CdBC being intermediate between Cu:CuBC and Pb:PbBC. Comparisons of the mean values of these ratios with those of three other studies of the binding capacities of waters including regions of the northeastern United States and northern Europe (Table 10) show that the ratios agree rather well for all the metals over the range of waters studied. Thus, while the studies include two regions that have metal-binding capacities apparently controlled by inorganic ligands, e.g., New Hampshire and Europe, and two regions in which organic matter is considered important for controlling the binding capacity of at least two of the metals, e.g., Maine and this work, the ratios of metal to binding capacity in all these waters are similar and low. These results would suggest that a certain metal-buffering capacity



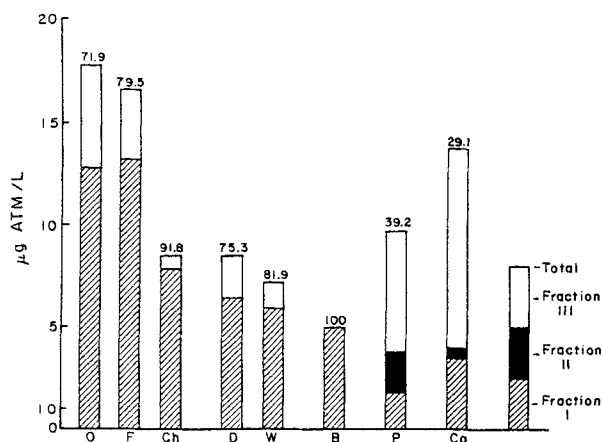
**Figure 4.** Distribution of CuBC among ultrafilterable fractions of eight southeastern United States waters sampled November 26-28, 1979. Fraction I = material  $<0.45 \mu\text{m}$  but  $>52 \text{ \AA}$ ; Fraction II = material  $<52 \text{ \AA}$  but  $>13 \text{ \AA}$ ; Fraction III = material  $<13 \text{ \AA}$ ; percent of total CuBC in Fractions I + II is indicated in numbers above bars.

exists in these waters regardless of the ligands controlling metal speciation. Further work on this topic would appear warranted considering the importance of metal-buffering capacity of waters to bioavailability.

The results of this study indicate that organic complexing is important in the case of copper and lead and that the distribution of organic matter in the waters studied is varied and may in some cases be predominantly larger molecules or colloids which can be removed by ultrafiltration. The binding capacities of ultrafiltered water samples were measured to determine the effect of these ultrafilterable fractions on the total binding capacities of metals (Figs. 3-5).

Cadmium-binding capacities are generally low and no significant differences could be found between the non-ultrafiltered waters and those that had been ultrafiltered to remove particles  $>52 \text{ \AA}$  and  $>13 \text{ \AA}$ , respectively (Fig. 3). However, for both Cu and Pb, significant portions of the metal-binding capacities of the waters could be removed by ultrafiltration (Figs. 4 and 5). Copper-binding capacity was most significantly affected by the removal of the larger particles through ultrafiltration, while in most cases, high percentages of the PbBC were also taken out by removal of larger diameter, ultrafilterable organic matter. Two commonalities between the





**Figure 5.** Distribution of PbBC among ultrafilterable fractions of eight southeastern United States waters sampled November 26–28, 1979. Fraction I = material  $<0.45 \mu\text{m}$  but  $>52 \text{ \AA}$ ; Fraction II = material  $<52 \text{ \AA}$  but  $>13 \text{ \AA}$ ; Fraction III = material  $<13 \text{ \AA}$ ; percent of total PbBC in Fractions I + II is indicated in numbers above bars.

distributions observed in Figures 4 and 5 are: the predominance of Fraction I (material  $<0.45 \mu\text{m}$  but  $>52 \text{ \AA}$ ) in containing material capable of binding both Cu and Pb relative to Fraction II ( $<52 \text{ \AA}$  but  $>13 \text{ \AA}$ ); and the lesser importance of both ultrafilterable fractions in the Peace River and the Caloosahatchee River relative to the other waters studied.

The reduction of metal-binding capacity due to removal of organic matter by ultrafiltration has been previously reported (Alberts and Collins 1980). However, the exact mechanism for the reduction is not understood. Based simply on the amount of organic carbon removed by the ultrafilters (Table 11), it would appear that most of the binding capacity should be in Fraction I. However, in both the Peace River and the Caloosahatchee River, for both Cu and Pb, and in the Suwanee River at Fargo, Georgia, with respect to Cu, Fraction II contained a significant portion of the metal-binding capacity. Yet, Fraction II did not contain a commensurate increased DOC in those instances to warrant the simple explanation. An alternative hypothesis is that the character of the organic matter in the two fractions differs with respect to the number of available binding sites. This latter hypothesis would appear valid based on current concepts of the nature of naturally occurring macromolecular organic matter, and is substantiated to some extent by the data of Alberts and Evans (1979) which show that, in the Peace River and the Suwanee River at Fargo, the total acidity of the organic matter (meq/g org.) in Fraction II was greater than in Fraction I. However, this latter type of data is scant and given the observed changes in organic matter distributions discussed earlier this mechanism must be considered speculative.

The greater relative importance of Fraction III ( $<13 \text{ \AA}$ ) in the total binding capacities of Cu and Pb in the Peace River and the Caloosahatchee River indicates more binding is occurring with ligands of a small size. While it is possible that these ligands may be organic, it is more reasonable to assume that this binding is primarily due to inorganic ligands. This hypothesis is given support by the fact that both of these rivers have increased conductivities, pH values, and chloride and sulfate concentrations. Greater inorganic binding in these cases agrees with the model predictions for Cu. Despite the lack of an inorganic ligand term in the predictive model for PbBC, it must be remembered that the Pb model accounted for only 69% of the variability. This indicates that the model is far from perfect and an inorganic term, such as sulfate, may be warranted in predicting PbBC (Giesy and others 1978).

## Summary and Conclusions

The Cd, Cu, and Pb binding capacities were measured for water samples from four rivers and two swamps in Florida and Georgia. The variability of metal-binding capacities among locations was studied with respect to dissolved organic carbon, as well as the distribution of organic carbon and metal-binding capacities among ultrafilterable fractions. In addition, the relative importance of the inorganic ligands ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) in controlling the metal binding capacities of the waters was determined. Partitioning of the variability explained by the organic and inorganic constituents of the waters was examined by correlation and principal components analyses. Predictive models of the Cu, Cd, and Pb binding capacities of the waters were constructed by multiple regression analysis. CdBC was influenced primarily by inorganic ligands (presumably  $\text{Cl}^-$ ) in all cases, while PbBC was determined to a large extent by DOC. However, there was some indication that inorganic ligands contribute to the PbBC in systems with relatively high concentrations of dissolved solids. Copper-binding capacities were determined by both inorganic and organic ligand concentrations. These results are in agreement with studies conducted in Maine waters (Giesy and others 1978) which were of relatively low pH. However, the results are contrary to other observations in New Hampshire (Truitt and Weber 1981) and northern Europe (Giesy and Briese 1980) which showed that in waters of higher pH and hardness, organic binding did not significantly contribute to the total metal-binding capacity. Wilson (1978) has also noted that humic materials may affect trace metal speciation in some cases and not in others. The dichotomy of the results clearly shows the need to understand the chemistry of the waters being investigated. In soft-acidic waters, with high dissolved organic carbon concentrations, such as those studied here and in

Table 11 Percentage of Cu and Pb binding capacities and DOC in ultrafiltrate fractions

	Cu		Pb		DOC	
	Fraction <sup>a</sup> I	Fraction <sup>a</sup> II	Fraction I	Fraction II	Fraction I	Fraction II
O	100	0	7.19	0	44.3	7.9
F	41.5	51.2	79.5	0	53.9	4.4
Ch	100	0	91.8	0	78.8	0
D	100	0	75.3	0	32.9	10.5
W	100	0	81.9	0	37.0	3.4
B	100	0	100	0	40.4	0.9
P	26.7	20.0	18.6	20.6	18.8	1.7
Ca	0	9.3	25.5	3.6	20.7	1.9

<sup>a</sup>Fraction I = 4,500 Å > % > 52 Å; Fraction II = 52 Å > % > 13 Å

Maine, the DOC is an important factor in controlling the binding capacity of some metals. However, in neutral to basic systems, inorganic ligands become dominant. Finally, the chemistry of the metal must be considered as Cd is controlled by inorganic ligands in both types of systems.

Despite the differences in controls on binding capacities, it has been shown that in all systems studied the ratio of metal in the water to the measured binding capacities is low. This finding indicates that for a wide range of water types and geographical locations, the metal-buffering capacities of waters for Cd, Cu, and Pb do not appear to be near saturation. The cause and stability of this buffering capacity is yet to be ascertained.

In this study, it has been shown that a significant fraction of the CuBC and PbBC can be removed by ultrafiltration. The CdBC was unaffected by ultrafiltration in all cases. The removal of CuBC and PbBC was most pronounced when submicron particles <0.45 μm but >52 Å were removed from the water. This corresponded, in most cases, to the removal of a significant portion of the organic matter in the water. Further removal of particles <52 Å but >13 Å did not significantly affect the binding capacities of most waters for Cu and Pb.

Finally, the distribution of carbon among various size fractions, as determined by ultrafiltration, indicated that almost all of the DOC in the waters examined was found in fractions <0.45 μm but >52 Å, and <13 Å. This distribution is considerably different than that observed in these same rivers one year earlier and emphasizes the need to better understand the seasonal distribution of organic matter within a system before extrapolating results between systems.

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