



## Colloidal trace metals, organic carbon and nitrogen in a southeastern U.S. estuary

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### Abstract

We have used cross-flow ultrafiltration on eleven 0.45- $\mu\text{m}$ -filtered samples taken across the salinity gradient in the Ochlockonee Estuary. We sequentially ultrafiltered the samples using 10- and 1-kD filters (1 kD = 1000 daltons). The results indicate that total Fe and Mn behave nonconservatively in the estuary and that the removal is from the high-molecular-weight (HMW; > 10 kD) fraction although Mn is removed at lower salinity than Fe. For Ni, Cu and Cd, the HMW fraction is very important in the river but these elements are quickly converted from HMW to low-molecular-weight (LMW) species with increasing salinity. Carbon in the HMW fraction is strongly correlated with Fe but only weakly correlated with Fe in the smaller size fractions. The two important processes controlling the behavior of metals, carbon and nitrogen in the estuary are colloid aggregation and desorption or dissociation.

### 1. Introduction

In the last several years the application of cross-flow filtration (CFF; Whitehouse et al., 1990; Bueseler et al., 1996-this issue) to aquatic systems has made it possible to separate colloidal size material (> 1 kD, 1 kD = 1000 daltons) from the fraction that has been traditionally described as dissolved (< 0.45  $\mu\text{m}$ ). Colloids are potentially very important in controlling the cycling of many elements that may either be scavenged onto Fe-oxyhydroxides or complexed with large aggregates, and have been shown to exist in high concentrations in the marine environment (Koike et al., 1990; Wells and Goldberg, 1992, 1993).

It has been shown, using CFF, that a large fraction of the organic carbon in open-ocean and coastal

waters is colloidal (Benner et al., 1992; Guo et al., 1994). It might therefore, be expected that colloids will play a very important role in controlling the cycling of dissolved organic carbon (DOC) in an estuary that has very high concentrations of dissolved humic substances. These humic and fulvic acids may then be removed via aggregation during the mixing process (Sholkovitz, 1976; Sholkovitz and Copeland, 1981; Fox, 1983). However, to date the number of investigations of organic colloids in estuaries has been quite limited. In the Krka River and Estuary, Croatia (Sempéré and Cauwet, 1995) the colloidal carbon fraction comprises as much as 50% of the total even though it is not a very organic-rich system (total DOC < 150  $\mu\text{M}$ ). However, in the Venice Lagoon, Italy (Martin et al., 1995) the colloidal fraction only accounts for only

10–25% of the filtered ( $< 0.4 \mu\text{m}$ ) DOC concentration (total DOC from 200 to  $400 \mu\text{M}$ ). Using the more conventional stirred-cell ultrafiltration apparatus, Sigleo et al. (1982) separated organic colloids (as much as 50% of the total DOC) from the bulk sample in the Patuxent River, Maryland, and identified most of the compounds as biological in origin, either carbohydrates, lipids or amino acids. No lignin material was found. These studies represent a basis for comparison among a variety of estuarine systems.

The estuarine geochemistry of many trace elements has been extensively studied and recently reviewed (Church, 1987; Cutter, 1991). In particular, the geochemistry of Fe as it moves from fresh waters with high concentrations (a few  $\mu\text{M}$ ) to saline waters with very low concentration (a few  $\text{nM}$ ) has been studied both in the laboratory and in the field (Eckert and Sholkovitz, 1976; Sholkovitz, 1976; Boyle et al., 1977; Sholkovitz and Copeland, 1981; Fox, 1988). It has been shown that the major form of Fe in some rivers is Fe-oxyhydroxides (Boyle et al., 1977; Mayer, 1982; Fox and Wofsy, 1982; Fox, 1988; Hunter and Leonard, 1988) which may be coated with natural organic matter (Sholkovitz and Copeland, 1981). Some of the Fe in estuaries may also be organically complexed (Matsunaga et al., 1984). As shown in laboratory experiments (Eckert and Sholkovitz, 1976; Sholkovitz, 1976; Sholkovitz and Copeland, 1981), the colloidal Fe-oxyhydroxides are destabilized and aggregate upon mixing river water with seawater. While these types of mixing experiments are useful for elucidating the potentially important parameters controlling the kinetics of aggregation, they require verification with field measurements. Total dissolved Fe ( $< 0.45 \mu\text{m}$ ) measurements almost always display non-conservative estuarine profiles (Holliday and Liss, 1976; Boyle et al., 1977; Figuerés et al., 1978; Church, 1986; Windom et al., 1988; Byrd et al., 1990) with few exceptions (Paulson et al., 1989; Shiller and Boyle, 1991). These field studies generally attribute the non-conservative nature of Fe to the same flocculation processes that are observed in the laboratory. However, few investigators have attempted to isolate the Fe-oxyhydroxide and organic carbon aggregates. Dai and Martin (1995) report that virtually all the Fe in the Ob and Yenisey Rivers, Russia, is high molecular weight ( $> 10 \text{ kD}$ ). A better understanding of how

the aggregation of Fe and organic carbon occurs will allow us to identify the relevant estuarine processes and to quantify the flux of metals and organic carbon to the coastal ocean.

These Fe-oxyhydroxides are very efficient scavengers of other trace metals (Millward and Moore, 1982). Therefore, this colloidal Fe-oxyhydroxide phase may control the concentrations of some of the other metals. In the Patuxent Estuary the winter time colloidal material consisted mainly of kaolinite and illite clays but it was enriched in several metals (Sigleo and Helz, 1981), suggesting scavenging onto the surface of the colloids. In estuaries in Texas it has been shown that colloids play an important role in the cycling of Al, Mn, Fe, Cu, Zn, Cd, Ag, and Pb (Benoit et al., 1994) as well as Th,  $^{210}\text{Pb}$  and Be (Baskaran and Santschi, 1993). For the trace metals (Benoit et al., 1994), ultrafiltration was only conducted on a limited number of samples; however, the correlations between the partitioning coefficient ( $K_D$ ) and suspended particulate material for all samples supports a Brownian-pumping model (Honeyman and Santschi, 1989). In the Venice Lagoon (Martin et al., 1995) colloids accounted for 54% of Mn, 87% of Fe, 18% of Ni, 46% of Cu, 34% of Cd and 58% of Pb in the traditional dissolved phase ( $< 0.45 \mu\text{m}$ ). This suggests that the colloidal fraction is important in controlling the flux of metals from the river to the coastal zone.

We will demonstrate the importance of colloidal material in transporting metals, organic carbon and nitrogen to the Ochlockonee Estuary, Florida. In the estuary, transitions between size classes and removal from solution occur via desorption from colloids and the flocculation of the high-molecular-weight material. This data set represents a synoptic view of an estuary with very little biological activity to affect the cycling of metals or organic carbon.

## 2. Methods

### 2.1. Study area

The Ochlockonee Estuary is a shallow (1–2 m), well-mixed estuary located in northwest Florida (Guentzel et al., 1996). At the time of sampling, a salt wedge existed only in the channel that was

dredged to a depth of 5–6 m. A dam located 105 km above the estuary controls the flow and no major tributaries enter below the dam. The river flow is such that the average flushing time for the bay is ~ 10 days (Kaul and Froelich, 1984). Below the dam, the river drains a forested watershed with spodosols (characterized by high Al, Fe and organic carbon) bordering the lower river (Pollman and Canfield, 1991). Above the dam the soils are a mixture of ultisols and entisols (more highly weathered clays). The nutrient geochemistry of the estuary has been extensively studied and presented elsewhere (Kaul and Froelich, 1984).

## 2.2. Sample collection

Eleven 20-l samples were collected across the salinity gradient between January 24 and February 2, 1994. Samples were collected from a 24-ft (7.32 m) fiberglass boat using a peristaltic pump with acid-cleaned tubing and in-line filtration (0.45- $\mu$ m polypropylene cartridge filter, MSI Inc.). The tubing was held at depth with an epoxy-coated weight. The tubing was allowed to purge 4–5 volumes before sampling began. Samples for total dissolved metals, carbon and nitrogen were collected as independent samples immediately prior to the collection of the sample to be used for cross-flow ultrafiltration. Samples were collected from high salinity to low salinity in an effort to prevent contamination of low-concentration (high salinity) samples with high-concentration (low salinity) samples. Samples were stored on ice in the dark for the 30-min transport to the shore-based clean laboratory.

## 2.3. Cross-flow ultrafiltration (CFF)

The samples were sequentially processed by CFF using 10- and 1-kD filters in a clean laboratory supplied with Class-100 high-efficiency particulate filtered air (HEPA). Acrylic filter holders (Filtron Centrasette) were used with stacked polysulfone filter cassettes (Omegasette screen channel). Total filter areas of 5 and 20 ft<sup>2</sup> (0.465 and 1.86 m<sup>2</sup>) were used for the 10- and 1-kD membranes, respectively. The recirculating flow rates were ~ 3 l/min and permeate flow rates were 100 ml/min. No transmembrane pressure was applied on the 10-kD filter while ~

10–12 psi (69–83 kPa) of transmembrane pressure was used with the 1-kD filters. Permeate samples were collected when the concentration factor was ~ 2. Final concentration factors were between 7 and 10. Processing time for each ultrafiltration step was < 1.5 h with total processing time never exceeding 3 h. The ultrafiltration systems were rinsed with 2–3 l of clean water (Barnstead NANOpure System) between each sample and then 0.5–1 l of sample was allowed to flush the membrane and discarded before the system was run in the recirculate mode. Samples for trace metals were collected in acid-cleaned 1-l FEP Teflon bottles. Subsamples for carbon and nitrogen were collected in either 125-ml glass bottles or 30-ml glass scintillation vials with Teflon lined caps and frozen immediately. All glassware was cleaned by baking at 525°C for 4 h.

Before sampling, the ultrafiltration systems were subjected to rigorous cleaning with dilute HCl and clean water. Blanks were checked during this cleaning period and the cycle of HCl and clean water was repeated until blanks for metals and organic carbon were below our detection limits. Blanks were again checked immediately prior to processing of samples and they were never large enough to be significant. While these blanks were conducted with clean deionized water and not saline water they are a good estimate for potential contamination.

Perhaps a better estimate of contamination is to calculate mass balances for the samples. Mass balances were calculated (Table 1) by summing the three fractions and dividing by the total concentration from the independent sample. Any system with mass balance > 100% probably indicates contamination, while samples with < 100% mass balance likely indicate scavenging onto the filter membrane or sample reservoir. The mass balances are not perfect, but considering a propagation of sampling and analytical errors on four separate sub-samples, any sample with mass balance of  $100 \pm 20\%$  could be considered “quantitative”. Based on Fe mass balance, only three of the samples fall far outside this range; generally with the sum of the fractions much less than the total dissolved sample ( $S = 4, 11$  and  $28.5$ ). It is likely that for some of these samples there was adsorption to the membranes. However, in general the trends show smooth systematic changes with salinity. Another possible explanation for the differ-

Table 1  
Trace-metal, carbon and nitrogen concentrations in the total dissolved, HMW, MMW and LMW fractions

D.L.	Fraction	Salinity										
		0.03	0.30	0.45	1.70	4.00	4.50	6.70	8.70	11.00	19.00	28.50
<i>Iron (nM):</i>												
0.18	total dissolved	6980.00	6180.00	5190.00	4880.00	5600.00	3040.00	2330.00	2370.00	3310.00	428.00	40.80
	HMW	4540.00	4360.00	4480.00	3660.00	2180.00	1830.00	1070.00	780.00	515.00	76.20	5.66
	MMW	232.00	452.00	429.00	630.00	664.00	577.00	578.00	586.00	471.00	128.00	8.81
	LMW	156.00	305.00	205.00	159.00	181.00	209.00	334.00	223.00	188.00	122.00	8.16
	mass balance (%)	71	83	99	91	54	86	85	67	35	76	55
<i>Manganese (nM):</i>												
0.03	total dissolved	437.00	283.00	267.00	249.00	234.00	360.00	264.00	228.00	138.00	64.30	10.79
	HMW	133.00	14.20	6.34	3.54	4.55	1.65	9.29	0.06	0.06	0.06	0.06
	MMW	0.06	0.06	0.06	0.06	0.06	3.81	3.19	4.50	0.06	0.06	0.06
	LMW	305.00	256.00	278.00	207.00	200.59	245.00	236.00	214.00	134.00	74.50	10.74
	mass balance (%)	100	95	107	85	88	70	94	96	97	116	101
<i>Nickel (nM):</i>												
0.06	total dissolved	4.50	4.77	5.53	4.59	4.92	4.55	4.27	4.66	3.81	2.56	2.59
	HMW	2.02	1.48	1.35	0.56	0.39	0.18	0.17	0.24	0.20	0.12	0.10
	MMW	0.25	0.004	0.06	0.23	0.49	0.12	0.16	0.23	0.22	0.13	0.04
	LMW	0.97	1.92	1.29	1.91	2.46	2.73	2.90	2.91	2.58	2.58	2.95
	mass balance (%)	72	71	49	59	68	67	76	73	79	110	120
<i>Copper (nM):</i>												
0.06	total dissolved	4.63	3.49	3.87	5.05	5.44	3.84	4.07	3.67	2.87	2.40	2.03
	HMW	2.83	1.75	1.38	1.55	0.98	0.63	0.51	0.55	0.40	0.37	0.20
	MMW	0.25	0.03	0.09	0.46	0.66	0.10	0.39	0.29	0.30	0.51	0.11
	LMW	0.44	1.02	0.55	1.31	1.55	0.91	1.13	2.00	1.77	1.35	1.63
	mass balance (%)	76	81	52	66	59	43	50	77	86	93	95
<i>Cadmium (pM):</i>												
1	total dissolved	36.10	47.60	45.70	37.00	40.40	42.90	54.00	46.60	48.30	53.70	40.20
	HMW	17.60	12.40	21.60	2.69	1.97	3.29	3.18	4.59	2.48	4.35	2.36
	MMW	2.44	1.49	0.56	0.02	0.02	0.37	1.17	0.22	0.13	6.74	0.03
	LMW	12.01	25.30	34.40	36.30	42.30	47.60	48.20	40.80	35.40	34.30	32.00
	mass balance (%)	89	82	124	105	110	120	97	98	79	85	86
<i>Organic carbon (μM):</i>												
10	total dissolved	1050.00	1570.00	1550.00	1460.00	1103.00	1112.00	1025.00	879.00	676.00	569.00	189.00
	HMW	548.00	770.00	706.00	342.00	179.00	224.00	156.00	110.00	68.70	43.40	10.00
	MMW	207.00	383.00	386.00	686.00	381.00	143.00	269.00	230.00	206.00	53.70	35.30
	LMW	200.00	383.00	404.00	429.00		487.00	510.00	496.00	361.00	276.00	198.00
	mass balance (%)	91	98	97	100	> 51	77	91	95	94	66	129
<i>Nitrogen (μM):</i>												
1	total dissolved	32.00	69.90	34.20	40.50	37.10	26.90	25.90	20.50	15.90	16.50	8.50
	HMW	2.65	37.00	9.86	5.87	8.40	5.20	4.30	3.19	1.22	1.00	3.31
	MMW	5.73	5.64	4.25	11.90	7.68	2.71	5.09	6.96	4.26	2.14	1.74

Table 1 (continued)

D.L.	Fraction	Salinity										
		0.03	0.30	0.45	1.70	4.00	4.50	6.70	8.70	11.00	19.00	28.50
<i>Nitrogen (<math>\mu\text{M}</math>):</i>												
	LMW	7.70	12.80	13.60	31.00		11.90	17.40	13.70	9.40		3.60
	mass balance (%)	50	79	81	120	> 43	74	103	116	94	> 19	102
<i>C/N:</i>												
	total dissolved	32.90	22.50	45.40	36.10	29.70	41.30	39.60	42.88	42.52	34.50	22.20
	HMW	207.00	20.82	71.60	58.20	21.20	43.00	36.40	34.55	56.27	43.40	3.00
	MMW	36.10	67.79	90.80	57.90	49.50	52.90	52.90	33.00	48.28	25.09	20.20
	LMW	26.00	29.92	29.70	13.90		40.90	29.30	36.20	38.40		55.00

Missing values for nitrogen are samples that were broken in shipment. D.L. = detection limit; LMW = low molecular weight; MMW = medium molecular weight; HMW = high molecular weight.

ences is that even though the total dissolved and cross-flow ultrafiltration samples were collected within 20 min of each other, the salinities of the two samples were sometimes different due to changing salinity in the estuary. Therefore, the total dissolved sample with the salinity closest to the ultrafiltration salinity was used to calculate the mass balance. These differences could account for as much as a 20–30% difference in the mass balance especially for samples such as Fe and organic carbon which have a strong gradient in concentration with respect to salinity. For Ni and Cu there is a clear minimum in recovery between salinity 0.45 and 8. While these losses are probably due to adsorptive losses, it is interesting to note that both low-salinity samples with high colloidal concentrations and high-salinity samples with low colloidal concentrations show good mass balance.

We are aware of the potential artifacts with cross-flow ultrafiltration which may include: changes in the filter characteristics over time, dissociation and disaggregation of colloids, inaccurate filter cut-offs and variability between manufacturers (Buesseler et al., 1996-this issue; Gustafsson et al., 1996-this issue). Changes in permeate concentration as a function of concentration factor were shown not to be very significant for DOC for the Filtron systems (Buesseler et al., 1996-this issue), therefore samples taken at concentration factor 2 should be a reasonable estimate for the permeate concentration. Consid-

ering the possible changes in conformation and size of the organic colloids with salinity, we will refer to the different size fractions as follows. "Total dissolved" refers to the fraction that passes through the 0.45- $\mu\text{m}$  cartridge filter. For this study there are two colloidal fractions; high molecular weight (HMW) (between 10 kD and 0.45  $\mu\text{m}$ ) and medium molecular weight (MMW) (between 1 and 10 kD). The term low molecular weight (LMW) refers to the fraction that passes through the 1-kD filter.

#### 2.4. Analytical

Because of the high organic carbon concentration in this estuary, it was necessary to oxidize the organics before preconcentration of the metals. BrCl was prepared according to Bloom and Creccelius (1983), except that sub-boiling quartz distilled 6 M HCl was used instead of reagent grade 12 M HCl. 5 ml of BrCl per liter of sample were added and the samples were then UV (254 nm) oxidized directly in the FEP Teflon bottle under low intensity (730  $\mu\text{W}/\text{cm}^2$ ) for 24 h. After 24 h, if there was visible organic color another 5 ml BrCl per liter of sample was added and it was UV oxidized for another 24 h. After the oxidation was complete, 1 ml of 10 mM hydroxylamine hydrochloride was added to each 1 l sample to prevent excess BrCl from oxidizing the chelating agents during preconcentration. While this acidic oxidation is not likely to digest aluminosilicate mate-

rial, it would solubilize any amorphous Fe-oxhydroxides and the associated metals. A less than quantitative analysis of metals contained in colloidal aluminosilicates would likely only affect our Fe measurements such that the calculated colloid percentages would be minimum estimates.

Iron was analyzed by direct injection of 20  $\mu$ l of UV oxidized sample using a Perkin Elmer 5000 Atomic Absorption Spectrophotometer ( $D_2$  background correction) equipped with an HGA 400 graphite furnace and an AS 40 autosampler. The other metals were first preconcentrated by APDC/DDC complexation and chloroform extraction of a 500-ml sample (Statham, 1985; Landing and Bruland, 1987). Recoveries were checked using both NASS-3 and standard additions to seawater collected 16 km offshore in the Gulf of Mexico. Detection limits are given in Table 1. Dissolved organic carbon (DOC) and total dissolved nitrogen were analyzed by discrete injection (50–100  $\mu$ l) high-temperature catalytic oxidation (Williams et al., 1993). DOC was combusted to  $CO_2$  with subsequent non-dispersive infra-red detection and DON was combusted to NO which was detected by chemiluminescence. Both DOC and DON were calibrated using aqueous (glucose, nitrate and EDTA) and gaseous ( $CO_2$  and NO) standards. Appropriate system blank corrections were made for both DOC and DON calculations. Chloride was measured on a subsample of the LMW fraction using a Dionex 4500i ion chromatograph equipped with an AS4A column.

## 2.5. Reactivity experiments

### 2.5.1. Iron reduction

In order to understand the speciation of Fe we conducted kinetic reduction experiments using ferrozine as an indicator of Fe(II) (Stookey, 1970). 25 mmol of hydroxylamine hydrochloride were added per liter of sample which contained 250  $\mu$ M ferrozine. The appearance of Fe(II) was followed spectrophotometrically (570 nm) for 2 h. The data were linearized assuming first-order kinetics with respect to the concentration of Fe(III). Results from solutions of Ochlockonee River water were compared to standard solutions of Fe(III) complexed with EDTA and NTA as well as freshly precipitated amorphous Fe(III)-hydroxides.

### 2.5.2. 8-Hydroxyquinoline experiments

8-Hydroxyquinoline was immobilized on a vinyl polymer resin according to the procedure of Landing et al. (1986). Solutions of estuarine water were pumped through 1 ml of gravity-packed resin at a rate of 5 ml/min. The immobilized 8-hydroxyquinoline has been shown to be very efficient at chelating ionic and weakly complexed metals; however, our laboratory experiments indicated that strongly complexed Fe and Cu are not efficiently removed from solution. These experiments were designed to be a qualitative indication of strong organic complexation.

## 3. Results and discussion

The estuarine distributions of various molecular weight classes for trace metals, DOC and DON are a result of many processes which result in either input or removal from a size fraction or transfer of an element from one size fraction to another. In particular, Fe and DOC show large non-conservative removals from the HMW fraction (Table 1; Figs. 1 and 2), which is also reflected in the total dissolved

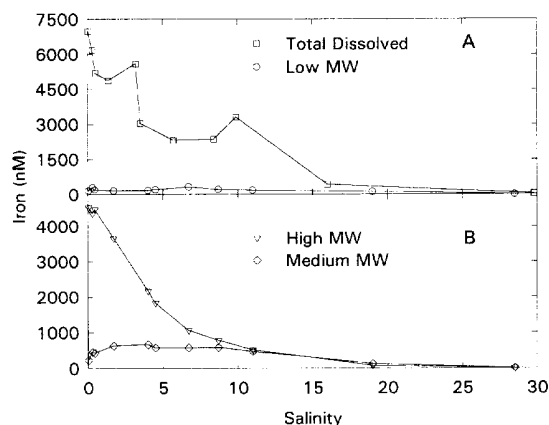


Fig. 1. Iron size fractions vs. salinity.

A. Total dissolved iron displays a non-conservative profile with removal of the HMW fraction. The concentration in the LMW fraction increases slightly at low salinity and then is mixed with the seawater end-member. The difference between the total dissolved and LMW fractions represents the colloidal fraction.

B. The HMW fraction is very nonconservative with removal before salinity 10. The MMW fraction increases and is then diluted with the seawater end-member similar to the LMW fraction.

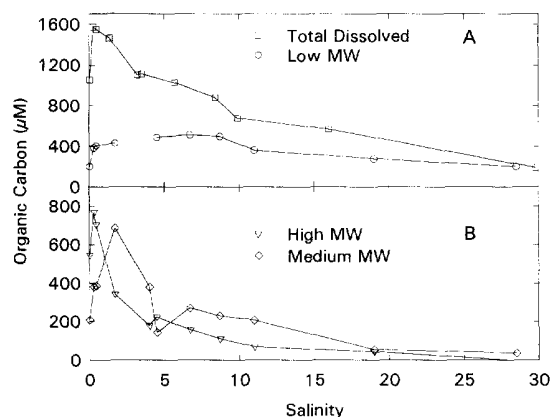


Fig. 2. Organic carbon size fractions vs. salinity.

A. Total carbon is nonconservative in the estuary and quite variable at low salinity. The LMW fraction displays input at low salinity and then dilution with the seawater end-member.

B. The HMW fraction is nonconservative with removal. As with Fe the MMW fraction is similar to the LMW fraction with input at low salinity and then mixing with the seawater end-member.

concentrations. This is contrasted by the MMW and LMW fractions which show modest concentration increases at low salinity.

In order to explain these salinity-dependent transformations in the estuary it is important to understand the speciation of the elements in the estuary. We determined the speciation of Fe in the river by conducting kinetic reduction experiments using hydroxylamine hydrochloride and ferrozine (Stokey, 1970; Landing and Westerlund, 1988). Ferrozine reacts very rapidly with  $\text{Fe}^{2+}$  to give a colored complex. However, if the Fe is complexed or present as oxyhydroxides, the reduction of Fe(III) by hydroxylamine and the complexation of  $\text{Fe}^{2+}$  by ferrozine are slowed. Approximately 20% of the total dissolved Fe in the river reacted at a rate similar to EDTA-complexed Fe(III) while the remainder reacted at a rate similar to freshly precipitated Fe(III)-oxyhydroxides. Therefore the HMW material in the river could be deduced to exist primarily as Fe(III)-oxyhydroxides with a small percentage of organically complexed Fe. This is not conclusive evidence for the existence of Fe-oxyhydroxides however, since conformational changes in the colloidal organic matter organics could result in complexed Fe that is kinetically very non-labile (Clark, 1987). The very high organic carbon to Fe molar ratio (Fig. 3) in the

HMW fraction ( $160 \pm 20$ ) suggests that there is a large amount of colloidal organic carbon which is not directly associated with the hypothesized Fe-oxyhydroxides. At the very least, it seems clear that, the same flocculation processes are affecting the concentrations of Fe and organic carbon in the HMW fraction.

As the salinity increases, the HMW fraction flocculates and is removed until at high salinity the LMW fraction is the dominant fraction. The MMW fractions for both Fe and organic carbon have mid-estuarine maxima which may be driven by the disaggregation of the HMW fraction rather than aggregation of LMW material. The LMW fraction does not exhibit the minimum one might expect at mid-salinity if aggregation of LMW material was producing MMW colloids. The LMW fraction is the dominant fraction at high salinities. The LMW iron is still complexed relatively strongly as it is unreactive to immobilized 8-hydroxyquinoline (Table 2). The cor-

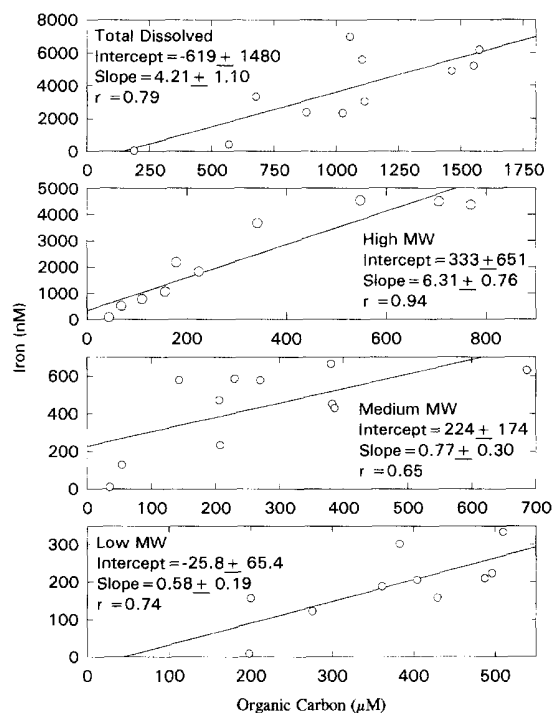


Fig. 3. Iron vs. organic carbon for the four size fractions. The correlation is best for the HMW fraction although still significant for the other fractions.

Table 2

Comparison of the percent of the total dissolved metal subject to rapid exchange onto immobilized 8-HQ and the percent metal in the LMW fraction in the river and at mid and high salinities

	%8-HQ	%LMW
<i>S = 0:</i>		
Mn	97	70
Fe	2	2
Ni	49	22
Cu	3	10
Cd	55	33
<i>S = 11:</i>		
Mn	100	100
Fe	12	6
Ni	82	68
Cu	8	67
Cd	67	73
<i>S = 19:</i>		
Mn	99	100
Fe	19	29
Ni	73	100
Cu	12	56
Cd	72	64

relations between Fe and organic carbon for both the MMW and LMW fractions are not as strong as for the HMW fraction, although still significant.

The size distribution of Mn in the estuary is much simpler (Fig. 4). Only in the river is there a significant HMW fraction. The most likely form of soluble Mn in freshwaters is  $Mn_{(aq)}^{2+}$ ; however, it may be complexed (Chiswell and Mokhtar, 1986). This complexation would likely be an outer-sphere type and would therefore be very labile. The remaining samples are dominated by the LMW fraction. At low, mid and high salinity, all the Mn in a total dissolved sample is removed from solution by the immobilized 8-HQ (Table 2).

Nickel, copper and cadmium (Figs. 5–7) may either be incorporated into the Fe-oxyhydroxide, sorbed onto the surface of the Fe-oxyhydroxide (Lion et al., 1982; Millward and Moore, 1982), or complexed with organic matter. Our data do not support an association of these metals with the Fe-oxyhydroxide matrix. The removal of the HMW fraction of these metals occurs at a much lower

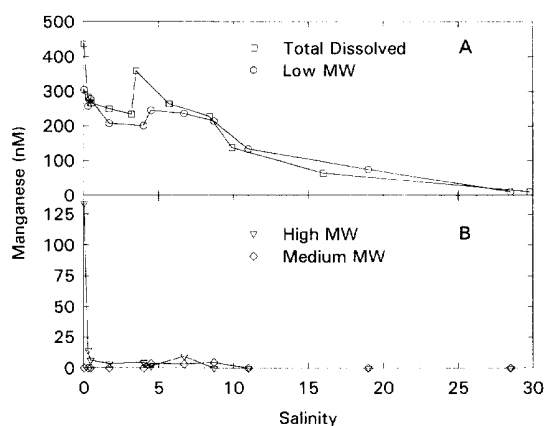


Fig. 4. Manganese size fractions vs. salinity.

A. Total dissolved and LMW fractions are almost identical throughout the estuary. There is removal from the total between the river and low salinity and then some indication for input around salinity 5.

B. Of the colloidal size fractions, only the HMW fraction in the river contains a large percentage of the total Mn.

salinity than for Fe. Also, the total concentrations of Ni, Cu and Cd remain relatively constant throughout the estuary as opposed to the large removal of Fe.

It is possible that Ni, Cu and Cd are either sorbed onto the surface of the Fe-oxyhydroxides or are

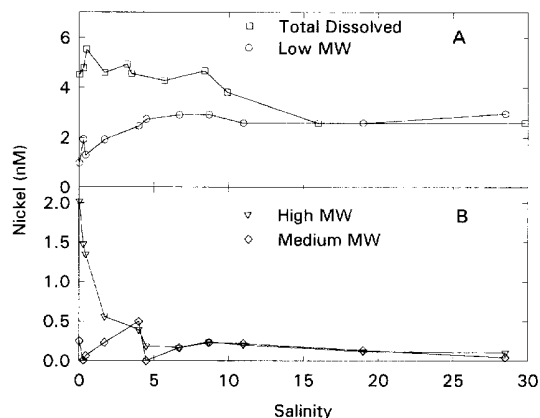


Fig. 5. Nickel size fractions vs. salinity.

A. Total dissolved Ni displays relatively conservative behaviour in the estuary. The LMW fraction increases in importance with salinity until above salinity 15 it is almost equal to the total dissolved.

B. The HMW fraction is nonconservatively removed in the estuary before salinity 10. The MMW fraction is quite variable at low salinity but is never the dominant fraction for Ni.



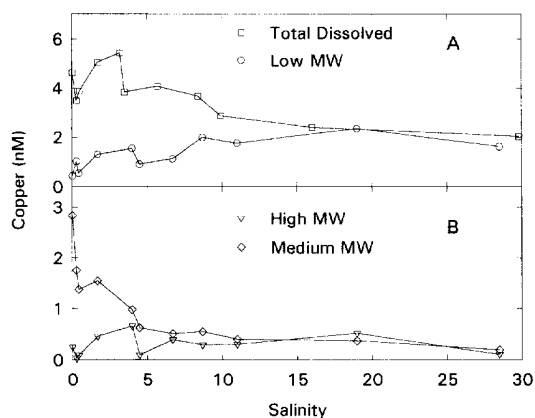


Fig. 6. Copper size fractions vs. salinity.

A. Total dissolved Cu is somewhat conservative in the estuary with an indication of an input at salinity 3–5. The LMW fraction increases conservatively until it is the dominant fraction above salinity 10.

B. The HMW size fraction is nonconservatively removed in the estuary below salinity 10. The MMW fraction is again variable but never the dominant fraction.

complexed by the organics that are coating the Fe-oxyhydroxide surface. When the river water mixes with the seawater, the metals are desorbed from the Fe-oxyhydroxide or dissociate from the organics and are replaced with Ca and Mg. This explanation is consistent with the relatively constant total concentration and with the shift from high to low molecular weight. In the Ogeechee and Savannah Rivers, total Cu is elevated above the ideal mixing line due to dissociation from particulates and large colloids (Windom et al., 1983). In the Ochlockonee, the particulate load is smaller and the dissociation would be primarily from colloids. The LMW material in the estuary may be composed of metal–organic complexes; however, more pass through the 1-kD filter, indicating either smaller complexes than in the river or complexes that were constricted by electrostatic interactions. The possibility of organic complexation is supported by the correlations between Ni and Cu in the MMW fraction with carbon. While the organic carbon concentration is several orders of magnitude greater than the metals, the trend is nearly identical with high concentrations in the river that are removed at low salinity followed by an increase which is ultimately diluted at high salinity. These metal–organic complexes show different labilities toward

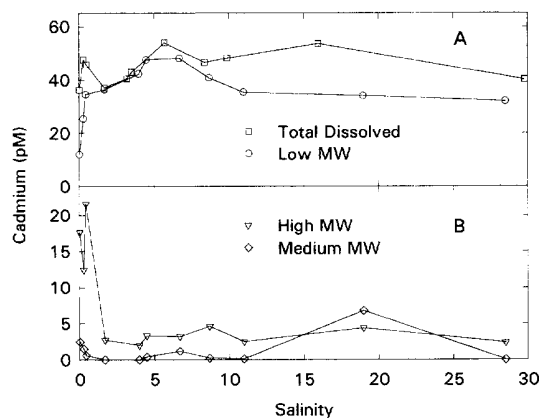


Fig. 7. Cadmium size fractions vs. salinity.

A. The total dissolved and LMW fractions are very similar in concentration between salinity 3 and 10.

B. Below salinity 5 the HMW fraction is an important fraction of total Cd. Above salinity 10 both the HMW and MMW fractions contribute to the total dissolved Cd concentration.

immobilized 8-HQ (Table 2). The Cu is very non-labile and therefore does not exchange onto the 8-HQ resin while Ni and Cd are more labile. Also, the lability of all metals increases as salinity increases. These results are in good agreement with the Irving–Williams order.

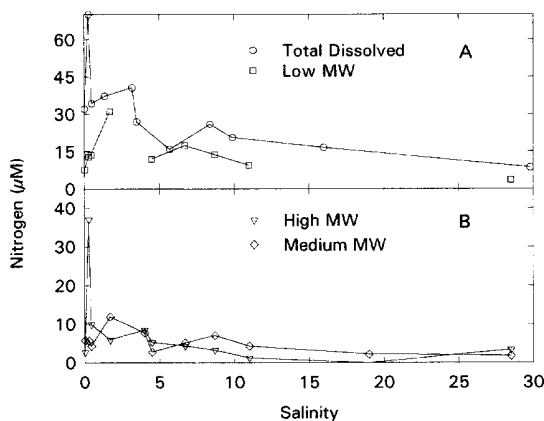


Fig. 8. Nitrogen size fractions vs. salinity.

A. Total nitrogen in the estuary decreases relatively conservatively through the estuary and is composed mainly of LMW material except at very low salinity.

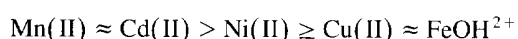
B. The HMW and MMW nitrogen is low and somewhat constant with the exception of a HMW sample at low salinity that is responsible for the increase in the total dissolved concentration.

For nitrogen (Fig. 8) it appears that there may be a large desorption of HMW material from particles at very low salinities which is then rapidly removed. Similar to carbon, the MMW and LMW fractions show a pattern of desorption and then relatively conservative mixing from salinity 8 to the seawater end-member. The C/N ratios (Table 1) reflect the similarity in the profiles with little variation as the fractions pass through the estuary. The fact that the ratio does not shift from a terrestrial signal to a marine signal may be due to the time of year the samples were taken. During the winter there is little productivity in the bay (Kaul and Froelich, 1984), therefore we did not observe a more "marine" signature in the C/N ratio at high salinities.

#### 4. Conclusions

Our data show that colloids play an important role in the cycling of many elements in the Ochlockonee Estuary. Iron exhibits non-conservative removal and is dominated by a HMW component that consists mainly of Fe-oxyhydroxides or non-labile organic complexes, although ~20% is still easily reducible and more likely to be bioavailable. This HMW fraction aggregates to form particles and also appears to disaggregate to form MMW material. Aggregation of the HMW DOC fraction also removes a large amount of the riverine DOC in the estuary. For Ni, Cu and Cd (elements which have relatively conservative total concentrations), colloids play an important role in the transport of these elements in the river. In the estuary, these elements dissociate or are desorbed from HMW material. Mn has a nonconservative total dissolved profile and only in the river is there a large amount of colloidal metal.

The reactivity of the trace metals also varies with salinity. For Fe, Ni, Cu and Cd, the reactivity increases as the salinity increases and the LMW fraction becomes more important. At the same time, Fe and Cu are much less reactive to 8-HQ even when the total dissolved concentrations are dominated by the LMW size fraction. At all salinities, the lability of the elements with respect to ligand exchange is roughly as predicted by the Irving–Williams order with:



While this data set is only a synoptic picture of a small organic-rich estuary, it demonstrates the importance of colloids in the transport of metals and organic carbon to the coastal zone. Positive identification of any colloidal Fe-oxyhydroxide or aluminosilicate phases would be useful in modeling adsorption/desorption processes. Our data add to the growing evidence which demonstrates the utility of cross-flow filtration for the isolation of HMW components from natural waters.

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