

THE ROLE OF SUSPENDED MATTER ON
TRACE METAL TRANSPORT IN AN ESTUARINE ENVIRONMENT

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THE ROLE OF SUSPENDED MATTER ON
TRACE METAL TRANSPORT IN AN ESTUARINE ENVIRONMENT

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SUMMARY

Suspended sediment collected during August, October, December, 1973, and April, 1974, from the estuarine zones of two major southeast Georgia rivers (Savannah and Ogeechee) were analyzed by radioisotope tracers (^{54}Mn , ^{65}Zn , ^{109}Cd , and ^{203}Hg) and a selective chemical leaching technique to determine the role of suspended material on metal transport in a Southeast Atlantic estuarine environment. The metal concentrations (Cu, Cd, Pb, Zn, Mn, and Fe) in the leached fractions, (adsorbed, reduced, oxidized, and residual) of suspended sediments from fresh water and saline environments were compared. Results indicated that suspended sediment can account for a significant portion of these metals in natural waters. Generally, the residual fraction (metals in lattice sites of crystalline detrital material) and the reduced fraction (metals precipitated and coprecipitated as metallic coatings) were the major sources of the trace metals in suspended sediment. The effect of a salinity change on the metal concentrations of the leached fractions was a function of the specific metal, season, and area of study. Comparison with the results of similar studies indicated the importance of regional differences in the character of suspended matter on the transport of trace metals.

CHAPTER I

INTRODUCTION

The purpose of this study was to investigate the interaction of selected trace and minor metals (Cu, Cd, Hg, Zn, Fe, Pb, and Mn) with suspended sediment through an estuarine environment. Interactions with the adsorbed, reduced, oxidized and residual fractions of suspended samples collected from the estuarine zones of the Savannah and Ogeechee Rivers (Figures 1, 2 and 3) were investigated by means of radioisotope tracers (^{54}Mn , ^{65}Zn , ^{109}Cd , and ^{203}Hg) and a selective chemical leaching procedure. Previous studies have described various sedimentological (Neiheisel and Weaver, 1967, and Windom et al., 1971a) and chemical characteristics (Windom et al., 1971b; Windom and Beck, 1971; Windom, in press) of these estuaries.

The use of radioisotope tracers enables an in situ investigation of suspended matter - trace metal adsorption reactions using metal spikes in the range of natural levels. Studies using ^{203}Hg have been successfully made by Bothner and Carpenter (1973) and DeGroot et al. (1971). ^{65}Zn and ^{109}Cd were used in studies by Holmes et al. (1974). Recent studies (Presley et al., 1972; Bothner, 1973; Gibbs, 1973; and Bruland et al., 1974) have shown the importance of studying the trace metal concentrations of various suspended and

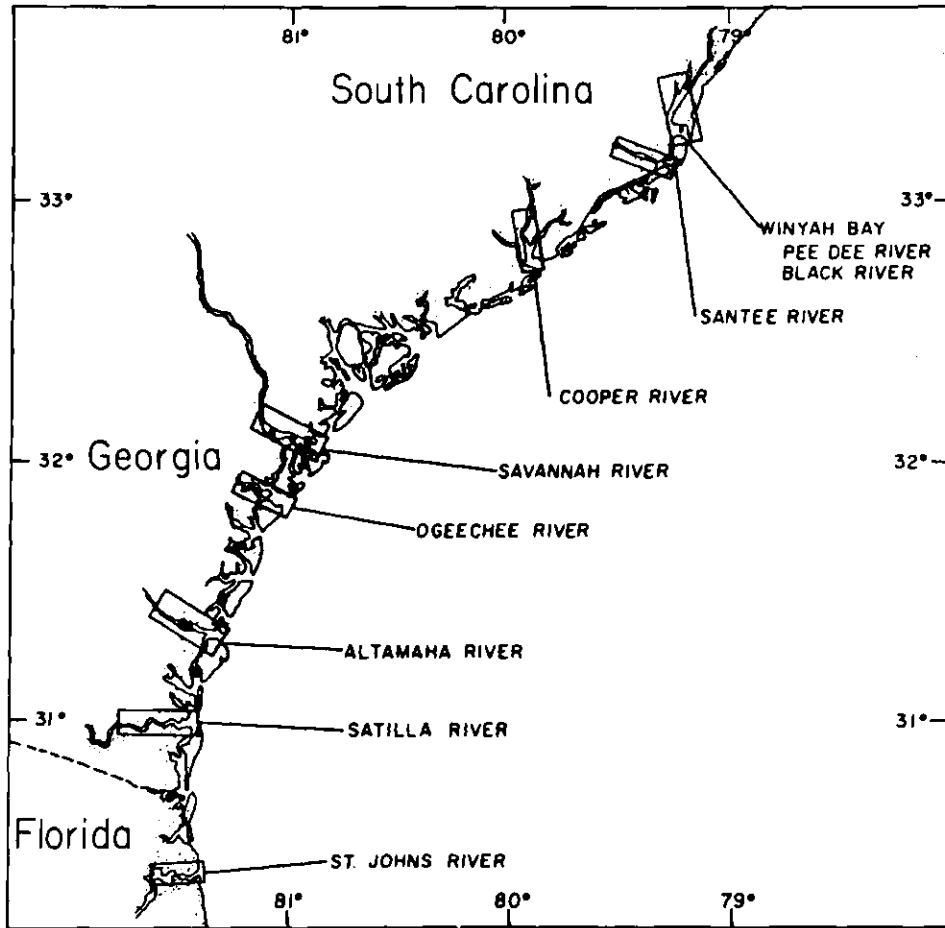


Figure 1. Study Area Showing Location of Savannah and Ogeechee Rivers

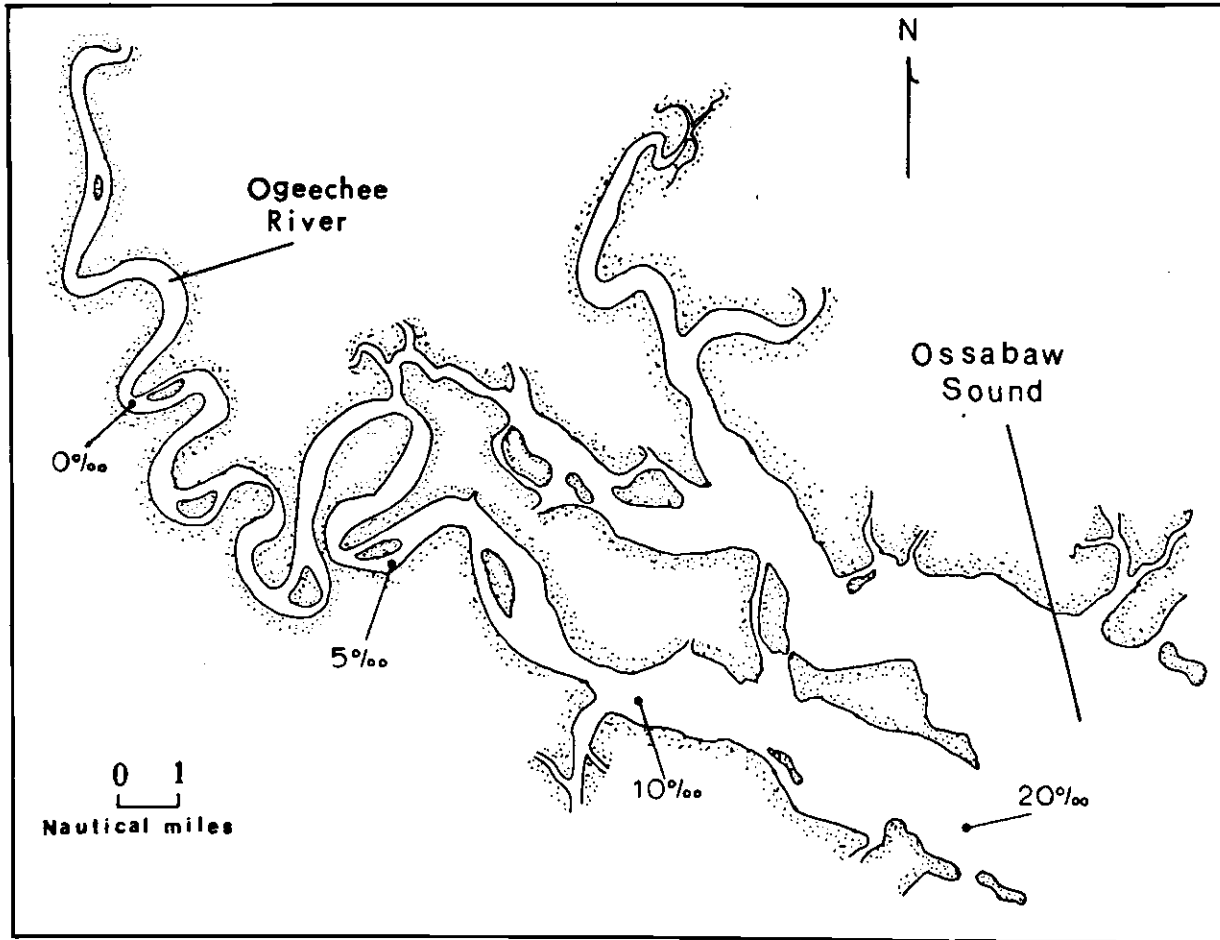


Figure 2. Approximate Locations of Sampling Stations on the Ogeechee River

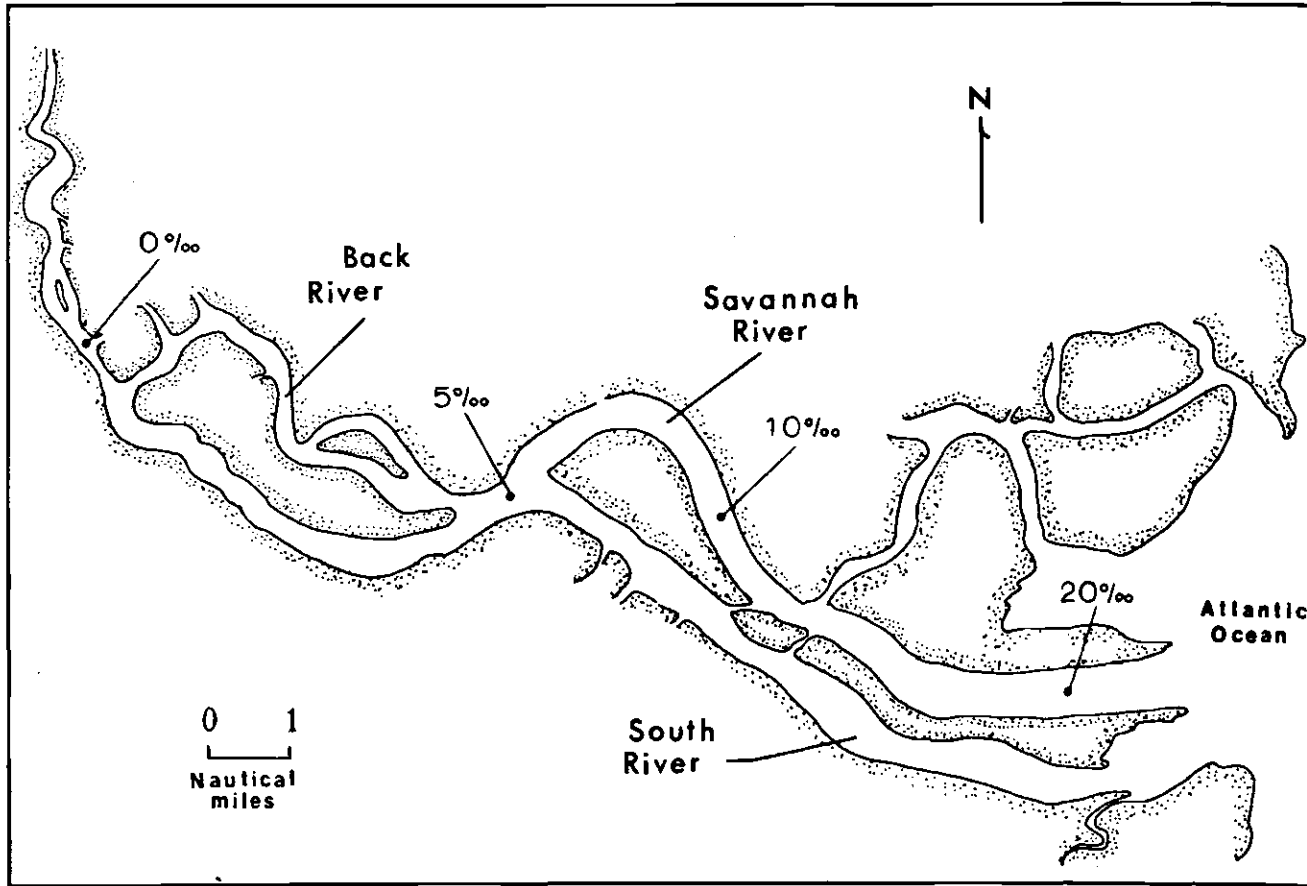


Figure 3. Approximate Locations of Sampling Stations on the Savannah River

bottom sediment fractions to elucidate mechanisms which may be significant in the distribution of metals. The selective leaching techniques prior to metal analysis used in these studies is primarily that of Presley (1969), expressing results as the metal concentration of four suspended sediment fractions: adsorbed, reduced, oxidized, and residual. It is important to note that while the metal concentrations of these leached fractions may be equated with a specific phase (for example: reduced fraction equals trace metals coprecipitated or complexed with hydrous Mn and Fe oxides, or oxidized fraction equals trace metals complexed or chelated by organic material) these leached fractions are in fact defined by the analytical procedures used. Various authors (e.g., Presley, 1969; Chester and Hughes, 1967; and Gibbs, 1973) have shown the validity of interpreting results from these analytically derived fractions in terms of specific mechanisms.

CHAPTER II

METHODS

Suspended samples were collected in August, October, and December, 1973, and April, 1974, for seasonal representation. Sampling stations were selected at salinities of 0‰, 5‰, 10‰, and 20‰ for the radioisotope tracer studies and 0‰ and 20‰ for the leaching studies. The location of the freshwater station did not exceed ca. sixteen and nine miles from the mouths of the Savannah and Ogeechee Rivers, respectively. Sampling stations were located at approximately the same sites for each sampling period (Figures 2 and 3). Samples were collected at depths of five to ten feet using a PVC Niskin sampler. Six liters of water were immediately transferred to six, one liter glass bottles. To each of the one liter samples one of the following radioisotopes was added: ^{54}Mn , ^{65}Zn , ^{109}Cd , or ^{203}Hg . ^{203}Hg was added as either mercuric chloride (^{203}Hg) or methyl mercury chloride ($^{203}\text{MeHg}$). After spiking, the bottles were capped with ground glass stoppers and either mechanically shaken or stirred to insure that solids remained in suspension. Experimental data showed that equilibration was reached after about four hours. As a precaution samples were allowed to equilibrate for about five hours, after which they were filtered through 0.45 micron

Millipore^(R) filters. The filters were then stored in plastic vials and returned to the laboratory for counting using a NaI detector connected to a single channel analyzer.

At salinities of 0‰ and 20‰, an additional 40 liters of water were collected. Within two hours of collection this water was centrifuged at ca. 12,000 RPM with a Sorvall SS-1 centrifuge with KSB continuous flow adaption and Kel-F (Teflon-like) coated centrifuge tubes. The flow rate of the sample was ca. 100 to 150 ml/min. The diameter of the smallest particle removed from suspension was 0.5 microns (see Appendix). After centrifugation (ca. seven hours) the centrifuge tubes were removed and placed in a freezer. After freezing, samples were warmed slightly and transferred to 50 ml polyethelene centrifuge tubes. These were capped, then re-frozen. All samples were chemically analyzed during May, 1974.

In addition to the water sampling at each station, pH, temperature, % TC (percent total carbon which in these samples is approximately equal to percent total organic carbon) and concentration of suspended matter were determined (Table 1). The % TC was determined on suspended matter collected on a 0.45 micron Millipore^(R) filter. The sample was scraped from the filter paper, dried in a 70° C oven overnight, and then analyzed on a Coleman Model 33 carbon-hydrogen analyzer. The concentration of suspended matter was determined by filtering a minimum of one liter of sample through a 0.45 micron Millipore^(R) filter (which had been prewashed, dried and weighed),

Table 1. Sampling Station Characteristics

Savannah River					
	Salinity	Temp	pH	%TC	Suspended Sediment Concentration
August	0°/∞∞	27	7.0	5.1	27 mg/l
	12°/∞∞	27	6.8	4.2	16
	18°/∞∞	30	7.4	9.4	38
October	0°/∞∞	23	-	3.3	53
	4°/∞∞	24	-	7.8	24
	9°/∞∞	24	-	5.6	22
	25°/∞∞	25	-	5.0	23
December	0°/∞∞	17	6.4	4.7	9
	6°/∞∞	17	6.9	4.8	26
	10°/∞∞	17	6.9	5.5	17
	24°/∞∞	19	7.2	2.7	14
April	0°/∞∞	19	5.5	3.7	28
	5°/∞∞	17	6.5	6.0	33
	10°/∞∞	18	6.8	6.4	15
	21°/∞∞	18	7.5	6.4	24
Ogeechee River					
August	0°/∞∞	30	6.8	8.1	23
	5°/∞∞	31	7.2	5.0	31
	10°/∞∞	30	7.1	4.1	22
	20°/∞∞	30	7.9	3.0	48
October	0°/∞∞	23	5.7	6.6	46
	5°/∞∞	23	5.8	5.6	71
	12°/∞∞	22	6.0	4.0	210
	20°/∞∞	22	5.9	3.9	54
December	0°/∞∞	17	7.2	7.1	17
	5°/∞∞	-	7.0	6.4	127
	10°/∞∞	16	7.6	3.1	49
	21°/∞∞	17	7.9	3.6	48
April	0°/∞∞	19	5.4	7.7	112
	5°/∞∞	19	6.7	6.7	28
	11°/∞∞	19	6.6	6.4	13
	20°/∞∞	20	7.5	6.6	21

drying overnight in a 70° C oven, and then reweighing.

The technique for the selective chemical leaching of the adsorbed, reduced, oxidized, and residual fractions is shown in Table 2. In this technique, centrifugation was carried out on an RC2-B Sorvall centrifuge at 12,000 RPM, for ca.14 minutes. Using equation (1) (see Appendix) and the previous values of R, S, n, and Δs , particles greater than 0.5 micron were removed from suspension. Decanting was done with a pipet to insure the samples were not resuspended. Step 1 removed the remainder of the original solution. Step 2, the addition of 1 N MgCl₂, removed those metal ions in the adsorbed fraction. Gibbs (1973) has found that 1 N MgCl₂ will not react with the reduced fraction. Step 3, treatment with 1M NH₂OH-HCl in 25% (v/v) HOAc (acetic acid) has been shown by Chester and Hughes (1967) to dissolve carbonates (relatively minor in these samples) plus acid soluble sulphides and organics and, most importantly, hydrous Mn and Fe oxide coatings without significantly disturbing the detrital fraction. This treatment was found to dissolve insignificant amounts of organic matter from samples similar to those in the present study. Treatment with 30% H₂O₂ (Step 4) dissolved a substantial portion of the remaining organic material without effecting the detrital fraction (Presley, 1969, and Jackson, 1956). The adsorbed, reduced, and oxidized fractions make up the authigenic phase of the suspended material. The remaining detrital material is composed of crystalline components,

Table 2. Technique for the Selective Chemical Leaching of Suspended Matter

The following procedure begins with the sample stored in its original solution. It should be noted that the volumes of reagents beyond the preparation step are for samples less than 0.7000 gm. For the remaining sample 0.7000 to ca. 2.0000 gm; reagent volumes were doubled.

Start: sample in original solution

Step 1: sample preparation

- a. Centrifuge and decant
- b. Add 10 ml of DDW (double distilled water), mix, centrifuge and decant
- c. Repeat step b.
- d. Using minimal DDW, wash sample into evaporating dish and dry over night in a 70° C oven
- e. Weigh sample and transfer to 50 ml centrifuge tube

Step 2: adsorbed fraction

- a. Add 10 ml of 1 N MgCl₂
- b. Shake for 5 minutes, centrifuge and decant; save
- c. Add 10 ml of DDW, shake 5 minutes, centrifuge and decant; save
- d. Combine supernatant liquids, take to known volume

Step 3: reduced fraction

- a. Add 10 ml of 1M NH₂OH - HCl in 25% (v/v) HOAc (acetic acid)
- b. Shake mildly for 4 hours, centrifuge and decant
- c. Add 10 ml of DDW, shake 5 minutes, centrifuge and decant; save
- d. Take supernatant liquids to known volume

Step 4: oxidized fraction

- a. Add 25 ml of H₂O₂ slowly till reaction with suspended sediment slows; let stand for 24 hours, centrifuge and decant; save
- b. Add 20 ml of DDW, shake 5 minutes, centrifuge and decant; save
- c. Take supernatant liquids to known volume

Step 5: residual fraction

- a. Transfer sample to Teflon beaker with minimal DDW
- b. Add 10 ml of 48% HF and 10 ml of concentrated HNO₃
- c. Allow samples to stand for two hours
- d. Add 5 ml of 70% HClO₄ and digest on hotplate until dense fumes of perchloric subside
- e. Wash the sides of the beaker with a minimum amount of water and take to dryness
- f. Add 2 ml of 10% HCl, heat on hotplate till all material dissolves and turns clear
- g. Filter through a pre-washed No. 41 Whatman filter into a 5 ml volumetric and make to volume with 10% HCl

Step 6: AAS analysis

- a. Analyze metals by "flame" or "heated graphite furnace" on atomic absorption spectrophotometer

predominantly clays. This residual fraction is dissolved by a combined treatment of HF-HNO₃ - HClO₄ (Step 5) according to the technique described by Smith and Windom (1972). In each step reagent blanks were taken through a procedure identical to that for the samples. To minimize metal contamination quartz sub-boiling distilled acids and water were used. Also, all chemical hardware used in these analyses was soaked in hot nitric acid and rinsed with large volumes of double distilled water. Metal concentrations (Fe, Zn, Mn, Cd, Pb, and Cu) were determined using both flame and flameless (heated graphite furnace) technique with a Perkin Elmer Model 403 Atomic Absorption Spectrophotometer.

CHAPTER III

RESULTS

The results of the radioisotope studies are summarized in Table 3. These data show the percentage of the isotope adsorbed on the suspended matter at various salinities relative to that for samples taken from fresh water. The results of the selective leaching analyses are reported in Tables 4 through 9. The metal concentrations are expressed on a dry weight basis and as a percentage of the total metal content of the adsorbed, reduced, oxidized, and residual fractions. In Tables 10 and 11 the seasonal data of Tables 4 through 9 have been summarized for 0‰ and 20‰ salinity for each of the above fractions. The results can be summarized as follows:

Iron

Over 90% of the total iron is in the residual fraction. For the authigenic fractions the Fe concentration is in the order reduced > oxidized > adsorbed, where the adsorbed fraction is relatively insignificant. Only the Fe concentration in the reduced fraction shows a correlation with salinity, decreasing with increasing salinity (Table 4). In the Savannah Estuary samples, the percent of total Fe in the various leached fractions remains constant with changing salinity

Table 3. Percentages of Radioisotopes Adsorbed Relative to Fresh Water Values*

Isotope	Salinity	Savannah River				Ogeechee River			
		Aug.	Oct.	Dec.	Apr.	Aug.	Oct.	Dec.	Apr.
^{109}Cd	5‰	-	12	67	9	20	92	219	52
	10‰	-	13	52	14	17	21	178	128
	20‰	-	12	50	9	9	105	91	61
^{65}Zn	5‰	-	41	19	26	26	75	13	259
	10‰	33	42	14	74	21	33	18	575
	20‰	42	29	0	69	14	293	21	259
^{54}Mn	5‰	-	37	5	1	48	194	46	82
	10‰	47	43	13	6	-	30	9	187
	20‰	27	93	63	34	23	314	71	196
^{203}Hg	5‰	-	387	154	192	78	9	41	551
	10‰	184	439	277	405	107	7	102	1260
	20‰	91	264	255	230	52	28	99	756
$^{203}\text{MeHg}$	5‰	-	750	185	158	74	8	23	197
	10‰	156	646	270	262	104	2	46	623
	20‰	91	96	345	285	50	23	64	880

*Values are in percent of radioisotope adsorbed per milligram of suspended sediment relative to the zero salinity value.

Table 4. Selective Leaching Data for Iron

Savannah River Estuary

Sampling Date	Salinity	(T) Total (ppm)	Adsorbed		Reduced		Oxidized		Residual	
			ppm	%T	ppm	%T	ppm	%T	ppm	%T
August	0‰	31900	<10	0	1547	5	176	1	30200	95
	20‰	36000	<10	0	1186	3	205	1	34600	96
October	0‰	---	---	-	---	-	---	-	---	--
	20‰	38500	<10	0	1211	3	319	1	37000	96
December	0‰	45700	<10	0	1662	4	97	0	44000	96
	20‰	35000	<10	0	1427	4	816	2	32700	93
April	0‰	49900	17	0	830	2	234	1	48800	98
	20‰	24000	<10	0	530	2	486	2	23000	96

Ogeechee River Estuary

August	0‰	35200	<10	0	1812	5	410	1	33000	94
	20‰	69800	<10	0	716	1	86	0	69000	99
October	0‰	33000	<10	0	1050	3	420	1	31500	96
	20‰	50600	<10	0	984	2	164	0	49500	98
December	0‰	34900	<10	0	1128	3	877	3	32900	94
	20‰	21800	<10	0	420	2	535	3	20800	95
April	0‰	32000	<10	0	977	3	2015	6	29000	91
	20‰	59200	<10	0	760	1	447	1	58000	98

(Table 10), but for the Ogeechee samples, the reduced and oxidizable Fe make up a smaller portion of the total in saline waters (Table 11). The average concentration of Fe in the Savannah Estuary samples is higher in the reducible fraction but lower in the oxidized and residual fractions and in the total, in comparison with Ogeechee samples. The oxidizable Fe shows a maximum concentration in April (ca. 2.4% of total Fe) and a minimum in August (0.4%). The residual, reduced, and adsorbed fractions remain relatively constant seasonally.

Manganese

Tracer studies for the Savannah River Estuary indicate that a substantial decrease in the adsorbed Mn occurs between 0‰ and 5‰. At higher salinities the suspended matter adsorption capacity increases. The degree of increase varies but does not exceed the adsorption capacity for Mn in freshwater suspended matter. The pattern for the Ogeechee River Estuary is not as clear. Suspended matter in saline waters commonly adsorbs more Mn than that in fresh water. Mn is primarily concentrated in the reduced fraction which accounts for 36 to 86 percent of the total. The oxidized, adsorbed, and residual Mn accounts for a significantly smaller percentage of the total (Table 5).

Appreciable changes occur in all leached fractions of the Ogeechee suspended sediment with changing salinity. Mn decreases in the adsorbed (30% to 9%), and oxidized fractions

Table 5. Selective Leaching Data for Manganese

Savannah River Estuary

Sampling Date	Salinity	(T)Total (ppm)	Adsorbed		Reduced		Oxidized		Residual	
			ppm	%T	ppm	%T	ppm	%T	ppm	%T
August	0‰	2364	318	14	1826	77	51	2	169	7
	20‰	948	194	21	605	64	25	3	124	13
October	0‰	-	-	-	-	-	-	-	-	-
	20‰	845	149	18	478	57	62	7	156	19
December	0‰	2138	651	30	1152	53	91	4	289	13
	20‰	1055	65	6	805	76	40	4	145	14
April	0‰	1804	330	18	1000	55	123	7	351	20
	20‰	668	109	16	360	54	68	10	131	20

Ogeechee River Estuary

August	0‰	1293	367	28	632	49	60	5	234	18
	20‰	712	72	10	265	37	62	9	313	44
October	0‰	692	200	29	286	41	95	14	111	16
	20‰	1132	38	3	916	81	29	3	149	13
December	0‰	1459	526	36	708	49	95	7	130	9
	20‰	842	42	5	573	68	153	18	74	9
April	0‰	1334	325	24	482	36	465	35	62	5
	20‰	884	179	20	536	61	78	9	91	10

(15% to 9%) while the reduced (44% to 64%), and residual fractions (11% to 19%) increase from 0‰ to 20‰ salinity (Table 11).

Mn concentrations in suspended sediments of the Savannah River Estuary decrease with increasing salinity in all fractions. This is true of only the adsorbed fraction in the Ogeechee Estuary. The suspended sediment of the Savannah Estuary also has higher concentrations of Mn in all but the oxidized fraction.

Seasonally, the adsorbed and reduced fractions contain more Mn during December, whereas the oxidizable Mn was at a minimum in April for both estuaries.

Zinc

The uptake of Zn decreases with increasing salinity with the predominant change occurring between 0‰ and 5‰. This pattern is more variable for the suspended sediment of the Ogeechee Estuary which occasionally shows an increase in uptake of Zn with increasing salinity (Table 3). The major reservoirs of Zn are the reduced and residual fractions. The Zn concentration of the oxidized fraction is less than the above two fractions but greater than the adsorbed fraction. The oxidized and adsorbed fractions are the only fractions which consistently decrease in Zn concentrations with increased salinity. The Zn concentration of the authigenic fractions is generally greater in the Savannah Estuary suspended

Table 6. Selective Leaching Data for Zinc

Savannah River Estuary

Sampling Date	Salinity	(T) Total (ppm)	Adsorbed		Reduced		Oxidized		Residual	
			ppm	%T	ppm	%T	ppm	%T	ppm	%T
August	0‰	225	27	12	95	42	24	11	79	35
	20‰	347	2	1	237	68	18	5	90	26
October	0‰	-	-	-	-	-	-	-	-	-
	20‰	226	5	2	121	54	14	6	86	38
December	0‰	297	44	15	102	34	34	11	117	39
	20‰	162	0	0	87	54	14	9	62	38
April	0‰	305	12	4	142	47	25	8	126	41
	20‰	171	0	0	95	56	19	11	57	33

Ogeechee River Estuary

August	0‰	230	13	6	127	55	18	8	72	31
	20‰	234	4	2	84	36	15	6	131	56
October	0‰	101	3	3	30	30	9	9	59	58
	20‰	164	0	0	82	50	6	4	76	46
December	0‰	109	12	11	36	33	11	10	50	46
	20‰	89	0	0	31	35	16	18	42	47
April	0‰	171	23	14	58	34	41	24	49	29
	20‰	160	0	0	103	64	14	9	43	27

samples (Table 6).

In the Savannah Estuary the reducible Zn increases from 41 to 59 percent with increasing salinity. The percent of Zn decreases in the adsorbed, oxidized, and residual fractions from 0‰ to 20‰ (Table 10). In the leached fractions of the Ogeechee Estuary, however, the percentage of Zn remains relatively constant with changing salinity (Table 11).

Seasonally, the average concentration of Zn in the various fractions is variable with total concentrations generally higher in August. The relative concentration of Zn is constant in the adsorbed fraction. The reduced fraction shows highest concentrations during August and April, and the maximum relative concentration for the oxidized fraction occurs in April (Table 6).

Cadmium

As in the previous cases of Mn and Zn, the radioisotope tracer studies indicate a considerable decrease in the amount of Cd adsorbed in saline relative to fresh water. For the Savannah Estuary the predominant decrease in Cd adsorption takes place between 0‰ and 5‰ and remains relatively constant through 20‰ salinity. Again, results for samples from the Ogeechee Estuary are more variable (Table 3). The relative concentration (percent) of total Cd in the residual fraction is highly variable which is also reflected in the total metal concentration. For the authigenic frac-

Table 7. Selective Leaching Data for Cadmium

Savannah River Estuary

<u>Sampling Date</u>	<u>Salinity</u>	<u>(T)Total (ppm)</u>	<u>Adsorbed</u>		<u>Reduced</u>		<u>Oxidized</u>		<u>Residual</u>	
			ppm	%T	ppm	%T	ppm	%T	ppm	%T
August	0‰	1.39	0.30	22	0.73	53	0.19	14	0.16	12
	20‰	0.58	0.02	3	0.49	85	0.04	7	0.03	5
October	0‰	-	-	-	-	-	-	-	-	-
	20‰	0.18	0.00	0	0.13	70	0.03	18	0.02	11
December	0‰	0.56	0.09	16	0.40	73	0.03	5	0.04	7
	20‰	3.66	0.00	0	0.56	15	0.10	3	3.00	82
April	0‰	4.13	0.10	2	0.51	12	0.10	2	3.42	83
	20‰	2.10	0.23	11	0.66	32	0.11	5	1.10	52

Ogeechee River Estuary

August	0‰	0.42	0.01	3	0.33	77	0.07	16	0.02	4
	20‰	35.24	0.27	1	0.36	1	0.30	1	34.30	97
October	0‰	0.22	0.00	0	0.17	76	0.04	19	0.01	5
	20‰	4.89	0.00	0	0.16	3	0.06	1	4.66	95
December	0‰	0.17	0.00	0	0.03	19	0.06	38	0.08	45
	20‰	2.19	0.01	0	0.06	3	0.04	2	2.09	95
April	0‰	1.32	0.02	1	0.20	15	0.12	9	0.98	74
	20‰	1.01	0.05	5	0.67	66	0.09	9	0.20	20

tions the greatest relative concentration of Cd is found in the reduced fraction. For the Savannah Estuary the oxidized and adsorbed fractions contain similar concentrations but less than the reduced fraction. For the Ogeechee Estuary the amount of oxidizable Cd is notably greater than that of the adsorbable Cd (Table 7). The percent of Cd in each of the leached fractions of Savannah Estuary suspended sediment remains constant between 0‰ and 20‰ salinity (Table 10). However, in the Ogeechee Estuary the residual Cd is of much greater importance in the saline samples, increasing from 51% to 95% of the total Cd between 0‰ and 20‰ salinity (Table 11). This results in a relative decrease in oxidizable (14% to 1%) and reducible Cd (34% to 3%) of saline samples relative to fresh water samples.

No distinct seasonal pattern existed for the Cd concentrations of the various fractions.

Lead

Significant differences occur in the Pb concentration of the various leached fractions. The order of Pb concentration is reduced > residual > oxidized > adsorbed (relatively insignificant) with the reducible fraction making up ca. 75% and 60% of the total Pb in suspended sediments of the Savannah and Ogeechee Estuaries respectively. Total Pb concentrations are approximately twice as high in the Savannah Estuary (Table 8). The percent of the total Pb in the leached

Table 8. Selective Leaching Data for Lead

Savannah River Estuary

Sampling Date	Salinity	(T)Total (ppm)	Adsorbed		Reduced		Oxidized		Residual	
			ppm	%T	ppm	%T	ppm	%T	ppm	%T
August	0‰	183	<0.2	0	155	70	5.0	2	23.0	10
	20‰	180	<0.2	0	147	82	4.7	3	28.0	16
October	0‰	-	-	-	-	-	-	-	-	-
	20‰	130	<0.2	0	99	76	7.9	6	22.8	18
December	0‰	105	<0.2	0	87	83	0.0	0	17.6	17
	20‰	130	<0.2	0	97	75	15.3	12	17.1	13
April	0‰	136	<0.2	0	90	66	14.2	10	31.2	23
	20‰	90	<0.2	0	58	64	12.7	14	19.1	21

Ogeechee River Estuary

August	0‰	99	<0.2	0	70	71	4.2	4	24.4	25
	20‰	75	<0.2	0	37	49	5.5	7	32.4	43
October	0‰	63	<0.2	0	40	64	5.9	9	16.8	27
	20‰	73	<0.2	0	53	73	1.1	2	18.6	26
December	0‰	55	<0.2	0	30	55	8.8	16	16.3	30
	20‰	48	<0.2	0	27	56	8.4	18	12.8	27
April	0‰	61	<0.2	0	27	44	17.1	28	17.1	28
	20‰	62	<0.2	0	47	76	5.4	9	9.8	16

fraction remains constant between 0‰ and 20‰ salinity (Tables 10 and 11).

Seasonally, total Pb, concentrations are highest in August, reflected in the higher Pb concentration of the reduced and, to a lesser extent, residual fractions during this sampling period. Oxidized Pb concentrations are at a maximum in April. The relative concentration of Pb in the reduced fraction is relatively constant. The oxidized fraction is most significant in April and least important in August.

Copper

Cu concentrations are highest in the residual fraction with the range of Cu concentration among the adsorbed, reduced and oxidized fraction about equivalent. Total Cu values for the Savannah Estuary suspended sediments are about twice those of the Ogeechee Estuary samples. It is notable that unlike other metals analyzed (except Mn), the adsorbed Cu often accounts for an appreciable portion of the total (Table 9). Changes in the concentrations of Cu with salinity are similar for both estuaries (Tables 10 and 11). The adsorbed fraction increases in importance in saline water, whereas the oxidized and reduced fractions decrease. Relative Cu concentrations in the detrital fraction of the Savannah Estuary samples increases from 40% to 53% of the total between 0‰ and 20‰, while the Ogeechee samples remain effectively unchanged.

Table 9. Selective Leaching Data for Copper

Savannah River Estuary

Sampling Date	Salinity	(T) Total (ppm)	Adsorbed		Reduced		Oxidized		Residual	
			ppm	%T	ppm	%T	ppm	%T	ppm	%T
August	0‰	96.1	0.4	0	34.0	35	30.0	31	31.7	33
	20‰	50.5	2.5	5	10.0	20	7.0	14	31.0	61
October	0‰	-	-	-	-	-	-	-	-	-
	20‰	40.5	7.3	18	3.0	7	5.0	12	25.2	62
December	0‰	53.3	8.8	17	11.0	21	2.0	4	31.5	59
	20‰	41.7	13.5	32	3.0	7	7.0	17	18.2	44
April	0‰	90.0	17.3	19	13.0	14	26.0	29	33.7	37
	20‰	48.2	9.0	17	6.0	12	12.0	25	21.2	44

Ogeechee River Estuary

August	0‰	42.0	9.1	22	3.0	7	6.0	14	23.9	57
	20‰	39.3	0.3	1	4.0	10	4.0	10	31.0	79
October	0‰	33.0	5.9	18	1.0	3	11.0	33	15.1	46
	20‰	31.2	9.0	29	1.0	3	2.0	6	19.2	62
December	0‰	23.6	5.6	24	5.0	21	2.0	9	11.0	47
	20‰	41.2	26.6	65	1.0	2	4.0	10	9.6	23
April	0‰	29.9	6.3	21	2.0	7	10.0	33	11.6	39
	20‰	48.2	27.0	56	3.0	6	7.0	15	11.2	23

Total concentrations are greatest in April and August. A maximum in the Cu concentration occurs for the adsorbed and oxidized fractions during April. Maximum concentrations occur in reducible and residual Cu in August.

Mercury

Hg-suspended sediment interactions were analyzed by radioisotope tracers (Table 3). The behavior of methyl mercury and mercuric chloride showed only slight differences in their relative degree of uptake. Hence the following applies to both inorganic and methyl mercury.

For the Savannah Estuary the adsorption of Hg increases with salinity. Data for the Ogeechee Estuary are more variable. During October, Hg adsorption is substantially less in saline waters. In April, suspended sediments in fresh water have a much lower adsorption capacity. August and December results were intermediate in nature.

With data for the mean dissolved concentration of Fe, Mn, Cu, Cd (Windom, in press), Pb (unpublished data), and Zn (Windom and Smith, 1972), it is possible to calculate the overall significance of suspended matter on trace metal transport in the Savannah and Ogeechee estuaries (Table 12). Percentages of metals listed for the various leached fractions are the average of the metal concentrations at 0‰ and 20‰ salinity. Results indicate that suspended matter is an important source of Fe, Mn, Zn, Pb and to a lesser degree, Cu

Table 10. Average Values of the Percent of Total Metal in Each Leached Fraction at 0‰ and 20‰.

Savannah River

Metal	Salinity	Total (ppm)	Adsorbed	Reduced	Oxidized	Residual
Fe	0‰	42500	0	3	0	96
	20‰	33400	0	3	1	95
Mn	0‰	2102	21	63	4	13
	20‰	879	15	64	6	16
Zn	0‰	276	10	41	10	39
	20‰	227	3	59	7	32
Cd	0‰	2.03	8	27	5	59
	20‰	1.63	4	28	4	64
Pb	0‰	141	0	78	4	17
	20‰	133	0	75	8	16
Cu	0‰	79.8	11	24	24	40
	20‰	45.2	18	12	17	53

Table 11. Average Values of the Percent of Total Metal in Each Leached Fraction at 0‰ and 20‰.

Ogeechee River

Metal	Salinity	Total (ppm)	Adsorbed	Reduced	Oxidized	Residual
Fe	0‰	33800	0	4	3	93
	20‰	50400	0	1	1	98
Mn	0‰	1194	30	44	15	11
	20‰	893	9	64	9	19
Zn	0‰	153	8	41	13	38
	20‰	162	1	46	8	45
Cd	0‰	0.53	1	34	14	51
	20‰	10.83	1	3	1	95
Pb	0‰	70	0	60	13	26
	20‰	65	0	63	8	28
Cu	0‰	32.1	21	9	23	48
	20‰	40.0	39	6	11	44

Table 12. Percentages of the Total Metal Transported by Solution and the Leached Fractions

<u>Mechanism</u>	<u>Fe</u>	<u>Mn</u>	<u>Zn</u>	<u>Pb</u>	<u>Cu</u>	<u>Cd</u>
Savannah Estuary						
1. solution	27	41	55	32	77	94
2. adsorbed	0	18	1	0	3	0
3. reduced	4	30	25	34	5	2
4. oxidized	0	2	2	26	5	0
5. residual	68	7	18	7	11	5
Ogeechee Estuary						
1. solution	11	39	34	36	73	79
2. adsorbed	0	13	3	0	8	0
3. reduced	2	32	29	40	2	1
4. oxidized	2	8	7	7	4	0
5. residual	85	9	28	17	12	19

and Cd in these estuaries. Comparison with the findings for Fe, Mn, and Cu of a similar study on major river systems (Gibbs, 1973) shows significant differences in the distribution of metals between the solution and various suspended fractions. For example, in southeast Georgia estuaries, Fe is almost exclusively in the solution phase and residual fraction of suspended sediment. In the major river systems, the reduced and residual fractions are most important. Locally, the percent of total Mn and Cu found in the various phases is solution > reduced > adsorbed and solution > residual, respectively. In the Yukon and Amazon Rivers (Gibbs, 1973), the order of importance is reduced > residual > adsorbed for Mn and the Zn concentration in the residual fraction is much greater than that in the remaining phases.

CHAPTER IV

CONCLUSIONS

Data from Windom (in press), Windom et al., 1971a, and Windom et al., 1971b, indicate the suspended sediment of the Savannah and Ogeechee Estuaries is typical of that found in Southeastern estuarine systems. A significant portion of the Savannah River drainage basin lies in the Piedmont Province which results in sediments relatively kaolinite rich with ca. 65% of total clays (Neiheisel and Weaver, 1967). The Ogeechee River drains predominantly from the Coastal Plain. In the Ogeechee Estuary, however, its clay mineral suite is similar to that of the Savannah Estuary (Windom et al., 1971b). This detrital material accounts for a major portion of the total Fe, Zn, Cu and Cd, and to a lesser degree Mn and Pb. The metals contained in this detrital fraction of suspended sediment are in lattice sites of crystalline material which are effectively inert to the uptake and release of trace metals during transport across a salinity gradient (except for exchange sites on clays). Changes in the metal distribution of this residual (detrital) fraction are then controlled by sedimentological processes such as mixing with offshore sediment (Neiheisel and Weaver, 1967), resuspension of relic sediments, changes in drainage characteristics or

flocculation.

Of greater importance in the transport of trace metals through an estuarine environment are the authigenic fractions (adsorbed, reduced, and oxidized) since they may be salinity dependent. The radioisotope tracer study indicates that the uptake capacity of Zn, Cd, and Mn by the authigenic phases of suspended sediment is less (greater for Hg) in a saline relative to a fresh water environment. The predominant change appears to occur between 0‰ and 5‰ salinity.

Authigenic Fe, Mn, Zn, Cd, and Pb are primarily concentrated in the reduced fraction. These metals are coprecipitated with hydrated Fe and Mn oxide phases as metallic coatings on detrital material (Jenne, 1968; Chester and Hughes, 1967; Gibbs, 1973). The percent of reducible Pb does not appear to change with salinity. The reduced fraction of suspended sediment in higher salinity waters appears to contain relatively less Fe and Cu than does that of fresh water. The reverse appears to be true for Zn, Mn, and Cd. The concentration of these metals in the reduced fraction is also apparently dependent on difference in the suspended sediment of each estuary.

The adsorbed fraction which represents these metal ions which can be exchanged with the dominant ions of estuarine waters is important to the transport and fate of Mn

and Cu and to a lesser extent, Zn and Cd. The adsorbed Mn, Zn, and Cd decreases in saline water, but Cu increases. The amount of adsorbed Fe and Pb is insignificant.

The average oxidizable Fe, Zn, Mn, and Pb accounts for less than 10% of their total in suspended sediment. For Cu and Cd the portion of oxidized metal in suspended sediment can be appreciable. Generally, there is a decrease in the percent of metal which is oxidizable in saline water. Differences in the suspended material of each estuary have a significant effect on such patterns.

Leaching studies on West Coast marine surface sediments (Bruland et al., 1974, and Presley, 1969) have resulted in similar percentages of total Fe and Pb in the various leached fractions. Results for Cd, Mn, and Zn, however, were more variable. The effect of the various leached fractions of suspended sediment on the transport of metals through a Southeastern Atlantic estuarine system has been shown here to be considerably different than that for a major river system, such as the Yukon or Amazon River (Gibbs, 1973). Thus, regional differences in the character of suspended sediment have an important effect on the significance of suspended sediment transport of trace metals.

APPENDIX

The size of the suspended material which will be removed from solution is dependent on factors such as salinity, temperature, centrifugation time and density of the suspended matter. An SS-1 Sorvall centrifuge was run at 12,000 RPM and 100 ml/min., a radioisotope was injected into the system and the radioactive outflow monitored. The elution of radioisotope was plotted against time, the resulting curve was integrated to give a residence time (t) at which 75% of the incoming solution remains in the centrifuge (t = 1.5 minutes). Using this time plus equation 3-6 of Jackson (1956):

$$t = \frac{63.0 \times 10^8 (\eta) \log_{10} (R/S)}{(Nm)^2 (D\mu)^2 \Delta s}$$

where t = 75% residence time in minutes

Nm = RPM

η = viscosity in poises at the existing temperature

Δs = difference in specific gravity between the solvated particle and suspension liquid

$D\mu$ = particle diameter in microns

R = radius in cm of rotation of top of the sediment in tube

S = radius in cm of surface of suspension in tube
a value for D_p can be calculated. Selecting a high value
for η (0.00723) (Jackson, 1950, p. 131) and minimum value
for Δs (0.100) and calculating R and S for an SS-1 angle
head rotor (R = 9.0 cm, S = 7.6 cm) the diameter of the
smallest particle removed from suspension will be ca. 0.5
microns.

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